PART ONE

THERMAL AND PHOTOSENSITIZED DIMERIZATIONS OF 1, 3-CYCLOHEXADIENE

PART TWO

PHOTOSENSITIZED ISOMERIZATION OF THE STILBENES: FURTHER STUDIES

Thesis by

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ABSTRACT

Part One

Thermal dimerization of 1, 3-cyclohexadiene gives 4:1 mixtures of *endo* and *exo* tricyclo[6. 2. 2. $0^{2,7}$]dodeca-4, 9-diene, 1 and 2. Photosensitized dimerization of cyclohexadiene gives 90% yields of three products in about 3:1:1 ratio. The major photodimer was shown in two ways to be *trans*-*cis*-*trans*-tricyclo[6. 4. 0. $0^{2,7}$]dodeca-3, 11-diene, 3. One of the minor photodimers was shown to be *exo*-dicyclohexadiene, 2; the other photodimer was assigned the structure *cis*-*cis*-*cis*-tricyclo[6. 4. 0. $0^{2,7}$]dodeca-3, 11-diene, 4. Photodimerization of 2-cyclohexenone and its photoaddition to cyclohexene are described. The mechanism of the photosensitized dimerization of cyclohexadiene is considered. Quantum yields for the sensitized dimerization are lower than the expected value by varying factors depending upon the particular sensitizer. This effect is interpreted in terms of formation of a sensitizer triplet-cyclohexadiene complex which can break apart either to yield sensitizer ground state plus diene triplet or the ground states of both species. The photoaddition of sensitizers to cyclohexadiene is discussed; it is concluded that in some cases at least the diene triplet is the reactive intermediate leading to sensitizer-diene adducts. Thermal rearrangements of the dicyclohexadienes are studied. At higher temperatures, 3 rearranges smoothly to give 1 as the only product, and 4 rearranges to give 2. Surprisingly, various catalysts are able to effect the reverse conversions at and below room temperature. Kinetic studies of these rearrangements are described as are heat of combustion measurements which show that the cyclobutanes 3 and 4 are less stable than the thermal dimers 1 and 2. A discussion of the significance of these results is also given.

Part Two

Reinvestigation of the Hammond-Saltiel description of the photosensitized isomerization of the stilbenes is reported. Most of the gross features of their theory are confirmed but many changes in detail are required by new data. Greater than 5 kcal/mole exothermicity in the energy transfer step is not, as previously reported, sufficient to insure that the process rate is diffusion controlled. A discussion of the meaning of a diffusion controlled process is given. Various factors are considered as possible sources of inefficiency in exothermic energy transfer. Quantum yield measurements for sensitized stilbene isomerization show there is only very limited wastage of quanta. Transfer of energy from sensitizers with triplet energies below 62 kcal/mole to the stilbenes and especially to *cis*-stilbene is governed not only by the sensitizer triplet energy but also by other factors which are characteristic of the sensitizer. These effects are discussed in terms of energy transfer to *cis*-stilbene *via* an intermediate complex of sensitizer triplet and stilbene. Results with sensitizers containing bromine indicate that these substances cause stilbene isomerization by light induced liberation of bromine atoms and not, in general, by electronic energy transfer. This finding casts doubt on some of the evidence adduced in support of nonvertical energy transfer to *cis*-stilbene. The nature and reactions of stilbene triplets are discussed with special reference to reversible energy transfer to *trans*-stilbene, azulene quenching effects and self quenching due to *trans*-stilbene. The implications of this study in the study of other photosensitized reactions are presented.

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PART ONE

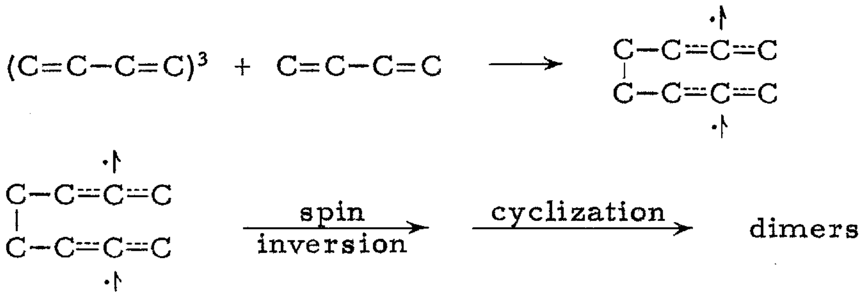
THERMAL AND PHOTOSENSITIZED DIMERIZATIONS OF 1, 3-CYCLOHEXADIENE

INTRODUCTION

Photosensitized dimerizations have been reported for butadiene, isoprene, cyclopentadiene and several related systems (1-6). It is now generally accepted that these reactions have as intermediates the triplet states of the diene and that the mechanism involves four discrete steps.*

$$(1)\quad \underset{\text{ground state sensitizer}}{S} \xrightarrow{h\nu} \underset{\text{excited singlet of sensitizer}}{S^1} \longrightarrow \underset{\text{lowest triplet of sensitizer}}{S^3}$$

$$(2)\quad S^3 + C{=}C{-}C{=}C \longrightarrow S + (C{=}C{-}C{=}C)^3$$



$$(3)\quad (C{=}C{-}C{=}C)^3 + C{=}C{-}C{=}C \longrightarrow \begin{array}{l} C{-}C{=}\overset{\cdot\uparrow}{C}{=}C \\ | \\ C{-}C{=}\underset{\cdot\uparrow}{C}{=}C \end{array}$$

$$(4)\quad \begin{array}{l} C{-}C{=}\overset{\cdot\uparrow}{C}{=}C \\ | \\ C{-}C{=}\underset{\cdot\uparrow}{C}{=}C \end{array} \xrightarrow[\text{inversion}]{\text{spin}} \xrightarrow{\text{cyclization}} \text{dimers}$$

Some representative examples of photosensitized dimerizations are given on the following page.

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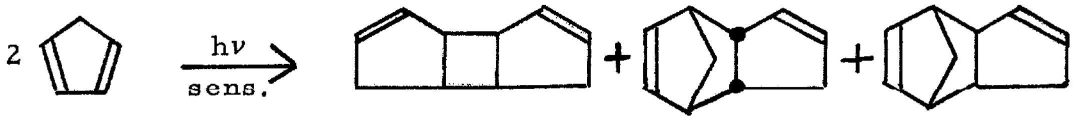
*A different mechanism for these reactions has been proposed by G. O. Schenck and R. Steinmetz, Bull. Soc. Chim. Bel., **71**, 781 (1962). For a summary of the strong arguments against Schenck's mechanism, see reference 6.



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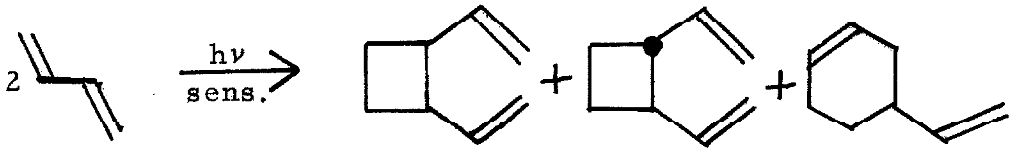
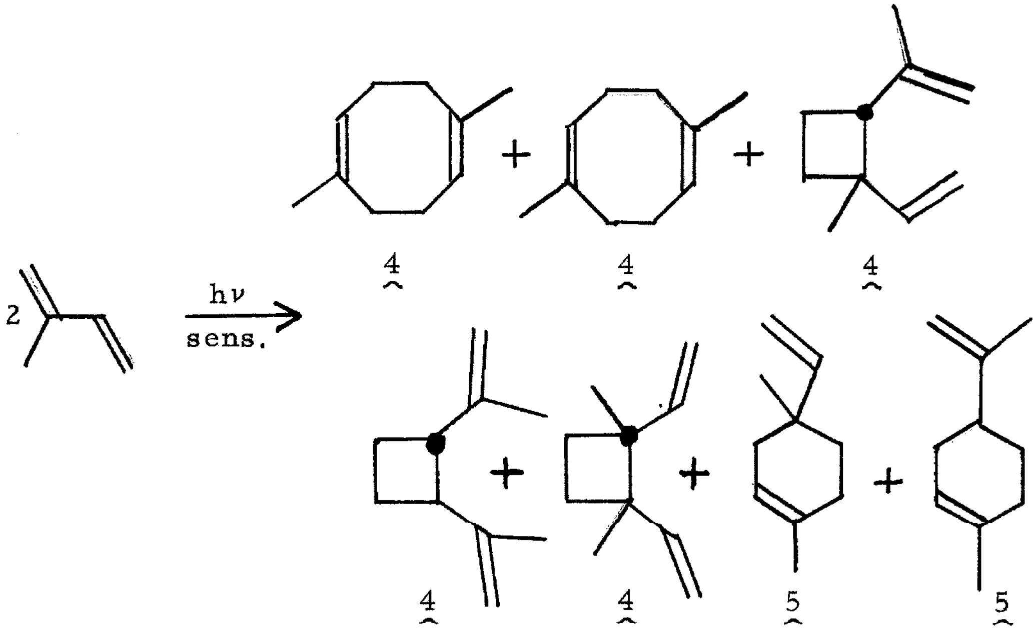
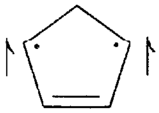




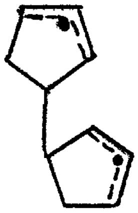
Dimerization of cyclopentadiene gives three dimers in about a 1:1:1 ratio which is independent of the sensitizer. Because the diene system in cyclopentadiene is constrained to the five-membered ring it must exist in a *cisoid* conformation in the ground state and the only triplet state which can be produced by energy transfer in solution is the *cis* triplet, 6.



6

The observed dimer ratio thus reflects only the characteristic reactions of the diene triplet (7).

Cyclopentadiene triplets, and the triplets of all other dienes studied so far, react with ground state diene so as to preserve two allylic radical systems in the biradical formed. Two such biradicals, 7 and 8, are possible in the cyclopentadiene system.



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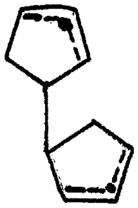


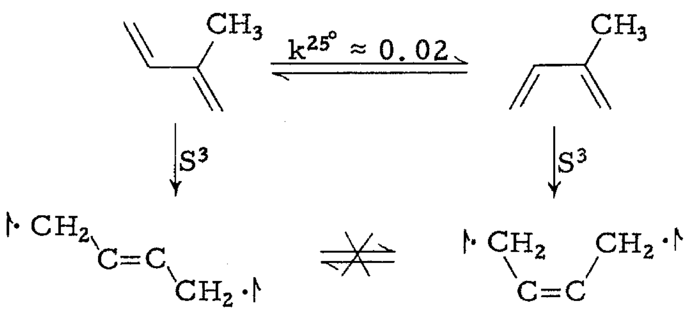
8

Clearly 1 and 2 are formed from 7 and 3 is formed from 8; consequently we see that 7 is formed about twice as fast as 8. This lack of selectivity reflects the fact that formation of either 7 or 8 in reaction 3 is highly exothermic. Closure of 7 and 8 to yield dimers is kinetically controlled and somewhat more selective than formation of the first bond. Due to the stepwise nature of the reaction, as demanded by the necessity for spin inversion in the biradical, the observed dimers do not correspond to those predicted by the rules elucidated recently by

Woodward and Hoffman for concerted cycloaddition reactions of dienes (8, 9). The failure to observe other products theoretically derivable from 7 and 8 may be due to their rearrangement under the conditions of the sensitized dimerization; however, sensitized dimerization of cyclopentadiene at −40° yielded no new dimers (10).

Dimerization of the acyclic diene, isoprene, gives seven products, 4 + 5, and in this case there is a regular variation of the amount of cyclohexenes formed, $\Sigma = 5/4 + 5$, with the triplet energy of the sensitizer. A plot of Σ against the triplet energy of the sensitizer is given in Figure One.

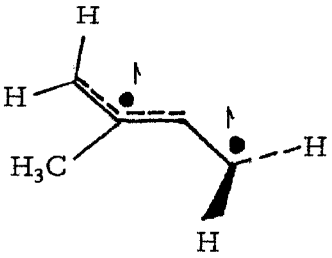
The dependence of Σ upon sensitizer triplet energy was explained by Liu and Hammond (3, 6) as being due to excitation of isoprene from both the s-*cis* and s-*trans* conformations of the ground state diene. Although these conformers are in rapid rotational equilibrium in the ground state, triplet states formed from them are configurationally stable because of the partial double bond between the central carbons of the diene system. Thus, excitation of s-*cis* isoprene gives the *cis*-triplet, 9, while excitation of s-*trans* isoprene gives the *trans* triplet, 10.



10

9

Although classical theories of energy transfer suggest that 9 and 10 be produced initially with the planar configuration of the ground state, the planar forms of these triplets probably have very little configurational stability and rapidly undergo rotational relaxation by twisting one of the terminal methylenes to give the perpendicular triplets 11 and 12.



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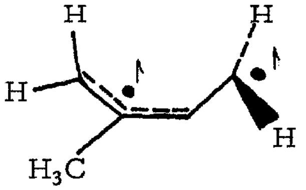
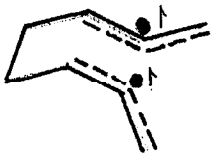


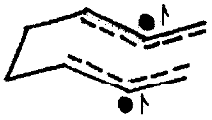
12

The perpendicular forms are predicted by theoretical calculations (11) and indicated by experimental results in fairly similar systems (12) to be of considerably lower energy than the planar forms of the triplets. All available evidence also suggests that rotational relaxation processes of this kind occur at rates much greater than those of other reactions of the triplets (12). Consequently, the diene triplets which become kinetically free probably have the perpendicular conformation regardless of the energy of the sensitizer which excited them.

Because of the overwhelming excess (98%) of s-trans isoprene in solution at room temperature, only two intermediates are important as dimer precursors. These are the biradicals 13 and 14, formed respectively by reaction of *cis* and *trans* triplets with s-*trans* ground state isoprene.



13



14

methyl groups not indicated

The allylic radical systems should maintain their stereochemistry during the lifetimes of 13 and 14 and it is, therefore, to be expected that the products derived from both intermediates should be characteristic of the monomer triplet from which they were formed.

The three cyclobutanes obtained from isoprene could be derived from either 13 or 14, but the cyclohexenes, since they have *cis* double bonds, should probably be produced only from 13 which has an incipient *cis*-double bond. Formation of the cycloöctadienes, which contain two *cis*-double bonds presents a special problem. The amounts of these compounds produced exceeds that which could be formed from intermediates derived from reaction of *cis*-triplets with s-*cis* ground state diene. Furthermore, formation of the cycloöctadienes is correlated with formation of cyclobutanes. Possibly the cycloöctadienes are derived from thermal rearrangement of unstable substances such as *cis*-*trans* or *trans*-*trans*-1, 5-cycloöctadiene or *cis*-1, 2-divinylcyclobutanes, all of which are possible products of cyclization of 13 and/or 14. Liu and Hammond (3, 6) concluded from the above argument that, subject to some reservations about cycloöctadiene formation, Σ gave a measure of the relative number of cis triplets produced by a given sensitizer.*

The energy necessary to produce the planar trans triplet of isoprene was found to be 59 kcal/mole (6, 14) and the energy required to produce the cis-triplet was estimated [using cyclohexadiene (14) as a model s-cis diene] to be 53 kcal/mole (6).

Previous studies of triplet energy transfer in solution indicated that as long as the triplet energy of the sensitizer exceeds by 3-5 kcal/mole or more that necessary to excite a substrate, energy transfer to that substrate will proceed at the diffusion controlled rate (15, 16). When this is the case the dimer ratios observed will depend only upon the relative amounts of the two ground state conformers in the equilibrium mixture and upon the decay processes of the diene triplets. There should then be observed a "high energy region" in which all sensitizers give the same Σ. Experimentally, it is found that all sensitizers with triplet energies exceeding 60 kcal/mole do in fact give identical Σ's.

For sensitizers having excitation energies less than 60 kcal/mole, energy transfer to the transoid conformer yielding the planar trans triplet is endothermic and the rate for this process will drop, resulting in an increasingly selective excitation of the s-cis conformer

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*This does not mean that cyclobutanes cannot be produced from **13**, just that all cyclohexenes come from **13**.

as the energy of the sensitizer decreases. This again is confirmed by experiment; Σ increases for sensitizers with energies below 60 kcal/mole.

As the sensitizer energy falls below 53 kcal/mole, production of both planar triplets becomes endothermic and the rates of production of both should decrease sharply, with the ratios of excitation rates tending to a limiting value of the order exp(-7000/RT). This prediction is not confirmed; Σ does not become constant, but rather decreases for sensitizers having energies below 50 kcal/mole, and approaches in the low energy limit a value similar to that obtained with high energy sensitizers. It is, therefore, clear that some process(es) in addition to energy transfer of the Franck-Condon type must operate to cause the observed diene dimerization.

At the present time, the most likely process by which dimerization is effected by low energy sensitizers appears to be nonvertical transfer of triplet excitation energy to both s-*cis* and s-*trans* diene conformers, with movement of diene nuclei during the instant of energy transfer thereby producing the perpendicular triplets directly. Such a mode of energy transfer solves the problems of energetics because it is no longer necessary to pass through the high energy planar forms of the triplets. Production of **13** and **14** by low energy sensitizers would also explain why, although Σ decreases, the ratios of products apparently derived from particular biradicals (**13** or **14**) remain the same as in the high energy case. Nonvertical energy transfer violates the Franck-Condon principle and has been an unpopular

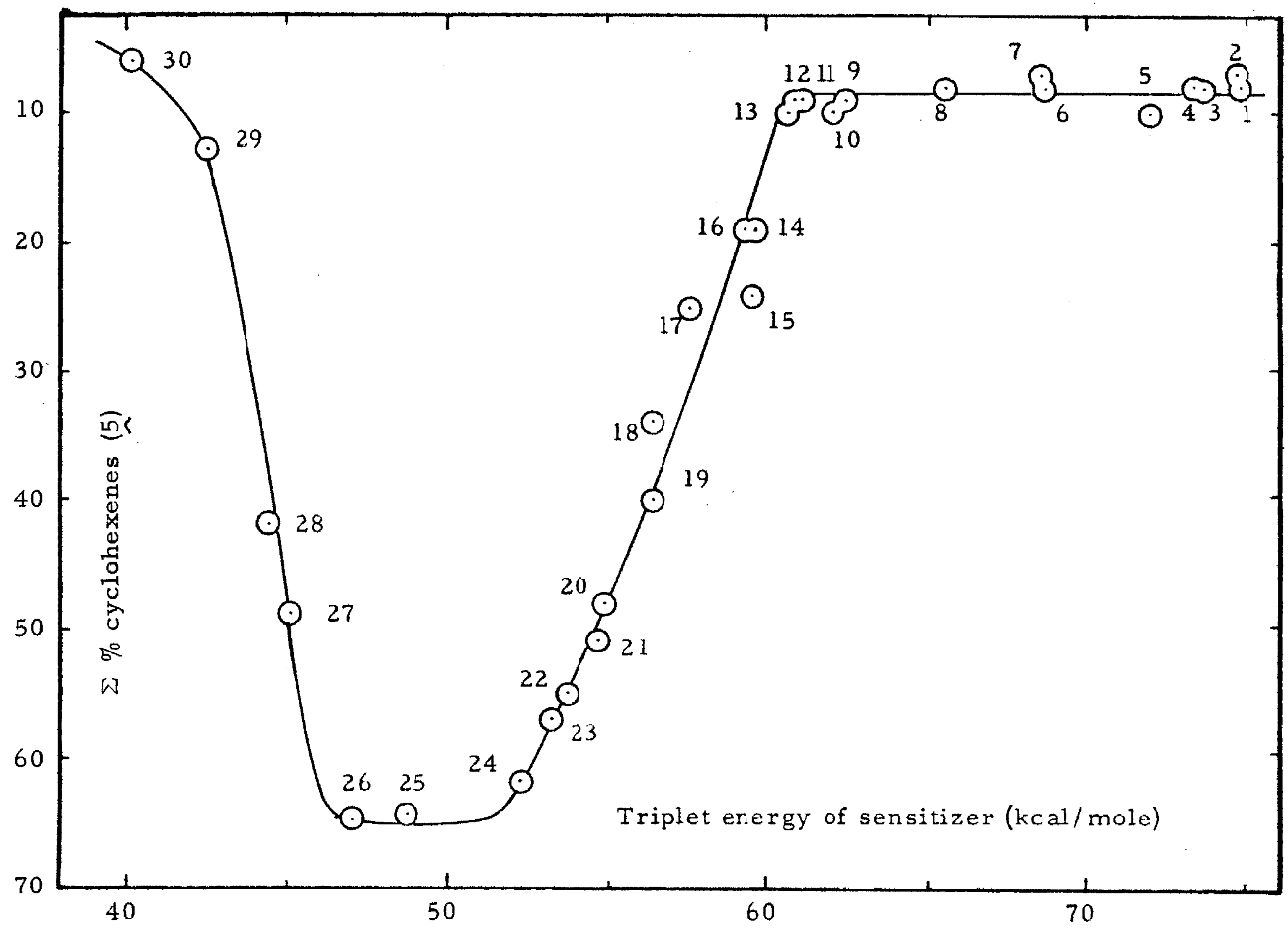


Figure I. Isoprene dimer composition vs triplet energy of sensitizer concept even in the laboratory in which it was first postulated. It has, however, been observed if not understood, in a number of systems and appears to be a bona fide electronic process of a new type. In the isoprene system nonvertical energy transfer has been considerably more successful in accommodating the data than any other explanation yet proposed.

Several other acyclic diene dimerizations have been investigated (6). Butadiene, piperylene and 2, 3-dimethylbutadiene all give dimer mixtures with compositions depending upon the sensitizer triplet energy in a way consistent with the interpretation given above.

Quantum yields for sensitized dimerization of isoprene as a function of diene concentration with and without added quenchers, were reported by Liu (6). The results shed considerable light on the rate of reaction 3, as compared to the rate of unimolecular decay of the isoprene triplet (reaction 5) and quenching of the same triplet by external quenchers, in Liu's case, azulene (reaction 6).

$$(5) \quad (C{=}C{-}C{=}C)^3 \longrightarrow C{=}C{-}C{=}C$$

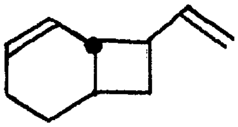
$$(6) \quad (C{=}C{-}C{=}C)^3 + az \longrightarrow az^3 + C{=}C{-}C{=}C$$

Changes in diene concentration do not alter the ratios of dimers produced; consequently, k_3/k_5 must be the same for both cis and trans triplets. If k_6 is assumed to be the same for both the cis and trans triplets, the quantum yield for dimerization can then be written as

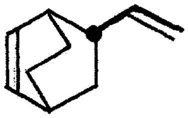
$$(7) \quad \frac{1}{\Phi} = \frac{1}{\underline{a}}\left(1 + \frac{k_5 + k_6[az]}{k_3[\text{isoprene}]}\right)$$

where a is the intersystem crossing yield of the sensitizer (17). Actually, experimentally it was shown that k_6 is slightly greater for the cis-triplet; the effect is, however, small and is ignored here. Liu (6) found that k_5/k_3 was about 20 moles/ℓ. and that $k_6/k_3 = 1.2 \times 10^3$. The rate of reaction 6 appears to be independent of solvent viscosity and cannot therefore be diffusion controlled (19). This result does not require that the energy of the relaxed isoprene triplets be lower than that of azulene because quenching of the perpendicular triplets is a nonvertical process. Using the ratios k_6/k_3 and k_5/k_3 and the fact that k_6 is less than the diffusion controlled limit, it follows that k_5 cannot exceed 10^7 sec.$^{-1}$; hence the lifetime of the isoprene triplet must be at least 10^{-7} sec. and is perhaps longer. A short lifetime is in agreement with theoretical arguments that perpendicular triplets ought to have very short lifetimes due to interactions of ground and excited state potential surfaces (20).

An interesting extension of photosensitized diene reactions is the cross addition of butadiene and cyclohexadiene (5, 6). Using mixtures containing 90% butadiene, Liu and Hammond isolated three cross adducts, two of which were identified as 17 and 18. The former is the only known example of a trans-fused ring system arising from reactions of diene triplets.



17

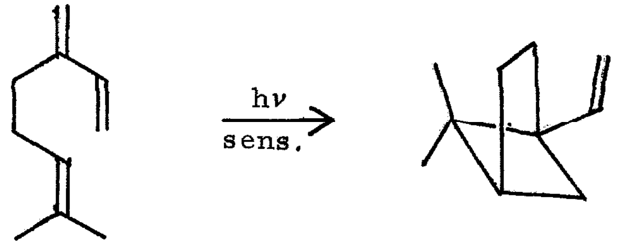


18

If the amount of butadiene is increased to 99% and a sensitizer such as fluorenone is employed to give predominantly excitation of s-cis butadiene, a fourth adduct is formed. In the 90% mixture, the ratios of cross adducts do not depend upon the triplet energy of the sensitizer, although changes are observed in the ratio of total adducts to diene dimers.

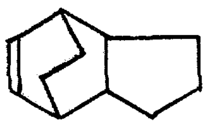
Most of the data available for this system are accommodated by assuming intermediacy of either or both cyclohexadiene and butadiene triplets in adduct formation, but the details of the reaction are not well understood. As the energy of the sensitizer falls below 60 kcal/mole, the energy necessary to promote s-trans butadiene to its planar triplet, the predominant triplet species in the 9:1 mixture presumably changes from trans butadiene triplet to cyclohexadiene triplet. This would not change the ratio of the adducts because addition of the triplet of either diene to the ground state of the other will give the same intermediate. There is, however, no guarantee that the triplets of both dienes actually do add to the ground state of the other; exclusive reaction by either path is consistent with the data. Formation of the fourth adduct in the 99:1 mixture was explained as arising from reaction of cis-butadiene triplets with cyclohexadiene. There seems no reason to believe that trans-butadiene triplets cannot also react with ground state cyclohexadiene.

Other substances can also react with diene triplets to give adducts. The most spectacular reaction is the photosensitized closure of myrcene, **19**, to give 1-vinyl-6,6-dimethylbicyclo[2.1.1]hexane, **20**.



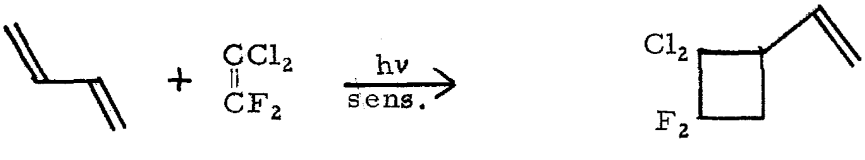
19 20

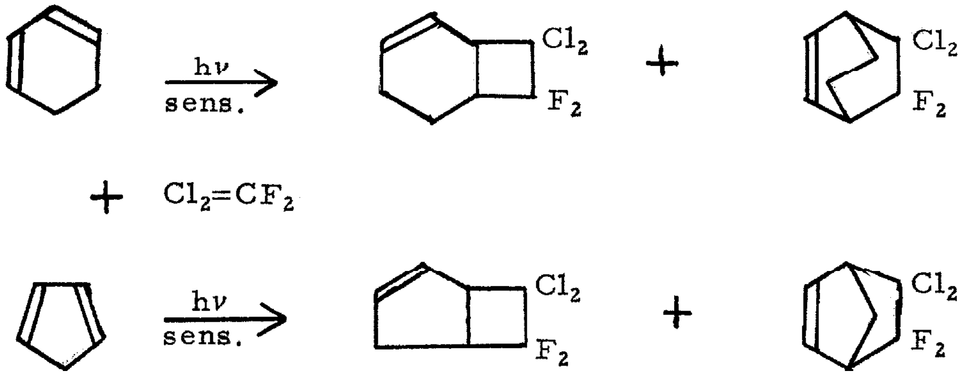
Attempts to extend this reaction to other systems have not proved very successful. Intermolecular additions of diene triplets to simple olefins have been confirmed only for addition of cyclohexadiene to give, among other products, an undecene tentatively assigned structure 21 (6).



21

Bartlett and Turro (21) have investigated the addition of diene triplets to 1, 1-dichloro-2, 2-difluoro ethylene. The triplets of cyclohexadiene, cyclopentadiene and butadiene all add to the olefin despite the fact that it is thermally inert toward these substances.





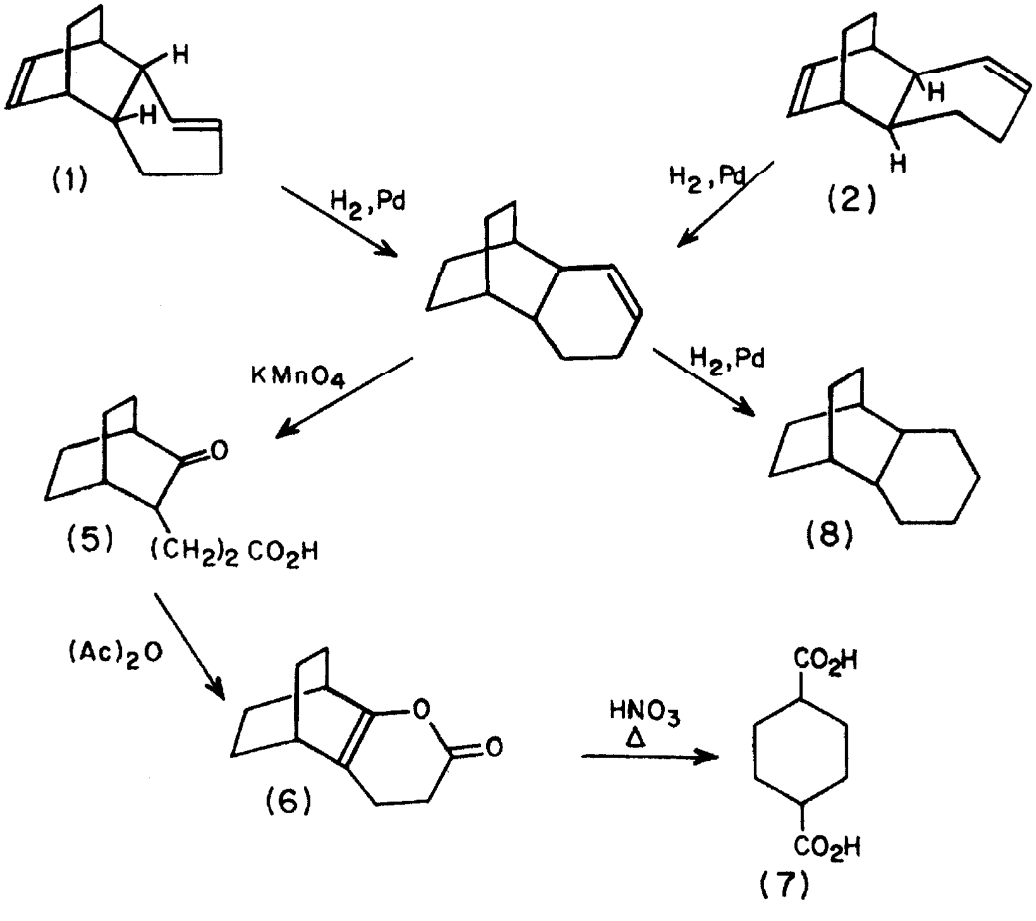
Some quantitative study was made of the addition of the cyclic dienes; under the experimental conditions only the diene triplets are produced and, as would be expected, the relative amounts of adducts and the ratio of adducts to dimers of the diene are independent of the triplet energy of the sensitizer.

We present here the results of a study of the thermal and photosensitized dimerizations of cyclohexadiene together with a study of the thermodynamic properties and kinetic behavior of the products.

RESULTS AND DISCUSSION

Thermal Dimerization of Cyclohexadiene

Alder and Stein reported isolation of a single product from the thermal dimerization of 1, 3-cyclohexadiene at 200° (22). The structure of the dimer was shown to be either 1 or 2 by the following chemical evidence



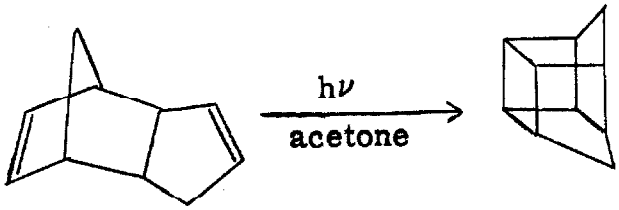
The dimerization was repeated and analysis of the products by vapor phase chromatography using Apiezon J columns showed two dimers in a 4:1 ratio. Since the analytical procedure of Alder and Stein could not have shown that **1** and **2** were different compounds because of the initial hydrogenation step, it was suspected that the two dimers observed were **1** and **2**. Hydrogenation of the dimers separately lead to the same saturated hydrocarbon, tricyclo[6.2.2.$0^{2,7}$]dodecane (**8**), confirming that the dimers are the *endo*-*exo* isomer pair **1** and **2**.

The major thermal dimer has b.p. 226° (746 mm.), $\underline{n}^{20}D$ 1.5250. Its n.m.r. spectrum in carbon tetrachloride consists of a quintet centered at τ 4.04, a broad region with maximum at τ 4.58, and broad partially resolved bands from τ 7.61 to 9.00. The relative areas of the three groups are 2:2:12. The infrared spectrum in chloroform shows principal maxima at: 3020 (s), 2920 (s), 1645 (w), 1440 (m), 1250 (m), 1160 (m), 1070 (m), 940 (m) and 865 (m) cm.$^{-1}$.

The minor thermal dimer has b.p. 229° (746 mm.), $\underline{n}^{20}D$ 1.5265. The n.m.r. spectrum in carbon tetrachloride consists of a quintet centered at τ 3.72, a broad band from τ 3.72 to 4.65, and a broad, partially resolved band from τ 7.70 to 9.25 in the saturated region with relative areas of 2:2:12. The infrared spectrum in chloroform shows maxima at: 3020 (s), 2920 (s), 1610 (w), 1440 (m), 1365 (m), 1250 (m), 1173 (m), 1075 (m) and 880 (m) cm.$^{-1}$.

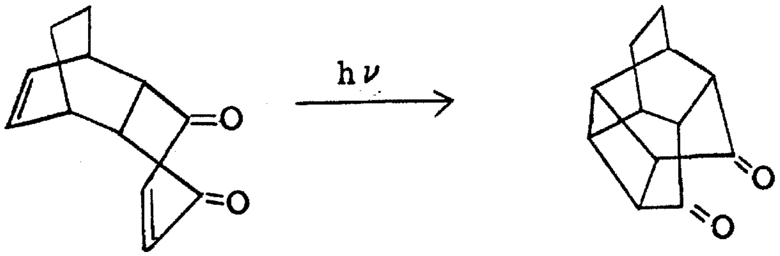
The major thermal dimer was assigned *endo* stereochemistry on the basis of the Alder rule (23). Because the minor product constitues 20% of the product mixture, application of the Alder rule to this system might be thought of questionable validity. Addition of vinyl acetate to cyclohexadiene, however, has recently been reported to give 86% endo- and 14% exo-5-acetoxybicyclo[2.2.2]octene-2, providing at least one example of an abnormal Diels-Alder reaction in which the Alder rule predicts the principal product in a mixture (24). Experiments were carried out to confirm that the observed product ratio actually represents relative rates of formation of the dimers in the primary dimerization process. Both dimers were shown to be stable to isomerization under the dimerization conditions and even for very low conversion of diene to dimer (<0.5%), the ratio of dimers was 4:1. Clearly, the observed product ratio is kinetically controlled in the original dimerization process.

Efforts to provide chemical evidence regarding the stereochemistry of the dimers have failed. Unlike endo-dicyclopentadiene, which closes readily upon irradiation in acetone to yield a cage isomer (25), neither of the dicyclohexadienes forms a cage isomer upon irradiation either in acetone, or in benzene solution with sensitizers such as benzophenone, β-acetonaphthone, benz[a]anthracene, eosin or 9,10-dibromoanthracene.



An attempt to synthesize *endo*-dicyclohexadiene from the known adduct of benzoquinone and cyclohexadiene (**9**) (26) was unsuccessful, but led to discovery of a very facile light-induced closure reaction. Upon irradiation either in solution or in the solid state, **9** is converted to **10** with high quantum efficiency.

The structure **10** is assigned to the closure adduct on the basis of its infrared spectrum, which shows a saturated carbonyl (1757 cm.$^{-1}$), the absence of carbon-carbon double bonds, and the presence of cyclobutane ring vibrations (935, 917, 800 cm.$^{-1}$). Because of problems of solubility and thermal instability, it has not been possible to measure the molecular weight of **10** and dimeric structures cannot be rigorously excluded. Structure **10**, however, is analogous to that assigned by Cookson, *et al.*, to the product obtained by photoisomerization of the adduct of cyclopentadiene and benzoquinone (27).

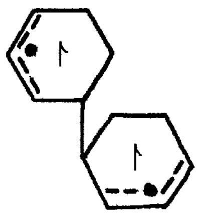


9 **10**

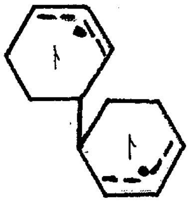
Products of the Photosensitized Dimerization of Cyclohexadiene

Irradiation of degassed solutions of cyclohexadiene and various sensitizers in benzene or isopentane solution resulted in 90% conversion to three dimers which were produced in approximately 3:1:1

ratio. A fourth dimer was produced in trace amounts. The dimers formed should by analogy with other diene dimerizations be derived from 11 and 12.

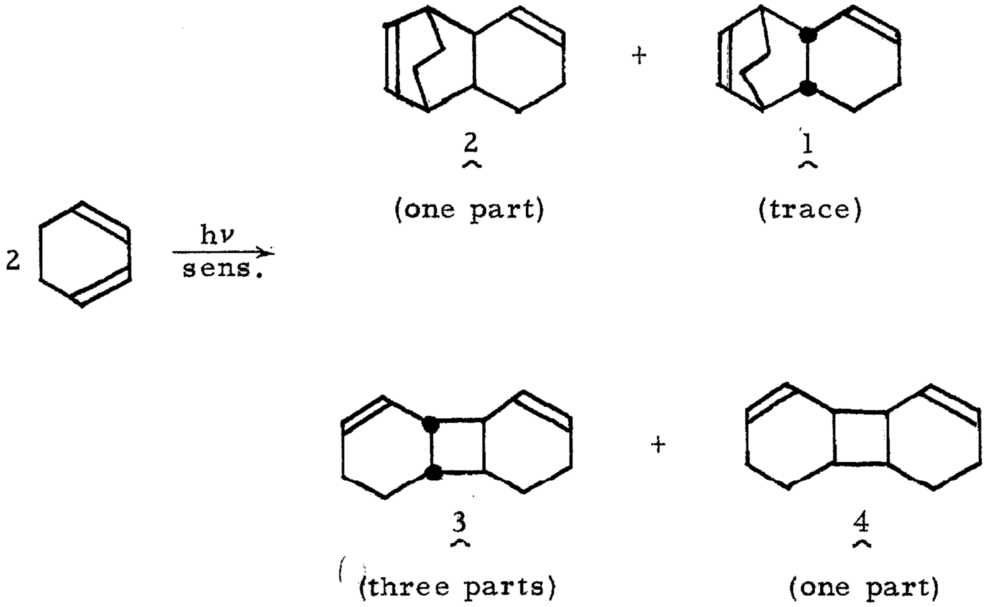


11



12

Structural evidence presented below indicates that the photosensitized reaction should be represented as



Dimers 1 and 3 can arise from 11 and 2 and 4 can arise from 12.

One of the minor photodimers was shown to be *exo*-dicyclohexadiene (**2**) by comparison with the thermal dimer. Comparison of v.p.c. retention times indicates the trace product is probably *endo*-dicyclohexadiene (**1**).

The infrared and n.m.r. spectra of the major photodimer are consistent with, but not definitive for, structure **3**. A partial structure proof was carried out by comparison with hydrocarbons obtained by chemical modification of the photoadducts formed from 2-cyclohexen-1-one and cyclohexene. Irradiation of degassed mixtures of the latter two compounds in Pyrex vessels results in 70% conversion to a mixture of four isomeric adducts, all having the composition $C_{12}H_{16}O$. The infrared spectrum of the mixture shows characteristic carbonyl absorption bands and bands between 850 and 1000 $cm.^{-1}$ such as are usually associated with vibrations of cyclobutane rings. We presume that the products are stereoisomers having structure **12**. The mixture of ketones reacted with 2,4-dinitrophenylhydrazine to give four dinitrophenylhydrazones which were separated by chromatography on silica gel. Treatment of the mixed ketones with sodium borohydride gives a mixture of isomeric alcohols, **13**. Conversion of the alcohols to the alkenes, **14**, could be accomplished either by acetate pyrolysis at 375° or by xanthate pyrolysis at 200°. From the xanthate pyrolysis, four isomers of **14** were obtained in 2:1:10:2 ratios.* The alkenes were

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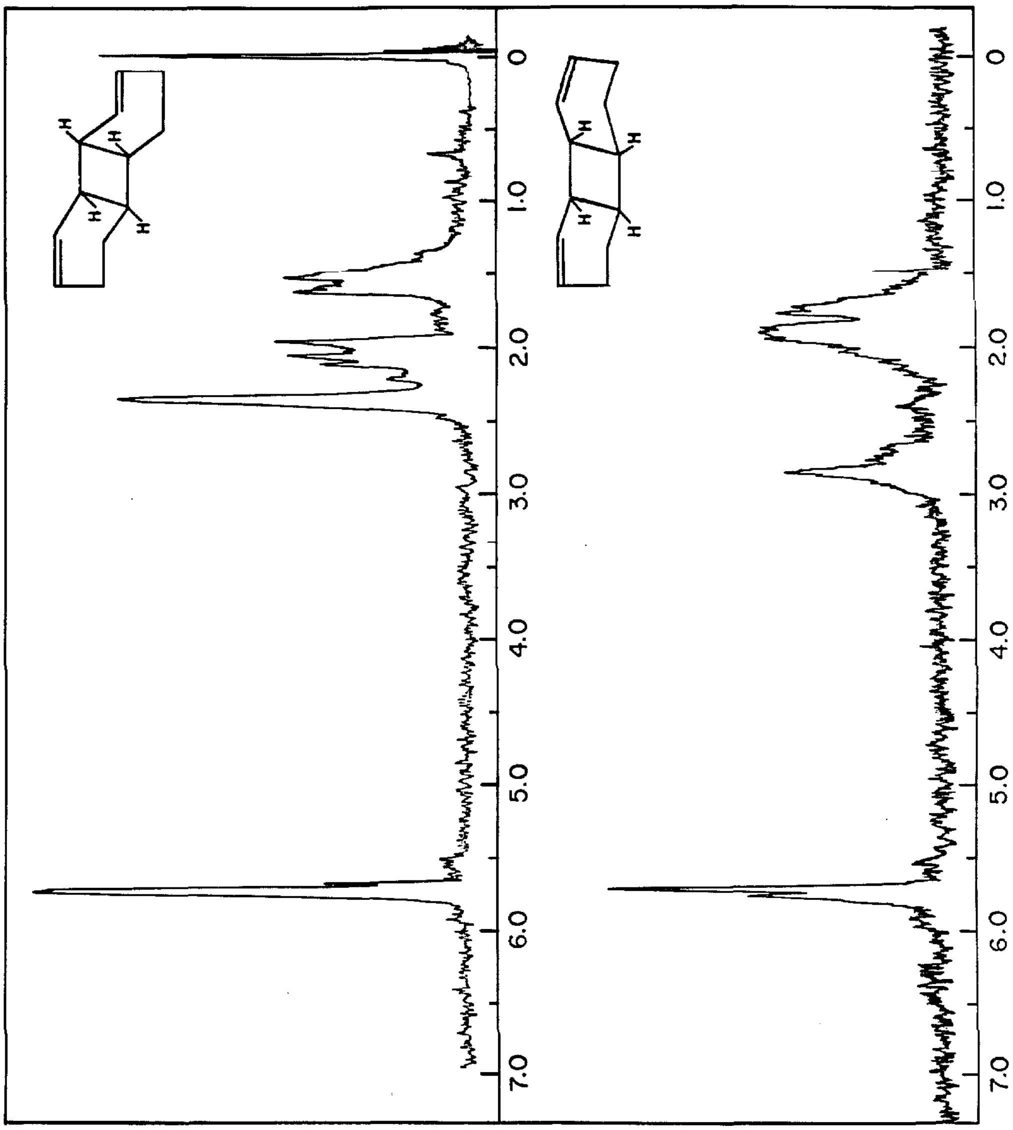
*Acetate pyrolysis gave the same four olefins in slightly different ratio.

separated by preparative v.p.c. with Apiezon J columns. Hydrogenation of the major isomer of the alkenes gave a saturated hydrocarbon 15, whose n.m.r. and infrared spectra were identical with those for the product of total hydrogenation of the major photodimer of cyclohexadiene.

The above reactions would seem to establish rigorously the presence of a cyclobutane ring in the major photoproduct. The asymmetrical disposition of the double bonds may be inferred from analogy to other photosensitized dimerizations of conjugated dienes and must be assumed to account for the thermal rearrangement of the compound (*vide infra*).

The third photodimer was assigned the stereoisomeric cyclobutane structure, 4. The n.m.r. spectrum of the compound is shown in Figure I. The sample used was known, by v.p.c. analysis, to contain small amounts of 2. The strong signal centered at τ 7.12 corresponds to the chemical shift characteristic of protons attached to cyclobutane rings. The broad bands lying between τ 7.8 and 8.4 are assigned to the methylene groups, two allylic and two nonallylic, in 4. The spectrum is rather similar to that of 3, which is also shown in Figure One. However, the latter shows a larger separation of the methylene resonances. The spectrum of 3 also contains a very closely grouped multiplet at τ 7.65. This is now assigned to protons attached to the four-membered ring, although the high-field position led us, at one time, to question the assignment of the structure of 3 and prompted initiation of the partial chemical proof of structure described above.

FIGURE I: N. m. r. spectra of (a) _trans_-_cis_-_trans_-tricyclo [6, 4, 0, $0^{2,7}$]dodeca-3, 11-diene and (b) _cis_-_cis_-_cis_ tricyclo[6, 4, 0, $0^{2,7}$]dodeca-3, 11-diene in carbon tetrachloride. The first spectrum gives parts per million relative to TMS internal standard, the second relative to TMS external. Both spectra recorded on Varian A-60 Nuclear Magnetic Resonance Spectrometer.


H
H
H
H
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
H
H
H
H
0
1.0
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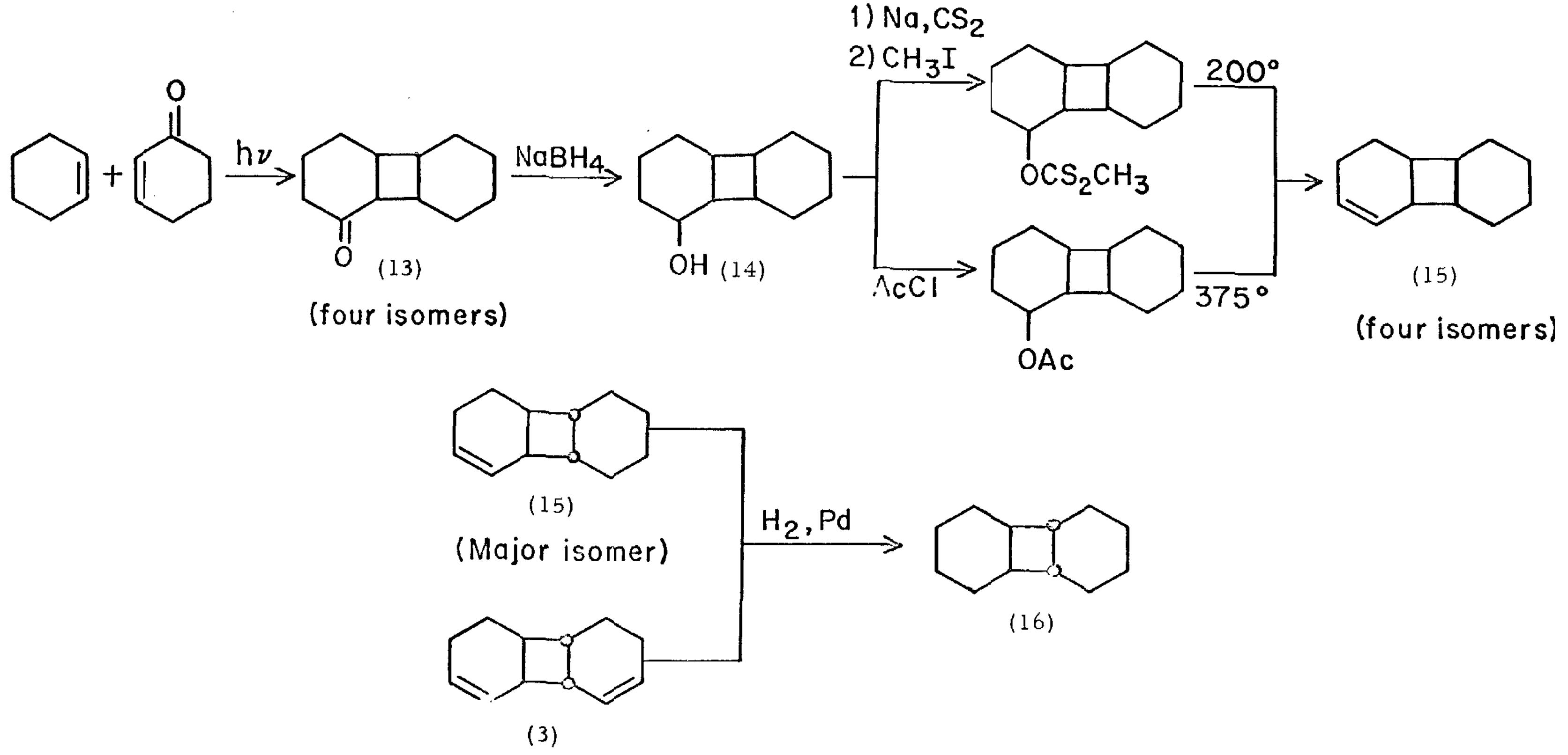
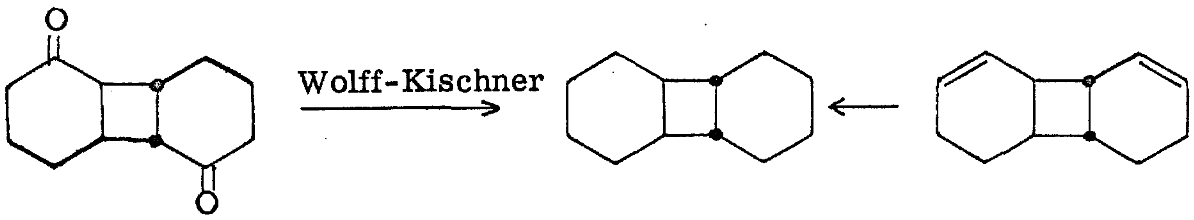
4.0
5.0
6.0
7.0

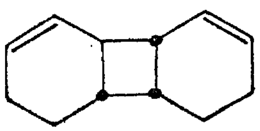

hν
(13)
(four isomers)
NaBH4
(14)
1) Na, CS2
2) CH3I
AcCl
OCS2CH3
OAc
200°
375°
(15)
(four isomers)
(15)
(Major isomer)
(3)
H2, Pd
(16)

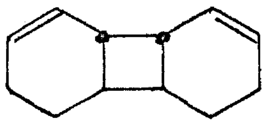
The infrared spectrum of 4 shows, *inter alia*, maxima at 1015, 975 and 850 cm.$^{-1}$ such as are normally found in the spectra of cyclobutane derivatives. Similar bands are found in the infrared spectrum of 3 at 1006, 930 and 865 cm.$^{-1}$.

After the partial structure proof given above for 3 had been completed, a more complete proof of structure was afforded by proving the identity of 16 with the Wolff-Kischner reduction product of the cyclohexenone dimer 17 which is known to have the *trans*-*cis*-*trans* ring fusion (29).

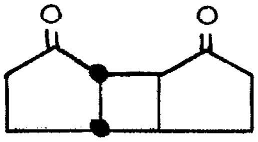


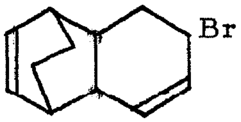
No information was obtained about the stereochemistry of the ring fusions in 4, but the stability of this compound (*vide infra*) leads us to prefer the all *cis* fused over the two possible *trans* fused isomers.



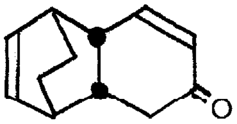


It was hoped that an independent proof of the stereochemistry of 17 could be provided by its synthesis through ring expansion of the known *trans*-*cis*-*trans*-tricyclo[5.3.0.$0^{2,6}$]decan-3,8-dione, 18. Since addition of diazomethane to 18 had been reported unsuccessful (29), 18 was treated with dimethylsulfoxinium methylide by the method of Corey (30). Reaction of 18 with the ylide under nitrogen in dimethylsulfoxide gave no volatile products and it was not possible to recover any of the starting material.


18



19



20

Treatment of a mixture of 1 and 2 with N-bromosuccinimide gave the bromodicyclohexadienes 19; however, treatment of 19 with potassium *t*-butoxide in dimethylsulfoxide gave only starting material and it was similarly not possible to prepare 20 by treating 19 with aqueous sodium dichromate and mineral acid.[*]

Several attempts were made to oxidize the cyclobutane derivatives 3 and 4 to biphenylene. All were unsuccessful.

Mechanism of the Photosensitized Dimerization

Without specifying the detailed nature of any of the reactions, we presume that formation of cyclohexadiene dimers in the sensitized

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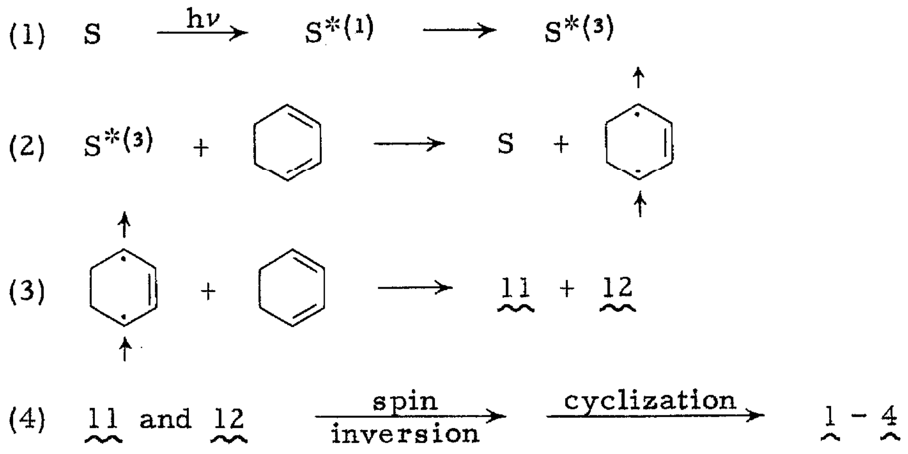
[*] 2-Cyclohexenone has been prepared from 3-bromocyclohexene in this way (*vide infra*, Experimental Section).

reaction occurs by the usual four step sequence



Only cis-cyclohexadiene triplets are possible and it is found that the ratio of dimers produced is independent of the sensitizer over a wide range of sensitizer triplet energies (31). Representative data are given in Table I. It is important to note that sensitizers having triplet excitation energies significantly less than that measured for cyclohexadiene [53 kcal/mole (14)], still give the same ratio of products. We infer from this observation that all sensitizers produce the same cyclohexadiene intermediates, presumably cyclohexadiene triplets.

Although all sensitizers give cyclohexadiene dimers in the same ratio some give also addition products with the diene. Duroquinone was reported by Schenck (32) to give a 1:1 adduct with cyclohexadiene — a result we confirm. 2-Cyclohexenone and 2-cyclopentenone had been reported not to add to cyclohexadiene (7), but do, in fact, give adducts when the enone is in excess. One other case of addition of sensitizer to diene is mentioned in Table I.

TABLE I

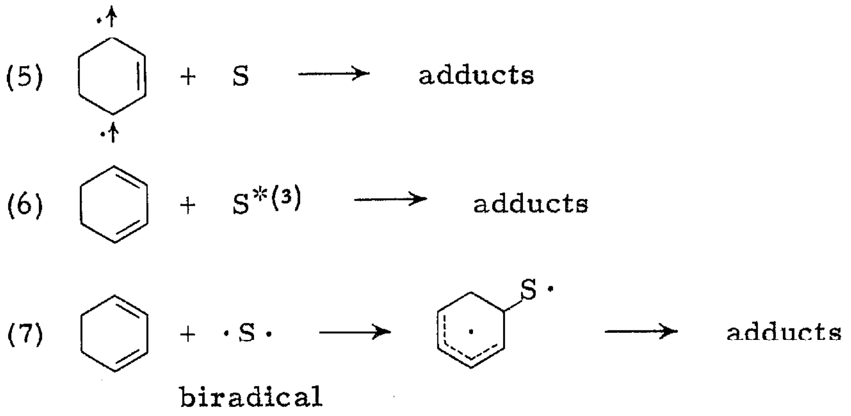
Product Ratios from Photosensitized Dimerization of Cyclohexadiene

Sensitizer	E_T (kcal/mole)	$\Sigma(\underset{\frown}{2} + \underset{\frown}{3})^a$ (%)
Benzophenone	69	89
Phenanthrene	61	89
2-Acetonaphthone	59	84
9-Fluorenone	53	89
Duroquinone[b]	53	84
1, 2, 5, 6-Dibenzanthracene	53	85
Benzanthrone	47	87
Cyclohexenone	?	85
Benzophenone imine[b]	?	92
Mesityl oxide	low	no reaction

[a] All measurements at 25°C irradiation temperature. Analysis on low temperature v. p. c. with Apiezon J columns.

[b] Observed other products in addition to cyclohexadiene dimers.

It is not clear that all cases of addition of sensitizer to diene involve the same mechanism. There are several mechanistic possibilities, including addition of diene triplets to sensitizer (reaction 5), addition of sensitizer triplets to diene (reaction 6), direct excitation of a ground state complex of diene and sensitizer with subsequent reactions from an excited state of the complex, and finally, formation of an adduct between a biradical formed from the sensitizer and the diene (reaction 7).



The last is, of course, the Schenck mechanism (*vide supra* page 1, footnote) and was postulated to explain the behavior of the duroquinone-cyclohexadiene system. Evidence presented below suggests that in the case of 2-cyclohexenone at least, addition of enone to diene occurs by reaction of diene triplets with the ground state of the enone.

Formation of diene-enone adducts is competitive with dimerization of the diene only when the enone is present in large excess. The ratio k_3/k_5 is of the order of 10. Representative data are given in Table II. Such variations as these are not satisfactorily explained except by assuming that reaction 5 and/or 7 accounts for at least part

TABLE II

Cyclohexadiene with 2-Cyclohexenone and 2-Cyclopentenone

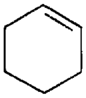
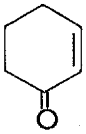
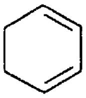
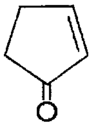
Reagents (volume fraction)				Products Observed
				
0	1	20	—	C
0	1	10	—	C
0	1	5	—	C + D
0	1	1	—	C + D
0	10	1	—	C + D Note a
5	1	0	—	A + B
4	1	1	—	A + C + trace B
5	1	3	—	A + C + trace B
5	1	5	—	C + trace A
0	—	25	1	C
0	—	10	1	C
0	—	2	1	C + E
0	—	1	1	C + E
0	—	1	2	C + E + F

Table II (continued)

Reagents	Products Observed
5 - 1 1	C + G
4 - 1 2	C + trace G
5 - 1 5	C

A = cyclohexene-cyclohexenone adducts (see text)

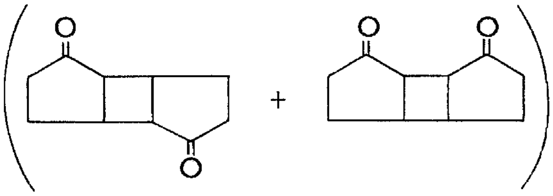
B = cyclohexenone dimers (reference 29)

C = cyclohexadiene dimers (see text)

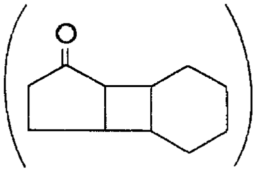
D = cyclohexadiene-cyclohexenone adducts (structures unknown)

E = cyclohexadiene-cyclopentenone adducts (structures unknown)

F = cyclopentenone dimers



G = cyclohexene-cyclopentenone adducts



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[a] Used 0.2 M 2-acetonaphthone as sensitizer.

of the adduct formation. Reaction 6 is eliminated altogether by the observation that adduct formation does not occur when a large excess of diene is used. Reaction 7 is not a satisfactory representation of the addition process because 2-acetonaphthone sensitizes the addition of 2-cyclohexenone to cyclohexadiene. The following reasoning indicates that the only active intermediate in the addition sensitized by acetonaphthone is the triplet of 1, 3-cyclohexadiene. The singlet energy of acetonaphthone is appreciably less than that of cyclohexenone and, therefore, transfer of singlet energy is unlikely. In any case, production of cyclohexenone singlets would lead to the appearance of cyclohexenone dimers under the conditions of our experiment. Since no dimers of cyclohexenone were observed, we presume no excited singlets of cyclohexenone were produced. Thus, energy transferred from 2-acetonaphthone to other components of the mixture must be triplet energy. Although the energy of the relaxed cyclohexenone triplet is of the order of 62 kcal/mole (33), the planar triplet has almost certainly a much higher energy. Even when the enone, as in our experiment, is present in tenfold excess over the diene, energy transfer from acetonaphthone to the diene should be preferred.* The

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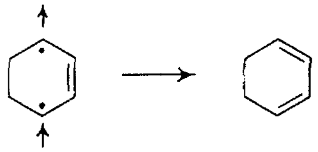
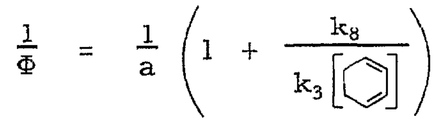
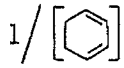
*This is perhaps the weakest part of the experiment. At the time the experiment was performed, it was thought that the triplet energy of 2-cyclohexenone was of the order of 72 kcal/mole, in which case the argument given in the text is quite solid. It is now evident that this is not the case; however, the relaxed cyclohexenone triplet is probably considerably twisted from the ground state configuration and not populated very rapidly; because the cyclohexadiene triplet is formed at nearly the diffusion-controlled rate, we feel that its formation will predominate under our conditions.

measured rate of quenching of acetonaphthone triplets by cyclohexadiene is about 4×10^9 ℓ./m.-sec. (34). The predominant reactive species in the addition reaction sensitized by 2-acetonaphthone must then be the cyclohexadiene triplet. The data are then correlated satisfactorily only by reaction 5.

If unimolecular decay of diene triplets (reaction 8) is included in the mechanistic scheme and the concentration of the diene is high enough to insure quenching of all the sensitizer triplets, then the dependence of the quantum yield for dimerization upon diene concentration is given by equation 9.

(8)


(9)


where a is the intersystem crossing yield of the sensitizer. For the linear diene isoprene, it will be remembered that Liu (6) found a linear variation of $1/\Phi$ with 1/  for diene concentrations up to pure isoprene.

For dimerization of cyclohexadiene the quantum yields for a given sensitizer achieve a limiting value for diene concentrations greater than 0.2 M, indicating the ratio k_8/k_3 [diene] is about 10^3 less for cyclohexadiene than for isoprene. Some quantum yields for cyclohexadiene dimerization effected by various sensitizers are given in Table III.

Why reaction with ground state diene as opposed to unimolecular decay should be so much more favored for cyclohexadiene than isoprene triplets is not clear. The difference could be due either to increased lifetime or increased reactivity of the cyclic diene triplet. It has been argued by Potts (20) that the cyclic triplet cannot profitably distort because ring strain largely cancels the gains made by reducing electron interactions. This would lead to increased lifetime of the cyclic as opposed to the acyclic triplet because of the absence in the former of the crossing of ground and excited potential surfaces which lead to the short lifetime of the latter. On the other hand, 2-cyclohexenone triplets evidently achieve considerable stabilization by some relaxation process which almost certainly involves some skeletal distortion, so it is not clear just how closely the ground and triplet state configurations of cyclohexadiene approximate each other. There seems then little basis for a priori predictions of the lifetime of the cyclohexadiene triplet. Similarly, it is difficult to make a priori estimates of k_3. If it is assumed that the isoprene triplet is, in fact, perpendicular and the cyclohexadiene triplet has a configuration similar to that of the ground state diene, then the latter should be a more energetic species and might perhaps, therefore, react more rapidly than the acyclic diene triplet. Of course this is pure speculation.

The quantum yields given in Table III present a very disturbing puzzle. Equation 9 demands that in the limit of high diene concentration, the quantum yield for dimerization equal the intersystem crossing yield of the sensitizer. In no instance has this been found to

TABLE III

Selected Quantum Yields for Photosensitized Dimerization of 1,3-Cyclohexadiene[a]

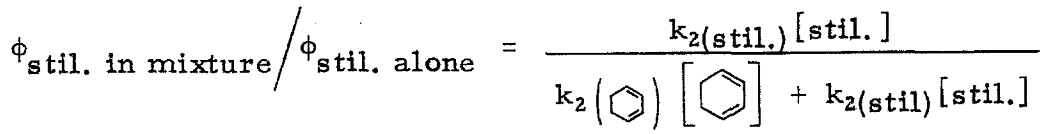
Sensitizer	E_T		ϕ_{dim}	ϕ_{ic}	k_q (in ℓ/m-sec.)
Benzophenone	68	0.2	0.90 ± 0.02	1.00	?
2-Acetonaphthone	59	0.2	0.62 ± 0.02	.84	4×10^9
1,2,5,6-Dibenzanthracene	52.5	0.2	0.10 ± 0.01	.85	3×10^8

[a] Reference 31.

be the case. With benzophenone about 10% of the incident quanta are wasted, with acetonaphthone, 25%, and with 1, 2, 5, 6-dibenzanthracene, 85%. This result cannot be due to failure to quench sensitizer triplets as in all cases measurements of k_2 indicate the rate of quenching of sensitizer triplets by cyclohexadiene to be at least three orders of magnitude greater than the measured rates of unimolecular decay of the sensitizer (34).

It could be argued that quenching due to impurities in the cyclohexadiene was responsible for the anomalous quantum yields. The presence of an impurity which quenched dibenzanthracene triplets at the diffusion-controlled rate could account for most of the measured rate of reaction 2 and then, in the quantum yield experiment, lead to the destruction of most sensitizer triplets before transfer of triplet energy to cyclohexadiene could occur. This possibility was excluded by the following experiment. Solutions containing dibenzanthracene, trans-α-methyl stilbene and cyclohexadiene were irradiated and quantum yields were measured for both isomerization of the stilbene and dimerization of cyclohexadiene. Under these conditions both the sum and ratio of quantum yields for the two processes could be exactly predicted using the relative concentrations of the two substrates together with the separately determined quantum yields for the photoreactions of the two substrates and the rates at which both quenched the triplets of dibenzanthracene, for example

(10)



$$\phi_{\text{stil. in mixture}} \Big/ \phi_{\text{stil. alone}} = \frac{k_{2(\text{stil.})}[\text{stil.}]}{k_2(⬡)\,[⬡] + k_{2(\text{stil})}[\text{stil.}]}$$

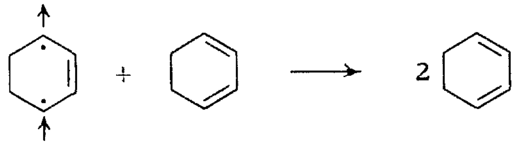
This result precludes the possibility that quenching by impurities is responsible for the low quantum yield observed for dibenzanthracene as sensitizer.

Our quantum yields were determined by monitoring the rate of production of cyclohexadiene dimers rather than the rate of disappearance of the monomeric diene. Consequently, it might be argued that side reactions such as abstraction of hydrogen from cyclohexadiene by benzophenone triplets are responsible for the quantum yield of less than unity obtained for dimerization effected by that sensitizer. No observed evidence supports this contention.

We discount the possibility that previously reported (18) intersystem crossing yields for the sensitizers used could be sufficiently in error to explain the observed discrepancies. The intersystem crossing yield reported for dibenzanthracene would, for example, have to be high by a factor of 8 in order to accommodate our results.

Another and more reasonable possibility is a bimolecular reaction of the diene triplet with the ground state diene which does not lead to dimer formation.

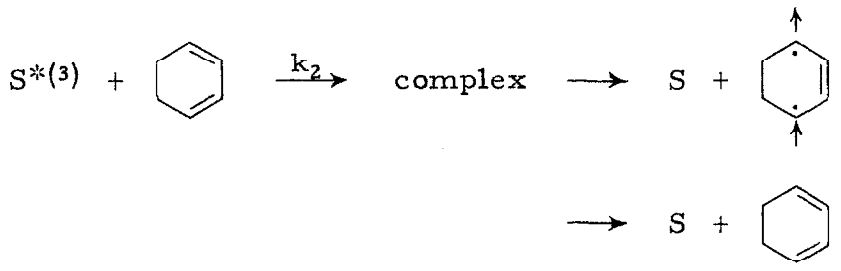
(11)



In essence reaction 11 represents "self-quenching" of cyclohexadiene triplets by cyclohexadiene. Self-quenching has been invoked to explain the results of photosensitized cis-trans isomerization of stilbene and there have been several reports of fluorescence from excited dimers (excimers) (6, 41). It should be noted, however, that formation of 11 and 12 must almost certainly be irreversible because of the single bond which is formed. The activation energy for cleavage of 11 or 12 would be great enough to insure that the probability of closure to products was unity. Hence, whatever the intermediate(s) in reaction 11, 11 and 12 cannot be candidates. The effect of reaction 11 would be to reduce the quantum yields for dimerization by the factor $k_3/(k_3 + k_{11})$. This poses a serious objection because unless $k_3/(k_3 + k_{11})$ depends upon the sensitizer, all sensitizers ought to give the same quantum yields for dimerization, $\phi = ak_3/(k_3 + k_{11})$. The quantum yields are, in fact, not identical but the observed product ratios are. This implys that the same triplets are ultimately produced by each individual sensitizer. Consequently, we feel that reaction 11 cannot alone explain the observed discrepancies.

At present, the most likely source of the energy wastage appears to be in the original energy transfer from sensitizer triplet to diene (reaction 2). The measured k_2's do not reflect whether diene triplets are actually produced upon quenching of a sensitizer triplet by diene; it is possible that varying fractions of encounters of different sensitizer triplets with cyclohexadiene result in production of diene triplets. A possible mechanism for this wastage might be formation of a complex between sensitizer triplet and cyclohexadiene with subsequent production of ground state sensitizer plus either ground or excited state diene.

(12)



This is not a "Schenck mechanism" because the reactive intermediate is still the triplet state of the monomeric diene. If reaction 12 were the energy wasting step then the ratio of dimers produced would be independent of sensitizer.

An explanation similar to the last given was tendered for benzophenone sensitized dimerization of coumarin in which it was found that $\Phi = 0.25$ in the limit of high coumarin concentration (43). In that case the present evidence is insufficient to eliminate the possibility that the inefficiency does not arise in the reactions of the coumarin intermediates.

Kinetic and Thermodynamic Relationships among the Dicyclohexadienes

The four isomeric dicyclohexadienes **1**–**4** undergo a remarkable series of interconversions. At elevated temperatures, **3** and **4** are converted respectively to **1** and **2** as the sole dimeric products. At and below room temperature in the presence of suitable catalysts, however, **1** is converted slowly to **3** and **2** to **4**. These extraordinary reactions may be summarized as

$$\mathbf{3} \quad \underset{\substack{0^\circ\\ \text{cat.}}}{\overset{180^\circ}{\rightleftharpoons}} \quad \mathbf{1}$$

$$\mathbf{4} \quad \underset{\substack{0^\circ\\ \text{cat.}}}{\overset{150^\circ}{\rightleftharpoons}} \quad \mathbf{2}$$

Rearrangement of the divinylcyclobutane derivatives **3** and **4** at higher temperatures is not unexpected as a number of divinylcyclobutanes have recently been reported to isomerize at similar temperatures (28). Production of cyclohexadiene in these reactions is extremely slow compared to the rate of rearrangement. Observation of a single rearrangement product from each cyclobutane seems to rule out cleavage-recombination mechanisms for the rearrangment. We believe that rearrangement occurs by cleavage of the cyclobutane ring to give two allyl radicals which subsequently recombine. A kinetic study of the rearrangements is summarized in Table IV.

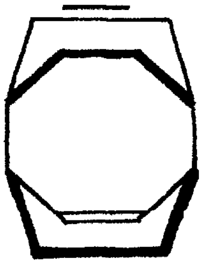
The results may be compared with those recently reported for the rearrangement of the 1, 2-divinylcyclobutanes (28). The cis isomer rearranges to 1, 5-cyclooötadiene with $\Delta\underline{H}^* = 23.7$ kcal per mole and $\Delta\underline{S}^* = -11.7$ e.u. The trans isomer rearranges to a mixture of products with $\Delta\underline{H}^* = 34.0$ kcal/mole and $\Delta\underline{S}^* = -1.2$ e.u. Obviously the rearrangements of **3** and **4** fall into the class, exemplified by trans-divinylcyclobutane, which is believed to involve formation of biradical

TABLE IV

Kinetics of Rearrangements of Tricyclo[6.4.0.$0^{2,7}$]dodeca-3,4-dienes at Elevated Temperatures

Temperature, °C	k × 10^6, sec.$^{-1}$	
	$3 \rightarrow 1$	
179.2	6.53 ± 0.12	
189.1	22.2 ± 2.1	ΔH^* = 36.8 kcal/mole
205.1	52.1 ± 3.1	ΔS^* = −3.2 e.u.
218.7	231 ± 1.5	
	$4 \rightarrow 2$	
164.0	51.5 ± 1.5	ΔH^* = 33.0 kcal/mole
179.3	196 ± 3	ΔS^* = +4.6 e.u.
188.7	574 ± 5	
205.1	2360 ± 250	

intermediates. Even though **4** is believed to be a *cis* compound, the result is not surprising since **4** cannot readily assume the conformation required to convert *cis*-divinylcyclobutane to cycloöctadiene in a concerted process; such a reaction of **4** would produce **21** rather than a dicyclohexadiene.



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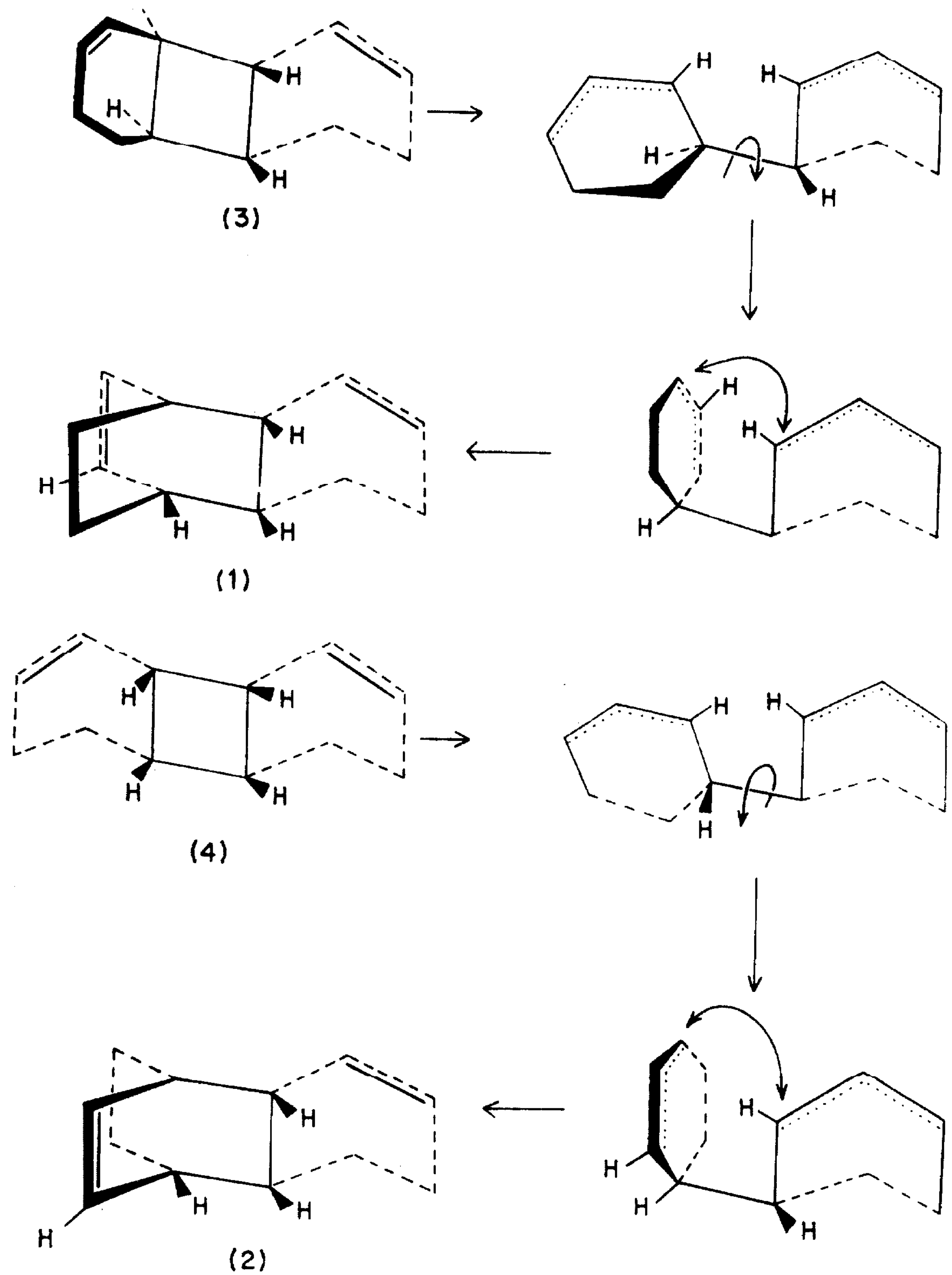
Rearrangements of **3** and **4** by the biradical mechanism would be expected to follow the observed courses. Since the biradical intermediates would have different stereochemistry, the paths of the reactions should not cross. The following equations show the postulated mechanism.



(3)

(1)

(4)

(2)

Reversion to Cyclobutanes. — Some samples of 1 and 2 slowly reverted to 3 and 4, respectively, at room temperature and below. These astonishing transformations were observed in samples collected from vapor chromatography on Apiezon J unless the chromatographed material was redistilled. Redistilled samples were indefinitely stable when stored in clean glass vials but underwent rearrangement when stored in contact with glass wool. At 25° the equilibrium ratio (3/1) is approximately 9. At temperatures up to 100° measurable conversion of 1 to 3 is observed. Measurement of equilibrium constants is not an easy matter because side reactions tend slowly to consume the photodimers.

The behavior of the two pairs of hydrocarbons is puzzling. Even the preliminary observations can be accommodated only if we presume that the Diels-Alder dimers have both substantially higher enthalpy and entropy contents than the isomeric cyclobutanes. This conclusion is very difficult to accept since the enthalpy contents of 3 and 4 should include about 20 kcal/mole strain energy attributed to the cyclobutane rings. Such strain is directly indicated by the heats of combustion of cycloalkanes (35) and is reflected in the kinetics of pyrolysis of cyclobutanes by what is presumed to be a biradical mechanism (28, 36). What few pertinent thermodynamic data available prior to this work were of little help in locating the source of the driving forces for the rearrangement reactions and we report here our own determinations of the heats of formation of the dimers 1-4 (Table V).

TABLE V

Enthalpies of Combustion and Formation of the Dicyclohexadienes

Substance	$\Delta H_c^{298°}$ (kcal/mole)	$\Delta H_f^{298°}$ (kcal/mole)	Source
1	-1675.4 ± 1.7	0.2 ± 0.7	This Thesis
2	-1684.0 ± 1.1	8.8 ± 1.1	This Thesis
3	-1686.8 ± 1.0	11.8 ± 1.0	This Thesis
4	-1698.1 ± 3.0	23.0 ± 3.0	This Thesis
1 + **2**[a]	-1681.5	$+1.6$	Reference 37
8	-1761	—	Reference 37

[a] Presumed a 4:1 mixture of **1** and **2** (*vide supra*). Our determinations imply such a mixture should have $\Delta H_c^{298°} = -1677.2$ kcal/mole.

The measured heats of combustion eliminate the possibility that the low temperature equilibria represent true thermodynamic equilibria between 1 and 3 and 2 and 4. Clearly adsorption upon the surface of the glass wool or the substantial amounts of polymer derived from the Megachrom processing drastically alters the energy relationships between 1 and 3 and 2 and 4. When the dimers are washed from the catalyst with solvent the apparent isomer compositions thus reflect a perturbed equilibrium. We find this explanation very unsatisfying and only hope that someone may be persuaded by its inelegance to find out what really is happening in this system.

endo-Dicyclohexadiene is indicated by our data to be the more stable of the two dicyclohexadienes, exactly the reverse of the situation which obtains with the dicyclopentadienes (37). This result is not very surprising, as the dicyclohexadienes should be more flexible than the dicyclopentadienes, thereby permitting 1 to assume less cramped conformations than those imposed upon dicyclopentadiene by the rigid cyclopentenyl systems. In addition, destabilization of 2 relative to *exo*-dicyclopentadiene might be expected, due to the greater size of the saturated bridge in 2. The magnitude of the difference between 1 and 2 (8 kcal/mole) is, however, somewhat greater than would be expected and may reflect a greater ability of the former to relieve eclipsed interactions by twisting the molecular skeleton. Such twisting operations are probably important in stabilizing bicyclooctane (38).

endo-Dicyclohexadiene does not appear to be an appreciably strained system. Its hydrogenation product 8 has $\Delta H_c^{298°} = -1761$

kcal/mole, a value very close to that prediced by Klages Rules (39, 40). Further, the enthalpy of hydrogenation of 1 to give 8 is calculated from the data in Table V to be −59 kcal/mole, only 4 kcal/mole different from the sum of the enthalpies of hydrogenation of cyclohexene and bicycloöctene (38). Taken together these data imply that destabilization of 1 due to strain amounts to less than 10 kcal/mole.

The stabilities of the cyclobutane derivatives 3 and 4 are of some interest. As would be expected, the all *cis* compound 4 is 23 kcal/mole less stable than 1, most of this difference presumably being accounted for by introduction in 4 of the four-membered ring. Although 3 is less stable than 1, it is an unusually stable cyclobutane derivative. Introduction of the four-membered ring in 3 results in less than 21 kcal/mole destabilization and it seems likely that 3 exists in a conformation involving a nonplanar cyclobutane ring. Several cyclobutane derivatives have been shown to have such twisted conformations (44).

In conclusion, it is worthwhile to point out that entropy effects have been ignored in this discussion of thermodynamic properties. While it is possible to adjust entropies of 1–4 so as to produce relative stabilities consistent with the observed rearrangements, the entropy differences required are so large as to be obviously incompatible with physical reality.

EXPERIMENTAL

Solvents

Dimethylsulfoxide. — Reagent grade dimethylsulfoxide was stirred with sodium hydride until added triphenylmethane turned red, and then vacuum distilled to give colorless and odorless material, m.p. 18°.

n-Pentane and Isopentane. — Technical grade *n*-pentane and pure grade isopentane were washed with concentrated sulfuric acid until the acid layer was no longer discolored, washed with dilute aqueous sodium bicarbonate and water, dried over magnesium sulfate and distilled from sodium. Only the middle fractions were used.

Ether, Carbon Tetrachloride, Chloroform and Benzene. — All of these reagents were reagent grade and, in the case of ether, anhydrous reagent, and were used as received.

Substrates

Cyclohexene. — Cyclohexene (reagent grade) was washed twice with 10% aqueous sodium bisulfite solution, with dilute sodium bicarbonate and with water, dried over magnesium sulfate and distilled from sodium. A middle fraction boiling at 80.5-81.0° was collected.

2-Cyclopentenone. — Aldrich Co. 2-cyclopentenone was distilled under vacuum immediately prior to use.

3-Buten-2-one. — Cal Biochem 3-buten-2-one was distilled just prior to use, b. p. 64-65° (746 mm.).

3-Methyl-3-penten-2-one. — Cal Biochem 3-methyl-3-penten-2-one was vacuum distilled just prior to use, b. p. 27° (1 mm.).

2-Cyclohexenone. — Aldrich Co. 2-cyclohexenone was vacuum distilled just prior to use, b. p. 44° (8 mm.).

Attempts to Prepare 2-Cyclohexenone. — A number of attempts were made to prepare cyclohexenone by treating 3-bromocyclohexene with sodium dichromate and sulfuric acid. Such treatment has been used successfully to prepare cyclohexenone from 3-chlorocyclohexene. In a typical preparation, freshly distilled 3-bromocyclohexene (160 g.) was added dropwise to one liter of rapidly stirred 15% aqueous sodium dichromate solution. Cooling of the reaction flask in ice kept the temperature of the reaction mixture below 10° throughout the course of the reaction. When all of the bromide had been added, 500 ml. of 50% aqeuous sulfuric acid (18 N) was added in small portions. The dark green mixture which resulted was extracted exhaustively with ether. The ether layer was twice washed with water, dried over magnesium sulfate and evaporated to dryness to yield the crude cyclohexenone as a dark red oil. Vacuum distillation of this oil gave 60-65% yields of a colorless oil having the physical properties of cyclohexenone. This material, however, rapidly discolored. It was found that washing once distilled material with dilute aqueous sodium bicarbonate, followed by drying and redistillation under vacuum gave a colorless product, b.p. 36–38° (6 mm.), n_D^{27} = 1.4858 (lit. n_D^{22} = 1.4868), with n.m.r. and infrared spectra consistent with 2-cyclohexenone. Melting point and mixed melting point of the 2,4-DNP were 162–163° and 162–164° respectively. Attempts to effect photodimerization of this material, however, led to rapid decomposition and the following modifications of the procedure were tested:

a) Washing once distilled material with: (1) sodium EDTA in 5% solution; (2) sodium bisulfite and sodium carbonate both as 5% solutions; (3) sodium bisulfite as a 5% solution.

(b) Passage of the enone with and without solvent through neutral alumina.

All of these procedures were followed by washing with water, drying over magnesium sulfate and redistilling under vacuum. None of these procedures produced photochemically acceptable material.

3-Bromocyclohexene. — 3-Bromocyclohexene was prepared in large quantities by stirring together for 48 hours at room temperature 800 g. of reagent grade N-bromosuccinimide, 2400 ml. of carbon tetrachloride and 1000 ml. of cyclohexene. Removal of the succinimide by filtration, evaporation under vacuum of the remaining cyclohexene and carbon tetrachloride and vacuum distillation of the residue gave 60–65% yields of 3-bromocyclohexene as a straw colored liquid, b.p. 31–32° (1 mm.), which rapidly discolored upon standing at 0°.

1,3-Cyclohexadiene. — In quantitative experiments, cyclohexadiene used was Aldrich Co. material distilled before use, b.p. 78–79°.

To provide the large quantities of cyclohexadiene necessary to the study of the structural and thermodynamic properties of the dicyclohexadienes, the following procedure was employed. 3-Bromocyclohexene (650 g.) was added dropwise over a 20 minute period to 2000 ml. of rapidly stirred, refluxing quinoline. Cyclohexadiene, which began to form after about 5% of the material had been added, distilled out of the solution through a long Vigreaux column and was collected in a vessel cooled in ice water. The distillate was washed once with dilute sodium bisulfite solution, dried over magnesium sulfate and distilled through a spinning band column, to give 250 g. of 1, 3-cyclohexadiene, b.p. 78-79° (746 mm.). Cyclohexadiene produced in this way was free from cyclohexene and benzene.

Sensitizers

All sensitizers used were purified as described in Part Two of this thesis except for benzophenone imine obtained from Dr. J. Bradshaw, mesityl oxide which was distilled by Dr. Turro and o-hydroxybenzophenone which had been recrystallized from alcohol by Dr. Turro. Duroquinone was recrystallized from benzene and sublimed under vacuum.

Syntheses

Photodimers of 1, 3-Cyclohexadiene. — Cyclohexadiene (Aldrich Chemical) (100 g.) and β-acetonaphthone (reagent grade) (9 g.) were dissolved in sufficient isopentane to give 500 ml. of solution.

Nitrogen was bubbled through the solution for 5 minutes and the solution was then irradiated for 24 hours with a 450 watt medium pressure mercury arc housed in an Hanovia immersion reactor. The reaction mixture was concentrated by rotary evaporation with aspirator suction, then vacuum distilled to give 92 g. (92%) of dimeric products, b. p. 34-39° (1 mm.). About 5 g. of higher molecular weight material was also recovered.

Anal. (of mixed dimers) Calcd. for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.66, 89.75; H, 10.19, 10.22.

The isomeric dimers were separated completely by v. p. c. on a 150 ft. long Apiezon J Golay column. The isomers were separated by preparative vapor phase chromatography with a Beckman Megachrom using eight 6 ft. Apiezon J columns. The dimers were not completely separated but could be obtained pure by taking cuts which eliminated mixed fractions. The first cut consisted of essentially pure **3**. The last cut consisted of **2** and **4** in 2:3 ratio from which the pure compounds were obtained by further preparative chromatography with a Wilkins Autoprep using a 12 ft. column of 35% Apiezon J on firebrick. During all v. p. c. work the column, injector and detector temperatures were kept below 160° to prevent thermal rearrangements of the photodimers.

Thermal Dimerization of Cyclohexadiene. — Cyclohexadiene (30.0 g.) was degassed twice by freeze-thaw cycles and sealed under vacuum in a thick walled tube. The tube was heated to 200° for 24 hours, cooled and opened, and the contents were distilled under vacuum to give 9.7 g. (32%) of dimeric products, b.p. 31–33° (1 mm.).

Rearrangement of the Photodimers. — Cyclohexadiene photodimers, (6.0 g.), distilled but not separated, were degassed twice by freeze-thaw cycles and sealed under vacuum in a thick walled tube. The tube was heated to 200° for 24 hours, cooled and opened, and the contents distilled under vacuum to give 5.0 g. (88%) of a 3:2 mixture of endo and exo dicyclohexadiene, identified by comparison with authentic samples. About 0.5 g. polymeric material and traces of monomer were obtained. Shorter heating times gave no polymer, but left some photodimer unconverted.

Anal. Calcd. for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.99; H, 9.88.

Hydrogenation of Thermal Dimers. — Cyclohexadiene thermal dimers (5.0 g.) in 3:2 ratio were dissolved in 25 ml. 95% ethanol (not denatured) and 0.5 g. of Engelhard platinum dioxide catalyst was added to the solution. The mixture was placed under hydrogen at room temperature and pressure until no more hydrogen was absorbed. The catalyst was then removed by filtration, 50 ml. of water was added, and the mixture extracted with 2 × 25 ml. pentane. The pentane layer was washed twice with water to remove ethanol, dried over magnesium sulfate, and evaporated to give 4.8 g. of tricyclo[6.2.2.$0^{2,7}$]dodecane, b.p. 233° (746 mm.), $n_D^{20} = 1.4445$, n.m.r. resonances at $\tau = 8.38$, 8.72; the infrared spectrum in chlorofrom showed maxima at 2950, 1465, 1125, 940, 860 cm.$^{-1}$.

Anal. Calcd. for $C_{12}H_{20}$: C, 87.81; H, 12.19. Found: C, 87.45; H, 12.44.

Hydrogenation of *trans*-*cis*-*trans*-Tricyclo[6.4.0.0^{2,7}]dodeca-3,11-diene. — The diene (400 mg.) was dissolved in 5 ml. 95% ethanol (not denatured) and hydrogenated in the same way as the thermal dimers. About 370 mg. (92%) of *trans*-*cis*-*trans*-tricyclo[6.4.0.0^{2,7}] dodecane, b.p. 233° (746 mm.), was obtained. Infrared maxima in carbon tetrachloride occurred at 2920, 2856, 2689, 1575, 1462, 1451, 1357, 1318, 1310, 1287, 1269, 1235, 1203, 1138, 1127, 1030, 980, 880, 850 cm.$^{-1}$. The n.m.r. spectrum in carbon tetrachloride showed maximum absorptions at τ = 7.88 and 8.50.

Anal. Calcd. for $C_{12}H_{20}$: C, 87.81; H, 12.19. Found: C, 87.32; H, 12.49.

Photoaddition of 2-Cyclohexenone to Cyclohexene. — A mixture of 30 g. cyclohexene (reagent grade) and 10 g. 2-cyclohexenone (Aldrich reagent chemical) was degassed twice by freeze-thaw cycles and sealed under vacuum in 15 × 125 mm. Pyrex tubes. The tubes were irradiated for 72 hours with a 450 watt medium pressure mercury arc in an Hanovia immersion reactor. Vacuum distillation of the contents gave 14.1 g. (70% based on cyclohexenone) of the adducts, b.p. 77-91° (1 mm.).

Anal. (of mixed adducts) Calcd. for $C_{12}H_{18}O$: C, 80.84; H, 10.11: Found: C, 80.79; H, 10.22.

Further distillation of the reaction mixture gave 2.1 g. (12%) of what appeared to be cyclohexenone dimers, b.p. 130-144° (1 mm.).

The 2, 4-dinitrophenylhydrazones of the mixed cyclohexene-cyclohexenone adducts were prepared by the method of Vogel (42). Separation of the DNP's was accomplished by column chromatography on a 2 × 28 cm. silica gel column eluted with 3:1 benzene-60-70 Ligroin. The silica gel used was prepared by mixing Mallinckrodt silicic acid and celite in 20:3 ratio and then heating over a Meeker burner for 6 hours. Four separate DNP's were obtained (none of which were identical to 2-cyclohexenone DNP), melting at 160-164°, 143-145°, 172-176° and 161-165°.

Reduction of Mixed Tricyclo[6. 4. 0. $0^{2,7}$]dodecan-3-ones. — The ketones (11 g.) were dissolved in 250 ml. of 95% ethanol (denatured) and the solution was cooled to 0° in an ice bath. The solution was stirred rapidly and a solution of 2. 5 g. of sodium borohydride in 30 ml. of 0. 1 N sodium hydroxide was added dropwise. After 3 hours, the reaction mixture was concentrated to 50 ml. by distillation, 150 ml. of water was added, and the mixture extracted with 4 × 50 ml. of ether. The ether layer was washed once with water, dried over magnesium sulfate and evaporated by boiling to give crude alcohols, which upon distillation gave 9. 0 g. (88%) of pure material.

Anal. (of mixed alcohols) Calcd. for $C_{12}H_{20}O$: C, 79. 94; H, 11. 18. Found: C, 79. 79, 79. 86; H, 11. 23, 11. 16.

Acetates of Mixed Tricyclo[6. 4. 0. $0^{2,7}$]dodecanols. — The alcohols were mixed with equal volumes of reagent grade acetyl chloride and allowed to stand for 5 minutes with occasional shaking. The reaction mixture was then diluted with water and the organic layer which separated was dried over magnesium sulfate to give 93-95% yields of the acetates. The infrared spectrum of the mixture in chloroform showed maximum absorption at 3075, 3043, 2957, 2880, 2420, 1763, 1650, 1535, 1457, 1383, 1265, 1230, 1032, 934 cm.$^{-1}$.

Pyrolysis of the Mixed Acetates. — A solution of 2.0 g. of the acetates in 15 ml. cyclohexane was dropped slowly through a pyrolysis tube packed with glass beads and heated to 375°. A small quantity of the desired alkenes was obtained; most of the acetates, however, failed to decompose and 0.85 g. of the acetates were recovered by washing the column repeatedly with cyclohexane.

Tricyclo[6.4.0.0^{2,7}]dodecane-3-xanthates. — The tricyclic alcohols (11 g.) were dissolved in 50 ml. dry ether. Freshly cut sodium slivers (1.4 g.) were added to the solution and the mixture was then stirred at room temperature for 24 hours, while 6 ml. (9.8 g.) of carbon disulfide was added in small portions. The sodium was then removed mechanically and stirring was continued for another hour. Methyl iodide (16.8 g.) was then added to the solution and stirring was continued overnight. After 14 hours, 1.0 g. additional methyl iodide was added and stirring continued for one more hour. The inorganic salts were removed by filtration and the ether solution was evaporated at 25° under reduced pressure to yield a red oil which was crystallized by allowing it to stand on a porous clay plate. About 2.0 g. of whitish crystals were obtained. Recrystallization from ethanol gave white crystals m.p. 35-46° (presumably a mixture of four isomers).

Pyrolysis of Tricyclo[6.4.0.$0^{2,7}$]dodecane-3-xanthates. — The xanthates (0.95 g.) were placed in a 25 ml. flask equipped with a reflux condenser and gas burette. The flask was heated to 205-210° for 65 minutes, then allowed to cool and the contents vacuum distilled to give 0.200 g. (40%) of a mixture of four alkenes in 2:1:10:2 ratios as determined by v.p.c. analysis on Apiezon J. The major isomer was obtained pure by preparative v.p.c. on the Autoprep using an Apiezon J column. The n.m.r. spectrum of the mixed alkenes showed most of the vinyl protons as an asymmetric multiplet with maxima at $\tau = 4.18$ and 4.23 and the saturated region as a broad band.

Hydrogenation of trans-cis-trans-Tricyclo[6.4.0.$0^{2\;7}$]dodec-3-ene. — The major component of the alkene mixture was washed from the collection trap of the Autoprep with 4.0 ml. absolute ethanol, 50 mg. of Engelhard 5% palladium on charcoal catalyst was added to the solution, and the mixture stirred under hydrogen at room temperature and atmospheric pressure until no more hydrogen was consumed. The catalyst was removed by filtration and 5.0 ml. water was added to the reaction mixture, which was then extracted with two 5 ml. portions of pentane. The pentane solution was washed twice with water, dried over magnesium sulfate, then evaporated by boiling to give the crude tricyclo[6.4.0.$0^{2,7}$]dodecane. After purification by preparative vapor phase chromatography with the Autoprep, the n.m.r. and infrared spectra of the alkane were identical to those of the product obtained by hydrogenation of the major photodimers.

Cycloheptanone with Dimethyl Sulfoxinium Methylide. — Trimethyl sulfoxinium iodide, prepared by the method of Kuhn and Trischman (45), (4.1 g.), and sodium hydride (0.78 g. of a 50% suspension in mineral oil), were dissolved in 20 ml. of dimethyl sulfoxide under a nitrogen atmosphere. The solution was stirred for 1 hour at 25°, then cycloheptanone (2.0 g.) was added and stirring was continued for another hour at 25° and an additional hour at 50°. Distilled water (80 ml.) was then added and the resulting mixture continuously extracted with pentane for 24 hours. The pentane layer was washed twice with water, dried over magnesium sulfate and evaporated to yield 1.2 g. of the epoxide (49% yield) as a colorless liquid.

Reaction of 18 with the Ylide. — The sample of 18 used was obtained from Dr. Turro and was recrystallized twice from carbon tetrachloride and sublimed under vacuum before use, m.p. 125.8-126.2° (lit. 125-126°) (46). Treatment of this ketone with the ylide prepared as above led to immediate production of a bright yellow color which subsequently turned first red then brown. No nonpolymeric materials could be obtained upon working up the reaction. A number of repeats of this procedure varying the reaction temperature and exposure time were unavailing. Reaction of cyclopentanone with the ylide similarly failed to give any volatile products.

Photodimerization of 2-Cyclohexenone. — The method used was that of Eaton (29). Twenty grams of freshly vacuum-distilled cyclohexenone were irradiated for 72 hours with a 450-watt Hanovia lamp through two layers of Pyrex. At the end of this period the excess cyclohexenone (2.6 g.) was removed under vacuum and the residue distilled to give 15.2 g. (87% based on unrecovered cyclohexenone) of a colorless oil, b.p. 125-128° (0.3 mm.). An attempt to chromatograph the mixture of dimers on Woelm neutral, activity grade 1 alumina led to a violent evolution of heat, but chromatography on Merck acid-washed alumina eluting with methylene chloride gave **17**; the corresponding *syn* isomer was removed by elution with ether containing 10% ethanol. Rechromatography of the major fractions gave the *anti* dimer (eluted by methylene chloride) as stout prisms, m.p. 53-55° (from hexane), and the *syn* isomer as white flakes, m.p. 79-80° (from hexane).

Wolff-Kischner Reduction of 17. — The dione (2.5 g.) was dissolved in 30 ml. of diethylene glycol. Hydrazine hydrate 85%, 30 ml. was then added and the mixture heated at 100° for 30 minutes. After the reaction mixture had cooled to room temperature, 8 g. of potassium hydroxide pellets were added and the mixture heated to 200° under nitrogen for 30 minutes. The alkane **16** was steam distilled from the reaction mixture. The aqueous distillate was washed three times with pentane; the pentane layer was then dried over magnesium sulfate and evaporated on the steam bath to yield crude **16**, which after preparative v.p.c. on Apiezon J, had n.m.r. and infrared spectra identical with those of the hydrogenation product obtained from the major photodimer.

***syn*-Tricyclo[6.2.2.$0^{2\,7}$]dodeca-4,9-dien-3,6-dione.** — Technical grade *p*-benzoquinone was passed through rosite (1 part Norite, 3 parts Celite by weight) in benzene solution and recrystallized from benzene, m.p. 114–115° (sealed capillary). Thirteen grams of the purified quinone and 40 ml. cyclohexadiene (Alrich Chemical) were stirred for 48 hours in the dark at room temperature. The solution was evaporated on a steam bath to give 17 g. (74%) of product, m.p. 94–95° (reported 94°) (12). The ultraviolet spectrum in methanol had λ_{max} = 2845 Å, (ϵ_{max} = 27,500). The infrared spectrum in a potassium bromide pellet had maxima at 3050 (s), 2960 (s), 2880 (s), 1690 (s), 1615 (w), 1280 (m), 1110 (m), 880 (m), 760 (m) cm.$^{-1}$. The n.m.r. spectrum in carbon tetrachloride showed a sharp singlet at τ = 2.76 (2 protons), a broader band at τ = 6.54–6.85 (2 protons), a triplet centered at τ = 7.06 (2 protons), and a broad quartet centered at τ = 8.54 (4 protons).

Anal. Calcd. for $C_{12}H_{12}O_2$: C, 76.53; H, 6.38. Found: C, 76.51; H, 6.36.

Photoisomerization of syn-Tricyclo[6.2.2.0^{2,7}]dodeca-4, 9-dien-3, 6-dione. — This substance was isomerized by either of two methods to give a cage compound in high yield:

a) An ether solution of the unsaturated ketone was allowed to evaporate on a flat glass plate, leaving a film of crystals which was then irradiated for an hour through Pyrex, giving a nearly quantitative yield of adduct.

b) An ether solution of the ketone was irradiated and gave in 1–2 hours quantitative yields of the adduct, (m.p. 165° with decomposition), which precipitated from solution as it was formed.

The adduct has infrared maximum absorptions (potassium bromide pellet) at: 3050, 2960, 1757, 1302, 1240, 1205, 1145, 1060, 935, 917, 880, 850, 760 cm.$^{-1}$. The n.m.r. spectrum of a dilute solution of the adduct in deuteroacetone showed only a broad band in the saturated region. The ultraviolet spectrum in methanol showed λ_{max} = 3000 Å (ϵ_{max} = 5).

Anal. Calcd. for $C_{12}H_{12}O_2$: C, 76.53; H, 6.38. Found: C, 76.58; H, 6.50.

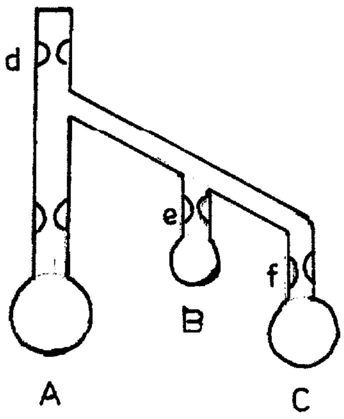
Attempted Aromatization of *cis-cis-cis*-Tricyclo[6.4.0.0^{2,7}]dodeca-3,11-diene. — The diene (25 mg., 0.00014 moles) and sulfur flowers (18 mg., 0.00056 moles) were heated to 150° in an evacuated sealed tube for 24 hours. The foul-smelling reaction mixture was dissolved in benzene and chromatographed on alumina by elution with 2:1 petroleum ether-benzene. Only low melting solids were obtained. Biphenyl may have been one of the products, but could not be positively identified. No evidence for biphenylene formation could be found.

A similar experiment with the *trans-cis-trans* isomer (**3**) also failed to give biphenylene.

The dimers were hydrogenated and heated with selenium for 72 hours at 275°. No reaction was observed.

Measurements of Heats of Combustion for the Dimers of 1,3-Cyclohexadiene

Cyclohexadiene photodimers were prepared in the usual way and separated on the Megachrom and Autoprep by application on a large scale of the separative techniques previously described. The separated dimers were twice vacuum distilled to remove monomeric and polymeric materials, dried over magnesium sulfate, and, finally, distilled in the special apparatus shown in the accompanying figure.



The apparatus was washed with a solution of orvus, a water soluble soap, rinsed repeatedly with distilled water, rinsed finally several times with methanol, dried in the oven overnight, removed from the oven and sealed until cold. After introduction of the sample into A, the apparatus was degassed by three feeze-thaw cycles at 10^{-3} mm. and sealed under vacuum at d. A forerun was then distilled into B to insure that no monomer was present in the final sample. This distillation was accomplished by simply cooling vessel B in liquid nitrogen and placing A in warm water (~50°). Tube B was cut off at constriction e. Finally the bulk of the sample was distilled into the container C, which was cut off at f. This procedure insured a dry sample, protected from oxidation reactions.

The heats of combustion of the dimer samples were measured by Mr. Al Kennedy at Rohm and Haas, Co., Redstone Arsenal, Huntsville, Alabama. The data are given on the following page, together with the relevant heats of combustion.

Dimer Composition[a]

(in mole %)

Sample	**3**	**1**	**4**	**2**
I	55.9	0	0	44.1
II	99.6	0	0	0.4
III	0	97.7	0	2.3
IV	21.0	0	44.4	34.6

[a] Dimer composition was determined by v.p.c. on the Apiezon J Golay column at 109°. The reproducibility of the analyses were ±1.0% or better.

Energy of Combustion in kcal/gram

Sample	I	II	III	IV
	-10,511.7	-10,529,6	-10,452.5	-10,540.8
	-10,504.6	-10,519.4	-10,446.1	-10,544.7
	-10,491.8	-10,525.2	-10,418.7	-10,524.1
	-10,503.7	-10,510.5	-10,438.6	-10,535.8
Average	-10,502.9	-10,521.2	-10,439.0	-10,536.4
	±5.4	±6.2	±10.2	±6.2

Assuming that different energies of interaction between the various dimers in solutions to be a negligible perturbation, the energies of combustion per gram of the dimers **1**-**4** can then be calculated by solving the following simultaneous equations

$$(1)\quad 0.559[\Delta E_c(3)] + 0.441[\Delta E_c(2)] = -10502.9 \pm 6.2 \text{ cal./g.}$$

$$(2)\quad 0.996[\Delta E_c(3)] + 0.004[\Delta E_c(2)] = -10521.2 \pm 6.2 \text{ cal./g.}$$

$$(3)\quad 0.977[\Delta E_c(1)] + 0.023[\Delta E_c(2)] = -10439 \pm 10.2 \text{ cal./g.}$$

$$(4)\quad 0.210[\Delta E_c(1)] + 0.444[\Delta E_c(4)] + 0.346[\Delta E_c(2)] = -10536.4 \pm 6.2 \text{ cal./g.}$$

The results of this calculation are given in Table VI. The heats of formation in the table are calculated from the following idealized equation.

$$12\ \text{C(graphite)} + 8\ \text{H}_2\text{(g.)} \longrightarrow \text{C}_{12}\text{H}_{16}\text{(liquid)}$$

Low Temperature Rearrangement of Thermal Dimers. — Samples of 1 and 2 obtained from vapor chromatography on Apiezon J columns were, especially with older v.p.c. columns, contaminated with varying amounts of high boiling material. Such samples reverted slowly to the photodimers at 25° and 0°, degassed and not degassed, and in various types of glass vessels. Analysis of samples was made using n.m.r., and v.p.c. techniques described in "Kinetic Study of High Temperature Rearrangements."

Samples of the thermal dimers were vacuum distilled and the purified materials were placed in clean glass vessels, both Pyrex and soft glass, degassed and in the presence of oxygen. An unpurified

TABLE VI

Combustion Heats of Dicyclohexadienes

Compound	$\Delta E_c^{298^\circ}$ cal. /g.	$\Delta E_c^{298^\circ}$ kcal/mole	$\Delta H_c^{298^\circ}$ kcal/mole	$\Delta H_f^{298^\circ}$ kcal/mole
1	−10438.9 ±10.2	−1673.0 ±1.7	−1675.4 ±1.7	+ 0.2 ± 1.7
2	−10493.1 ±7.5	−1681.6 ±1.1	−1684.0 ±1.1	+ 8.8 ± 1.1
3	−10510.6 ±6.2	−1684.4 ±1.0	−1686.8 ±1.0	+11.8 ± 1.0
4	−10582.0 ±18.5	−1698.1 ±3.0	−1698.1 ±3.0	+23.0 ± 3.0

All errors estimated assuming v.p.c. analysis was accurate.

sample, as a 15% solution in carbon tetrachloride, was stored in the presence of oxygen. After more than twelve months no rearrangement was observed in any of these cases.

It was found possible to effect rearrangement even of pure material by placing it in contact with Corning Pyrex brand glass wool (used as received). Degassed and nondegassed systems showed ~20% rearrangement in 41 days at 0°, as determined by n.m.r. analysis. The rate constant for rearrangement at 0° is thus about 10^{-8} sec.$^{-1}$.

A sample of unpurified **1**, from the Megachrom, which was allowed to stand for 9½ months at 25° (conditions which should have permitted complete rearrangement to **3**) showed 90% rearrangement by n.m.r. analysis. Samples of **3** collected from Apiezon J columns tended to *very slowly* form **1** unless purified. The difference in rates of formation of the two products is probably due to unequal contamination occasioned by passage through the Megachrom. The "equilibrium" value **3**/**1** at 25° is thus calculated to be about 9. Similar studies with **4** and **2** are not possible because of side reactions which appear to consume **4**. Available data seem to indicate, however, that at 25° (**4**/**2**) eq ≤ 1.

Kinetic Study of High Temperature Rearrangements. — Pure samples of the dimers were prepared as described above and distilled immediately prior to use.

Kinetic runs were performed according to the procedures described by Hammond and DeBoer (14), and will not be described here. Control experiments showed the absence of surface effects and confirmed that the rates obtained were reproducible.

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PART TWO

PHOTOSENSITIZED ISOMERIZATION OF THE STILBENES: FURTHER STUDIES

INTRODUCTION

Study of the photosensitized cis-trans isomerization of the stilbenes by Saltiel (1-5) led to definition of the general details of the mechanism of this and similar reactions and to accumulation of considerable information about the nature of electronically excited states and energy transfer in solution. We will be concerned here with further studies of this system which require reformulation of certain details of the mechanism of photosensitized isomerization reactions. Numerous detailed expositions of Saltiel's work on the stilbenes have recently appeared (4-6), and we give now only a brief description of the problems which led to the initiation of this work.

In Figure I are given the reported compositions (4) of the photostationary states established by prolonged irradiation of the stilbenes in the presence of various sensitizers having different triplet energies. For all of the sensitizers employed in obtaining the data in Figure I, the $S^0 \rightarrow S^1$ splittings are smaller than for either of the stilbene isomers; it was, therefore, presumed by Saltiel that only triplet energy transfer occurs in the sensitized reaction. With some sensitizers, side reactions compete with triplet energy transfer; all data in Figure I, however, were corrected for these processes.

To account for the data in Figure I, Saltiel and Hammond (4, 5) proposed the following mechanism.

(1) $S \xrightarrow{h\nu} S^1 \longrightarrow S^3$

(2) $S^3 + t \rightleftharpoons t^3 + S$

Photosensitized Isomerization of the Stilbenes

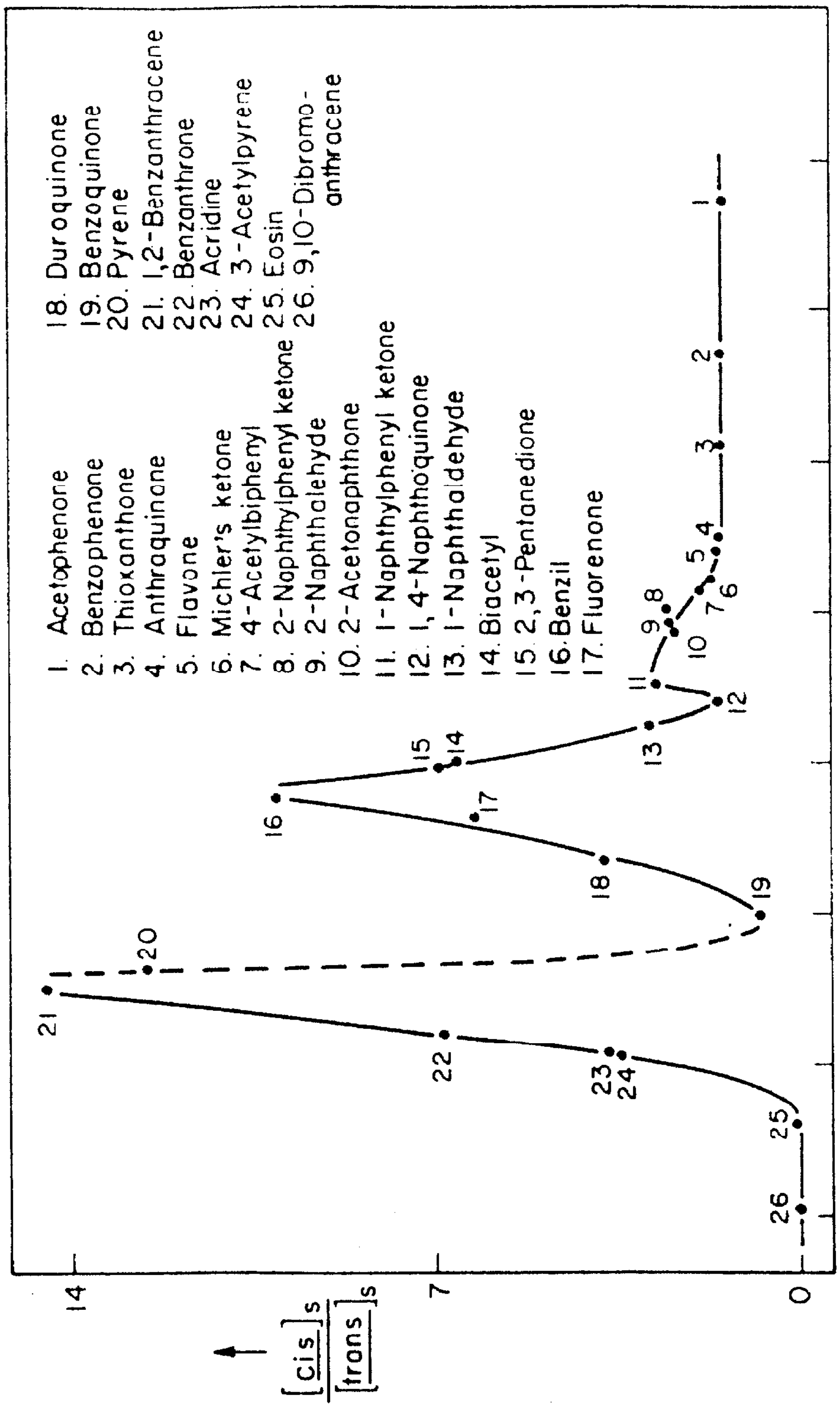

Figure I

(3) $S^3 + c \longrightarrow c^3 + S$

(4) $S^3 + c \longrightarrow p^3 + S$

(5) $c^3 \xrightarrow{\text{fast}} p^3$

(6) $t^3 \overset{\text{fast}}{\rightleftarrows} p^3$

(7) $p^3 \longrightarrow t$

(8) $p^3 \longrightarrow c$

(9) $t^3 \longrightarrow t$

(10) $t^3 + \underline{t} \longrightarrow 2t$

(11) $t^3 + Q \longrightarrow t + Q^3$

In their representation, and throughout this Thesis: S, S^1 and S^3 are respectively the ground singlet, first excited singlet and lowest triplet state of the sensitizer; t and c are trans and cis ground state stilbene; Q and Q^3 are the ground singlet and lowest triplet states of any substance capable of quenching stilbene triplets; and c^3, p^3 and t^3 are stilbene triplets with cisoid, twisted and transoid geometries respectively.

From the above mechanism a general expression can be derived for the stationary state cis/trans ratio of the stilbenes.

$$(12) \quad \left(\frac{c}{t}\right)_{\substack{\text{stationary}\\ \text{state}}} = \left(\frac{k_2}{k_3 + k_4}\right)\left(\frac{K_6 k_8}{K_6 k_7 + k_9 + k_{10}[t] + k_{11}[Q] + k_{-2}[S]}\right)$$

Data in Figure I were extrapolated to infinite dilution of the sensitizer and since there were no external quenchers, interpretation was possible in terms of the following simpler expression.

$$(13) \quad \left(\frac{c}{t}\right)_s = \underset{\text{excitation ratio}}{\left(\frac{k_2}{k_3 + k_4}\right)} \quad \underset{\text{decay ratio}}{\left(\frac{K_6 k_8}{K_6 k_7 + k_9 + k_{10}[t]}\right)}$$

Only the excitation ratio depends upon the particular sensitizer, and data in Figure I were interpreted solely in terms of the relative magnitudes of the rate constants k_2, k_3 and k_4.

Little was known from Saltiel's work about the nature of the nonvertical energy transfer process represented by reaction 4, beyond the facts that it must occur at a rate 3 to 5 orders of magnitude less than that for a diffusion-controlled process, and that nuclear motion of the stilbene occurs during the transfer of energy (4). Since the triplet energies of cis- and trans-stilbene are 57 and 50 kcal/mole respectively (7), rates of classical energy transfer for most sensitizers in Figure I are sufficiently high that reaction 4 does not provide a major source of excitation of the stilbenes. How reaction 4 was invoked to explain the behavior of low energy sensitizer-stilbene systems is considered below.

Triplet energy transfer represented by reactions 2 and 3 was believed to occur by an exchange mechanism, requiring close approach of donor and acceptor such as is achieved only during a collisional encounter in solution; hence, both k_2 and k_3 are limited by the rate of diffusion in solution (8-10). For all sensitizers having triplet energies greater than 62 kcal/mole, the same photostationary state was predicted, since with these sensitizers both reactions 2 and 3 are exothermic by several kcal/mole and would be expected to occur at the diffusion controlled rate (8, 9). The general increase in the photostationary cis/trans ratio as the sensitizer triplet energy decreased from 62 to 55 kcal/mole was attributed to decreases in k_3 while k_2 continued to be limited only by the rate of diffusion. The shallow minimum in the photostationary cis/trans ratio for sensitizer energies near 57 kcal/mole was attributed to an increase in k_3, due to resonance transfer of triplet energy to cis-stilbene. Another decrease in the photostationary cis/trans ratio as the sensitizer triplet energy dropped from 55 to 50 kcal/mole was attributed to decreases in k_2 as energy transfer to trans-stilbene becomes no longer substantially exothermic. The lower energy maximum in the photostationary cis/trans ratio was observed for sensitizers having triplet energies of about 48 kcal/mole and was again attributed to resonance transfer of triplet energy, this time to trans-stilbene (4, 5). It was postulated (4, 5) that the 0-0 band of the $S^0 \rightarrow T^1$ transition in stilbene had an energy of 47 kcal/mole and that the lowest energy transition observed by Evans (7) in the $S^0 \rightarrow T^1$ absorption spectrum of trans-stilbene was the 0-1 band. For sensitizers having triplet energies below 48 kcal/mole, the photostationary cis/trans ratio decreased sharply, approaching zero with sensitizers having triplet energies around 40 kcal/mole. This was attributed to very low rates of classical energy transfer (reactions 2 and 3) which allowed k_4 to dominate the excitation ratio.

Nonvertical energy transfer was first proposed to explain the behavior of the stilbenes with low energy sensitizers. On the basis of evidence discussed on the following page, it was inferred that the potential energy diagram for the stilbene triplets was best represented as in Figure II. As can be seen from that Figure, energy transfer from a sensitizer having a triplet energy of 45 kcal/mole to *cis*-stilbene to produce the *cisoid* triplet is a process with an activation energy of at least 12 kcal/mole. Such a process could not compete successfully with unimolecular decay of the sensitizer triplet (11). On the other hand, since the *cis* ground state is of higher energy than the *trans* ground state the direct conversion of *cis*-stilbene to either t^3 or p^3 (wavy lines in Figure II) should require only 45 kcal/mole so long as it is not necessary to pass through the high energy *cisoid* form of the triplet state. For several reasons nonvertical energy transfer is not amenable to study in the stilbene system, but a number of examples of conversion of flexible acceptors to triplets with nonground state geometry have been reported — this type of electronic transition may be considered well documented if not well understood (12). Figure II shows why nonvertical energy transfer to *trans*-stilbene is apparently not observed (4, 11); the most energetically favorable transition for *trans*-stilbene is probably the vertical one.

Considerable evidence was adduced to support the potential curve drawn in Figure II. Existence of the *transoid* triplet, t^3, was indicated by the ability of various substances to quench stilbene triplets with resultant production of *trans*-stilbene. Photostationary *trans*/*cis* ratios obtained with sensitizers having triplet energies less than 53 kcal/mole increased linearly with increasing sensitizer concentration, an effect attributed to reversibility of reaction 2. Addition of

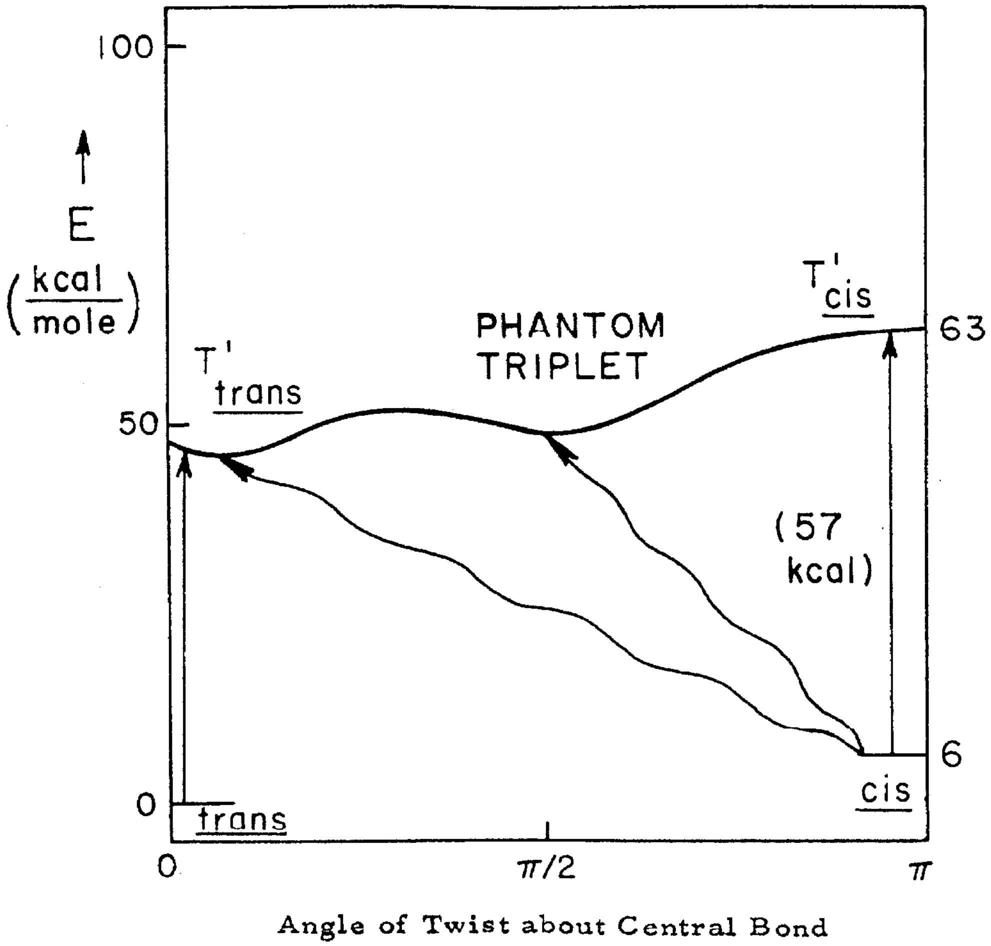

Figure II. Potential function for rotation in stilbene triplet states.

azulene, which has a triplet energy of less than 39 kcal/mole (12), led to linear increases in the photostationary trans/cis ratio, probably because of the occurrence of reaction 11. As required by the mechanism given above, the effect of added azulene upon the photostationary state was, after correction for reversibility of reaction 2, the same for all sensitizers. This extremely important result indicated that the same stilbene intermediates were produced by all sensitizers. Photostationary state and quantum yield data obtained with benzophenone as sensitizer indicated that decreasing the stilbene concentration favors decay of the stilbene triplets to give cis-stilbene. This effect was attributed to reaction 10, but this assignment must be regarded as questionable (vide infra).

Increasing the reaction temperature was found to increase the stationary cis/trans ratio; this suggested that at least one other triplet in addition to t^3 was capable of decaying directly to cis and trans ground states. This and all the data given previously could have been interpreted satisfactorily in terms of a single triplet whose decay processes were sensitive to the environment were it not for the fact that the α-methyl stilbenes, which display excitation behavior similar to that for the stilbenes, show none of the effects upon the decay ratio shown by the stilbenes (4). The behavior of the methyl stilbenes was adequately described in terms of rapid relaxation of cisoid and transoid triplets to a single twisted triplet of perhaps perpendicular geometry which in turn decays rapidly to the ground state isomers. The failure of the α-methyl stilbene triplet to interact with its environment led

Saltiel and Hammond (4, 5) to prefer the two-triplet mechanism for the stilbenes.

Quantum yield measurements were employed in the study of sensitized stilbene isomerization. Rather simple kinetic expressions can be derived for the initial quantum efficiencies for trans to cis and cis to trans conversion of the stilbenes. Equations 16 and 17 may be derived for the initial quantum yields for stilbene isomerization using the assumptions that: 1) reactions 10 and 11 may be neglected; 2) reaction 2 is nonreversible, and including the unimolecular decay of sensitizer triplets (reaction 15).

$$(15)\quad S^3 \longrightarrow S$$

$$(16)\quad \phi_{t\to c} = \underline{a}\left(\frac{k_{qt}(t)}{k_{qt}(t) + k_{15}}\right)\left(\frac{K_6k_8}{K_6(k_7 + k_8) + k_9}\right)$$

$$(17)\quad \phi_{c\to t} = \underline{a}\left(\frac{k_{qc}(c)}{k_{qc}(c) + k_{15}}\right)\left(\frac{K_6k_7 + k_9}{K_6(k_7 + k_8) + k_9}\right)$$

where $\underline{a}$ is the intersystem crossing yield of the sensitizer and k_{qc} and k_{qt} are the sums respectively of the rates of all processes which transfer excitation to cis- and trans-stilbene. Since $k_{15} < 10^6$ sec.$^{-1}$ for all cases of interest to us (11), we may write:

$$(18)\quad \phi_{t\to c} = \underline{a}\left(\frac{K_6k_8}{K_6(k_7 + k_8) + k_9}\right)$$

$$(19)\quad \phi_{c\to t} = \underline{a}\left(\frac{K_6k_7 + k_9}{K_6(k_7 + k_8) + k_9}\right)$$

Furthermore,

$$(20) \quad \phi_{t \rightarrow c} + \phi_{c \rightarrow t} = \underline{a}$$

Also

$$(21) \quad \left(\frac{c}{t}\right)_s = \left(\frac{k_{qt}}{k_{qc}}\right) \left(\frac{\phi_{t \rightarrow c}}{\phi_{c \rightarrow t}}\right)$$

If, as was presumed the case for high energy sensitizers, $k_{qt} = k_{qc}$, then:

$$(22) \quad \left(\frac{c}{t}\right)_s = \frac{\phi_{t \rightarrow c}}{\phi_{c \rightarrow t}}$$

Study of the quantum yields for α-methyl stilbene isomerization sensitized by benzophenone showed that $\phi_{t \rightarrow c} + \phi_{c \rightarrow t}$ did equal the intersystem crossing yield of benzophenone within experimental error (4, 13). Furthermore, the ratio of the quantum yields was the same as the observed photostationary <u>cis</u>/<u>trans</u> ratio. For stilbene isomerization sensitized by benzophenone, however, it was found that $\phi_{t \rightarrow c} = 0.44$ and $\phi_{c \rightarrow t} = 0.37$. The ratio $\phi_{t \rightarrow c}/\phi_{c \rightarrow t} = 1.2$, while the photostationary <u>cis</u>/<u>trans</u> ratio was 1.5. The sum: $\phi_{t \rightarrow c} + \phi_{c \rightarrow t}$ was 0.81 while the reported intersystem crossing yield for benzophenone was 1.00 ± 0.02 (13).

It was noted that insertion of $\phi_{c \rightarrow t}$ and the observed photostationary state into equation 22 gave a predicted value of $\phi_{t \rightarrow c} = 0.56$. If this were the value of $\phi_{t \rightarrow c}$ then $\phi_{t \rightarrow c} + \phi_{c \rightarrow t} = 0.93$, giving a value for intersystem crossing in benzophenone which was more nearly in agreement with other reported values (13). It appeared then that the observed quantum wastage occurred in conversion of trans to cis stilbene. A likely quantum wastage process was considered to be self quenching of transoid triplets by trans-stilbene (reaction 10). Were this effect large enough, it was argued, it could lead to the observed discrepancy. However, a study of the dependence of $\phi_{t \rightarrow c}$ upon stilbene concentration showed increases in $\phi_{t \rightarrow c}$ with decreasing stilbene concentration which were too small to account for the observed effects. The quantum yield for isomerization of cis-stilbene, $\phi_{c \rightarrow t}$, was not dependent upon the concentration of cis-stilbene. A study of the dependence of the stationary cis/trans ratio obtained with benzophenone as sensitizer likewise failed to show more than a mild increase with decreasing stilbene concentration. It was this anomaly which led to initiation of this work: a careful study of the behavior of the stilbenes with sensitizers having triplet energies well in excess of those of either isomeric stilbene. In what follows we describe the results of this and related studies of stilbene isomerization.

RESULTS AND DISCUSSION

General Considerations

We discuss photosensitized *cis*-*trans* isomerization of the stilbenes in terms of the mechanism outlined in reactions 1-11 of the Introduction, but omitting the self quenching of *transoid* triplet by *trans*-stilbene. This omission is discussed in a later section. The mechanism presumes that isomerization occurs only in the stilbene triplet states and that the reactions of stilbene triplets subsequent to their formation are independent of the sensitizer which produced them. While this often holds true, it is not invariably the case and care will be taken in what follows to insure that these conditions are satisfied by all sensitizer-substrate pairs discussed in terms of the above mechanism.

For stilbene isomerization without self quenching of *trans*-stilbene, the analogue of equation 13 is:

$$(23) \quad \left(\frac{c}{t}\right)_s = \left(\frac{k_{qt}}{k_{qc}}\right)\left(\frac{K_6k_8}{K_6k_7 + k_9 + k_{10}[az] + k_{-2}[S]}\right)$$

In most of the cases discussed here no quencher is added and the photostationary states are extrapolated to infinite dilution in sensitizer. Hence:

$$(24) \quad \left(\frac{c}{t}\right)_s = \left(\frac{k_{qt}}{k_{qc}}\right)\left(\frac{K_6k_8}{k_9 + K_6k_7}\right) = \left(\frac{k_{qt}}{k_{qc}}\right)\left(\frac{\alpha}{1-\alpha}\right)$$

where $\alpha = [K_6k_8/K_6(k_7 + k_8) + k_9]$. To the extent that α remains constant for different sensitizers, equation 24 means that photostationary state measurements may be used to determine the ratio k_{qt}/k_{qc}.

In addition to the photostationary state and quantum yield measurements reported here, another experimental approach to the study of k_{qt}/k_{qc}, flash spectrophotometry, has been employed with very good success (11). High concentrations of the triplets of selected sensitizers are produced by a bright Xenon arc flash of short duration (~5 μsec.). After decay of the flash, the rate of decay of the triplet-triplet absorption spectrum of the sensitizer was measured both with and without added quenchers — in the case of interest here, stilbene. Using this technique, values of k_{15} were determined for many sensitizers. Quenching constants k_{qt} and k_{qc} for many stilbene-sensitizer systems were also determined. Data useful to this work are given in Table I.

For purposes of discussion, we identify two classes of sensitizers along classical lines. The first class consists of sensitizers having triplet excitation energies greater than 62 kcal/mole which were believed to transfer excitation at an equal rate to both of the stilbenes. The second class consists of sensitizers of triplet excitation energy less than 62 kcal/mole for all of which energy transfer to <u>trans</u>- or <u>cis</u>-stilbene, or both, proceeds at less than the diffusion-controlled rate. A discussion is given of recent evidence bearing on the decay ratio of the stilbene triplets justifying the assumptions necessary to use of equation 24 to determine k_{qt}/k_{qc}. In general, the

TABLE I

Measured k_{qt} and k_{qc} Reported by Herkstroeter (11) for Various Sensitizers and the Stilbenes

Sensitizer	E_T	k_{qc}	k_{qt}
	(kcal/mole)	(in ℓ/m-sec.)	
Thioxanthone	65.5	5.0×10^9	5.0×10^9[a,b]
Phenanthrene	61.8	3.8×10^9	4.6×10^9
2-Acetonaphthone	59.3	3.4×10^9	4.9×10^9
1-Naphthylphenyl ketone	57.5	2.5×10^9	4.4×10^9
Chrysene	56.6	2.5×10^9	5.0×10^9
Fluorenone	53.3	9.0×10^8	3.6×10^9
1,2,5,6-Dibenzanthracene	52.2	9.0×10^8	3.3×10^9
Benzil	50.9[c]	2.6×10^8	1.8×10^9
Pyrene	48.2	5×10^7	7×10^8
1,2-Benzanthracene	47.2	6×10^7	3×10^8
Benzanthrone	47.0	6×10^7	2.5×10^8
3-Acetylpyrene	45.5	4.3×10^6	1.5×10^7
Acridine	45.3	2.5×10^6	5.8×10^6
9,10-Dimethyl-1,2-benzanthracene	44.3	8.6×10^5	1.6×10^6
Anthracene	42.6	7.6×10^4	1.1×10^5
3,4-Benzpyrene	41.9	8.7×10^4	7.5×10^4

Table I (continued)

[a] Averages of all reported values are given. Range of reported values is ± 10–20% of the average.

[b] For all sensitizers of energy higher than 1, 2, 5, 6-dibenzanthracene, the values of k_{qt} and k_{qc} were measured only by flashing solutions having the photostationary state compositions then using the observed ratio of cis and trans stilbene to divide up the total quenching into those parts attributable to cis and trans stilbene.

[c] Vide infra discussion of the triplet energy of benzil.

treatment given is topical rather than general; it became obvious in the course of this work that although extraction of information about excited state processes from study of photochemical reactions was eminently feasible, considerable care was necessary in the processing of the data to remove the effects of processes other than energy transfer. A critical examination of the Hammond-Saltiel treatment of the stilbene system is given together with new interpretations where indicated.

Photostationary States for the Stilbenes with High Energy Sensitizers

We define "high energy sensitizers" for a photosensitized isomerization reaction as those sensitizers with triplet excitation energies at least 5 kcal/mole greater than the triplet excitation energy of either of the substrates. For the stilbene system high energy sensitizers are those having triplet energies greater than 62 kcal/mole. Our definition is chosen to coincide with the often reported (4) tendency of the rate of quenching of a donor by an acceptor to approach the diffusion controlled limit provided the triplet energy of the former exceeds that of the latter by 5 kcal/mole or more. In the past it was presumed that the photostationary states obtained with high energy sensitizers should depend only upon α since the rate of transfer to both isomers is diffusion controlled. Early experiments tended to confirm this expectation for the stilbenes (Table I) and other systems were reported to exhibit similar behavior (4, 5, 10, 14-18).

Unfortunately, some of the data in Table II were determined using filter systems which admitted light absorbed very preferentially by the stilbenes (Table III). Because stilbene undergoes isomerization after itself absorbing light (4), achieving photostationary states containing up to 92% cis-stilbene, stationary states measured for the system acetophenone-stilbene using a Pyrex filter do not accurately represent the course of the sensitized reaction alone. Some of the data in Figure I must then not be representative solely of the sensitized isomerization process.

In Table IV are given the results of a detailed study of the photostationary states obtained with high energy sensitizer-stilbene systems. All the data in Table IV were obtained at 27-28° using uranium glass filters and were analysed under essentially identical conditions using well-established vapor phase chromatographic techniques. No isomerization of the stilbenes occurred under the conditions employed in the analytical procedure. The v. p. c. attenuator was found to be linear and the two isomers gave equal responses within experimental error. The error limits correspond in actuality to precision limits of the v. p. c. analysis and may not reflect the full extent of the actual errors. However, it was found that reproducibility of individual determinations was generally possible well within the precision limits.

Several aspects of the data in Table IV require comment. Samples of both cis- and trans-stilbene of purity comparable to those employed here have variously been reported to have extinction

TABLE II

Photostationary States Reported by Saltiel for High Energy Sensitizer-Stilbene Systems

Sensitizer Conc. (m/ℓ)	Total Stilbene Conc. (m/ℓ)	% *cis* Initially	Filter System	Temp. °C	Photostationary State in % *cis*
Acetophenone (E_T = 73.6 kcal/mole)[a]					
0.050	0.050	0	P[b]	28	59.3 ± 1.0
0.010	0.050	100	P	28	59.1 ± 0.5
Benzophenone (E_T = 68.5 kcal/mole)[a]					
0.050	0.050	0	P	28	59.6 ± 0.4
0.050	0.050	100	P	28	59.6 ± 0.8
Thioxanthone (E_T = 65.5 kcal/mole)[a]					
0.050	0.050	0	U	28	71.5 ± 0.2
0.050	0.050	100	U	28	58.9 ± 0.5
9,10-Anthraquinone (E_T = 62.4 kcal/mole)[a]					
0.008	0.050	0	P	28	60.0 ± 1.2
0.008	0.050	100	P	28	59.7 ± 0.3
Flavone (E_T = 62.0 kcal/mole)[a]					
0.05	0.050	0	U	28	61.7 ± 0.1
0.05	0.050	100	U	28	61.3 ± 0.6

[a] Reference 19.

[b] "P" represents a Pyrex filter, reported by Saltiel to transmit 41% of the light at 3130 Å. "U" represents a uranium glass filter which transmits only wavelengths longer than 3400 Å (*vide infra*).

TABLE III

Some Extinction Coefficients of the Stilbenes and Various Sensitizers[a, b]

Substance	ϵ (3660 Å)	ϵ (3150 Å)
trans-Stilbene	0	26,500
cis-Stilbene	0	4,480
Acetophenone	3	57
Benzophenone	66	108

[a] For more complete listings see Experimental Section.

[b] Hanovia lamps of the type used in these experiments give an intensity of about 25 watts around 3660 Å and 20 watts near 3130 Å. Pyrex (2 mm.) transmits about 25% of the light at 3130 Å (see Experimental Section).

TABLE IV

Photostationary States for Sensitized Isomerization of the Stilbenes

Sensitizer Conc. (m/ℓ)	Total Stilbene Conc. (m/ℓ)	% *cis* Initially	Filter System[a]	Temp. °C	Photo-stationary State in % *cis*
		Acetophenone (E_T = 73.6 kcal/mole)[b]			
1.00	0.048	0	P	28	56.2 ± 0.5
1.00	0.048	0	U	27	54.9 ± 0.3
1.00	0.048	100	U	27	55.8 ± 0.3
1.00	0.024	0	U	27	55.7 ± 0.3
1.00	0.024	100	U	27	55.1 ± 0.3
0.50	0.049	0	U	27	55.7 ± 0.6
0.50	0.049	100	U	27	55.9 ± 0.1
0.50	0.010	0	U	27	55.8 ± 0.3
0.50	0.010	100	U	27	55.9 ± 0.5
0.25	0.050	0	U	27	55.5 ± 0.3
0.25	0.050	100	U	27	55.0 ± 0.6
0.10	0.050	0	U	27	54.7 ± 0.2
0.10	0.050	100	U	27	56.0 ± 1.2
0.05	0.050	0	P	28	59.2 ± 0.5
0.05	0.050	100	P	28	58.8 ± 0.1
		Propiophenone (E_T ≈ 73 kcal/mole)[b]			
0.50	0.049	0	U	27	55.6 ± 0.5
0.50	0.49	100	U	27	55.4 ± 0.4
0.50	0.049	0	U	27	55.1 ± 0.6
0.50	0.049	100	U	27	56.2 ± 0.2
0.25	0.050	0	U	27	55.6 ± 0.1

Table IV (continued)

Sensitizer Conc. (m/ℓ)	Total Stilbene Conc. (m/ℓ)	% *cis* Initially	Filter System[a]	Temp. °C	Photo-stationary State in % *cis*
Propiophenone (E_T ≈ 73 kcal/mole)[b] (continued)					
0.25	0.050	100	U	27	55.5 ± 0.4
0.10	0.050	0	U	27	54.4 ± 0.7
0.10	0.050	100	U	27	55.4 ± 0.4
iso-Butyrophenone (E_T = 72.2 kcal/mole)					
0.75	0.048	0	U	27	56.5 ± 0.3
0.75	0.048	100	U	27	56.3 ± 0.6
0.50	0.049	0	U	27	54.9 ± 0.5
0.50	0.049	100	U	27	56.3 ± 0.1
0.25	0.050	0	U	27	54.5 ± 0.2
0.25	0.050	100	U	27	56.3 ± 0.2
Cyclopropylphenyl ketone[c] (E_T ~ 72 kcal/mole)[d]					
0.80	0.048	0	U	27	55.7 ± 0.3
0.80	0.048	100	U	27	55.9 ± 0.6
Deoxybenzoin (E_T ~ 72 kcal/mole)[d]					
0.05	0.050	0	U	27	55.6 ± 0.2
0.05	0.050	100	U	27	56.4 ± 1.1
Carbazole[e] (E_T = 70.1 kcal/mole)					
0.05	0.050	0	U	27	84.3 ± 0.4
0.05	0.050	100	U	27	85.8 ± 0.4

Table IV (continued)

Sensitizer Conc. (m/ℓ)	Total Stilbene Conc. (m/ℓ)	% *cis* Initially	Filter System[a]	Temp. °C	Photo-stationary State in % *cis*
		Diphenylene oxide[f] (E_T = 70.1 kcal/mole)			
0.10	0.0050	0	U	27	59.2 ± 1.1
0.10	0.0050	100	U	27	60.0 ± 0.6
		Dibenzothiophene (E_T = 69.7 kcal/mole)			
0.10	0.0050	0	U	27	—
0.10	0.0050	100	U	27	78.0 ± 1.0[f]
0.05	0.050	0	U	27	64.3 ± 0.4[g]
0.05	0.050	100	U	27	64.6 ± 0.5[g]
		o-Dibenzoylbenzene (E_T = 68.7 kcal/mole)			
0.05	0.050	0	U	27	59.5 ± 0.6
0.05	0.050	100	U	27	62.5 ± 0.2
		p-Bromobenzophenone (E_T = 68.7 kcal/mole)			
0.05	0.050	0	U	27	03.7
0.05	0.050	100	U	27	03.6
		Benzophenone (E_T = 68.5 kcal/mole)			
0.05	0.050	0	P	28	59.6 ± 0.3
0.05	0.050	100	P	28	59.7 ± 0.4
0.05	0.050	0	U	27	59.4 ± 0.1
0.05	0.050	100	U	27	59.6 ± 0.2
0.05	0.050	0	U	27	60.5 ± 0.3[m]
0.05	0.050	100	U	27	60.3 ± 0.2[m]
0.05	0.010	0	U	27	59.4 ± 0.1

Table IV (continued)

Sensitizer Conc. (m/ℓ)	Total Stilbene Conc. (m/ℓ)	% *cis* Initially	Filter System[a]	Temp. °C	Photo-stationary State in % *cis*
Benzophenone (E_T = 68.5 kcal/mole) (continued)					
0.05	0.010	100	U	27	59.6 ± 0.2
0.05	0.0050	0	U	27	60.1 ± 0.3
0.05	0.0050	100	U	27	59.8 ± 0.6
0.05	0.0010	0	U	27	63 ± 4
0.05	0.0010	100	U	27	62.7 ± 1.3
1.00	0.048	0	U	28	59.3 ± 0.1
0.50	0.049	0	U	28	59.4 ± 0.1
0.25	0.050	0	U	28	59.4 ± 0.1
0.10	0.050	0	U	28	60.7 ± 0.4
0.01	0.050	0	U	28	59.5 ± 0.1
0.005	0.050	0	U	28	59.2 ± 0.6
p-Diacetylbenzene[h] (E_T = 67.7 kcal/mole)					
0.05	0.05	0	U	27	59.5 ± 0.1
0.05	0.05	100	U	27	58.9 ± 0.6
Fluorene[f] (E_T = 67.6 kcal/mole)					
0.10	0.0050	0	U	27	75.8 ± 0.6
0.10	0.0050	100	U	27	78.4 ± 1.2
9-Benzoylfluorene[i] (E_T = 66.8 kcal/mole)					
0.05	0.050	0	U	27	66.4 ± 1.0
0.05	0.050	100	U	27	70.4 ± 1.2

Table IV (continued)

Sensitizer Conc. (m/ℓ)	Total Stilbene Conc. (m/ℓ)	% *cis* Initially	Filter System[a]	Temp. °C	Photo-stationary State in % *cis*
Triphenylene[j] (E_T = 66.6 kcal/mole)					
0.05	0.050	0	P	28	45.8 ± 0.2
p-Cyanobenzophenone (E_T = 66.4 kcal/mole)					
0.05	0.050	0	U	27	59.5 ± 0.6
0.05	0.050	100	U	27	61.0 ± 0.7
1,3,5-Triacetylbenzene (E_T ≈ 66 kcal/mole ?)[k]					
0.05	0.050	0	U	27	60.5 ± 0.6
0.05	0.050	100	U	27	60.1 ± 0.2
Thioxanthone (E_T = 65.5 kcal/mole)					
0.05	0.050	0	U	27	58.9 ± 0.3
0.05	0.050	60	U	28	59.3 ± 0.6
0.05	0.050	100	U	27	60.3 ± 0.4
Anthraquinone (E_T = 62.4 kcal/mole)					
0.05	0.050	0	U	27	63.7 ± 0.1
0.05	0.050	100	U	27	63.1 ± 0.7
Phenanthrene[e] (E_T = 62.2 kcal/mole)					
0.08	0.0050	0	U	27	65.0 ± 1.3
0.08	0.0050	100	U	27	63.9 ± 0.9

Table IV (continued)

Sensitizer Conc. (m/ℓ)	Total Stilbene Conc. (m/ℓ)	% *cis* Initially	Filter System[a]	Temp. °C	Photo-stationary State in % *cis*
		Flavone[e] (E_T = 62.0 kcal/mole)			
0.05	0.050	0	U	27	62.1 ± 0.8
0.05	0.050	100	U	27	62.1 ± 0.7
		2-Acetylfluorene (E_T = 62.0 kcal/mole)			
0.05	0.050	0	U	27	64.6 ± 0.4
0.05	0.050	100	U	27	64.9 ± 0.3

[a] "U" represents a uranium glass filter while "P" represents a Pyrex glass filter. Transmission properties of these filters are given in the Experimental Section.

[b] The source of the quoted triplet energies is reference 19.

[c] Some formation of side products with this sensitizer.

[d] Estimated value. Reported value (reference in b) is in error.

[e] Solutions turned yellow.

[f] Measured photostationary state for this sensitizer using the indirect method with acetophenone the original absorber of light.

[g] Determined with light absorbed directly by the dibenzothiophene.

[h] Solutions were chromatographed on neutral Al_2O_3, eluted with benzene before v.p.c. analysis.

[i] Observed partial decomposition of the sensitizer.

[j] Triphenylene, (ϵ_{3660} = 0, ϵ_{3130} = 910), does not absorb all the incident irradiation. See text.

[k] The reported phosphorescence spectrum (note b) of 1,3,5-triacetyl benzene is in error (L. Coyne and D. Valentine, unpublished). No emission was detected from this compound in MCIP at 77°K.

[l] Photostationary states for this compound measured by the indirect method with benzophenone being the initial light absorber.

[m] These points determined using zone refined benzophenone and *trans*-stilbene. Solutions were degassed by the procedure used in quantum yield determinations.

coefficients of the order of unity at 3660 Å (11). Many of the sensitizers employed in obtaining data in Table IV have rather low extinction coefficients at this wavelength. To show that the filter systems employed were adequate to insure a purely sensitized reaction, both cis- and trans-stilbene were irradiated through the filter system and the rates of conversion of each to the other upon irradiation using the uranium glass filter were found to be less than 1% of that observed with typical sensitizers. We conclude that the absorption reported for the stilbenes at 3660 Å is due to impurities.

Because of the strong absorption of the stilbenes at 3130 Å, only 3660 Å light may be used in effecting a purely sensitized reaction, a requirement which limits very severely the number and types of sensitizers which can be used. In fact, almost the only sensitizers which absorb light at 3660 Å and have triplet energies greater than 62 kcal/mole are acetophenone and benzophenone and their derivatives. An indirect technique was employed to gain information about the behavior of the stilbenes with substances with triplet energies greater than 62 kcal/mole which do not absorb light at 3660 Å. The principle involved is quite straightforward. Solutions of the potential sensitizer and the appropriate stilbene in 20:1 ratio, together with enough acetophenone or benzophenone to absorb all the light at 3660 Å, are prepared, irradiated and analysed in the usual way. The expected course of events is transfer of triplet energy from acetophenone (or benzophenone) to the proposed sensitizer followed by transfer from sensitizer to the stilbenes. Photostationary states obtained in this way will contain small contributions from direct transfer of triplet energy from acetophenone to the stilbenes. The size of this fraction depends upon the relative rates at which the stilbenes and the potential sensitizer quench the original light absorber.

In practice, judged by the results obtained, the indirect technique is of limited value. A problem arises with sensitizers such as fluorene which have labile hydrogen atoms, because the $n \rightarrow \pi^*$ triplets of acetophenone and benzophenone tend to abstract hydrogen from them leading to undesired side product formation.

In two of three cases tested, naphthalene and phenanthrene, the indirect method gave the same photostationary state that was observed by the usual methods using extremely dilute solutions of the stilbenes (11). With dibenzothiophene, however, there appears to be no correspondence between the photostationary state obtained with absorption of light directly into the dibenzothiophene and that found when acetophenone is the initial light absorber. Part of the problem may arise in analysis since the dibenzothiophene interferes with determination of trans-stilbene peak areas. At the present time it appears that some care must be exercised in interpreting data obtained using the indirect technique.

Photostationary state data in Table IV show, with a few exceptions discussed separately below, a definite trend toward lower cis/trans stationary stilbene isomer ratios as the triplet energy of the sensitizer is increased. The cis/trans ratio reaches a value of 1.27 with the highest energy sensitizers used ($E_T \sim$ 73-75 kcal/mole). It is of considerable importance to the subsequent discussion that the factors governing the photostationary states obtained with given sensitizers be correctly identified. Therefore, prior to any discussion of the variations in the stationary cis/trans ratios obtained in the high energy region we discuss certain sensitizers whose (unusual) behavior can be directly attributed to causes other than the energy transfer processes we wish to consider.

Carbazole gives a photostationary state unusually rich in cis-stilbene. This determination was reproducible, but even with carefully purified carbazole, reaction mixtures turned yellow upon irradiation. It is also not clear that the triplet energy reported for carbazole on the basis of its phosphorescence spectrum (19) is correct; some evidence exists that the reported emission is spurious (20).

Use of p-bromobenzophenone as sensitizer for stilbene isomerization leads to rapid establishment of a quasi-stationary mixture containing in excess of 96% trans-stilbene. Upon longer irradiation the mixtures show a trend toward further enrichment in trans-stilbene. Phosphorescence spectra obtained from 4-bromobenzophenone indicate its triplet energy to be of the order of 68.7 kcal/mole (20). Since photostationary states very rich in trans-stilbene are generally found only for sensitizers having triplet energies around 40 kcal/mole, we believe that the principal reaction pathway with this sensitizer is photoproduction of bromine atoms which effect isomerization. Evidence to support this claim is presented on page 136.

Use of triphenylene as a photosensitizer for stilbene isomerization is complicated by the fact that at all wavelengths of light accessible with our equipment stilbene absorbs more strongly than triphenylene. The single photostationary state in Table IV includes competition from processes initiated by absorption of light both into triphenylene and stilbene and is mentioned here only because it is so unusual. We mentioned earlier that isomerization of the stilbenes initiated by absorption of light into the stilbenes gives mixtures very rich in cis-stilbene; consequently, added triphenylene clearly has a very profound effect upon the reaction. It is easy, in fact, to calculate that the observed trans-rich photostationary state cannot be the result of any non-chain isomerization process initiated by light absorption into triphenylene. Determination of the processes involved in the isomerization is not easy. Stilbene and triphenylene do not form a ground state complex (20). Addition of triphenylene (which absorbs none of the incident irradiation) does not affect the photostationary states obtained with 1, 2, 5, 6-dibenzanthracene-stilbene systems (Table V) from which we infer that ground state triphenylene does not interfere with the decay processes of stilbene triplets. It would seem that triphenylene must affect stilbene isomerization through reactions involving excited singlets, although it has been reported that trans-stilbene fluorescence at room temperature is not quenched by triphenylene (20). At the present time this problem is not understood. An investigation of the behavior of triphenylene with the α-methyl- and α, α'-dimethylstilbenes, which show effects similar to those observed

TABLE V

Effect of Added Triphenylene upon Photostationary States Obtained with 1, 2, 5, 6-Dibenzanthracene As Sensitizer

Dibenzanthracene Conc. (m/ℓ)	Triphenylene Conc. (m/ℓ)	Total Stilbene Conc. (m/ℓ)	Initial % *cis*	Photo-stationary State in % *cis*[a]
0.0058	0	0.025	0	89.0 ± 0.7
0.0058	0	0.025	100	88.3 ± 0.1
0.0058	0.011	0.025	0	87.3 ± 0.5
0.0058	0.011	0.025	100	88.6 ± 0.2
0.0058	0.029	0.025	0	88.2 ± 0.3
0.0058	0.029	0.025	100	88.2 ± 0.1

[a] All measurements were made at 28° in benzene solutions using the uranium glass filter.

for stilbene but are more amenable to study, is in progress (20) and hopefully will provide a better understanding of the unusual photoreactions of this compound.

In the discussion which follows we do not treat any of the sensitizers discussed above or any sensitizers for which the reaction mixtures turned color during irradiation or for which appreciable decomposition of the sensitizer occurred during the isomerization. Specifically, we do not discuss the results obtained with flavone or 9-benzoylfluorene, both of which gave yellow reaction mixtures. 9-Benzoylfluorene also appeared to decompose appreciably during the photoreaction. 9, 10-Anthraquinone is also not discussed, not because of overt misbehavior of this sensitizer but because it has proven difficult to reproduce photostationary states obtained with this sensitizer.*

Discussion of the High Energy Region

With the exceptions previously discussed, the photostationary state data in Table IV show a generally monotonic decrease in the stationary cis/trans-stilbene isomer ratio as the sensitizer triplet energy is increased. Therefore, production of trans-stilbene in the sensitized reaction becomes more favorable as the triplet energy of the sensitizer increases. According to equation 24, this result might be accommodated by a decrease in the ratio k_{qt}/k_{qc} or by a change in

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*Compare, for example, our values with those reported by Saltiel in Table II.

α or by a combination of the two. Our discussion will presume that α is invariant for the sensitizers of concern. With the possible exception of quantum yield measurements to be discussed presently, there is no evidence to suggest that energy transfer to either stilbene isomer results in other than a mixture of t^3 and p^3 which is rapidly equilibrated before undergoing further reactions. Unfortunately, relative absorption coefficients do not permit measurement of the azulene effect for acetophenone derivatives, so it cannot be said with complete certainty that the stilbene intermediates obtained from these sensitizers are identical to those produced by other sensitizers. We regard the possibility that different intermediates are produced as very unlikely. By elimination, we conclude that the ratio k_{qt}/k_{qc} decreases as the sensitizer triplet energy increases from 62 to 74 kcal/mole. This result requires reexamination of the belief that substantially exothermic electronic energy transfers occur at the diffusion-controlled rate.

We now discuss some general features of diffusion-controlled reactions. If a physical or chemical change occurs upon the first encounter of the particular reactants in solution then its rate will be determined only by the rate at which the reactants diffuse together. A number of theoretical calculations of the rate of physical encounters of reactants in solution have been given (21-24). Generally it is assumed that the reactants are spherical and that interactions of the solvent with reactants are described satisfactorily by the bulk viscosity (η) of the solvent. A rather sophisticated treatment of this model by Noyes (23) led to derivation of equation 25.

$$(25)\quad k' = [4\pi\rho\, DN/1000]\,[1 + 4\pi\rho\, DN/1000\, k_c]$$

where ρ is the collision diameter, D is the bulk diffusion rate, N is Avogadro's number and k_c is the rate constant that would describe the reaction if the distribution of molecules were that given by equilibrium statistical mechanics and had not been perturbed by reaction. Noyes' equation predicts for diffusion-controlled reactions in benzene at 25° a rate constant of about 10^{10} ℓ/m-sec.

For obvious reasons, experimental tests of equation 25 and its analogues are not easy to carry out, chiefly because it is necessary to verify by other means that in any model system reaction really does occur in the first encounter. Recombination of iodine atoms in carbon tetrachloride at 25° is believed to satisfy the above requirement — also iodine atoms are presumably spherical, and thus satisfy the assumptions of the model used in deriving equation 25. When Noyes (24) measured the rate of recombination of iodine atoms in carbon tetrachloride, however, the measured rate was only about half that predicted by equation 25 for a diffusion-controlled process. Noyes argued that equation 25 might be expected not to predict accurately the rate of a diffusion-controlled reaction provided that upon close but non-nearest neighbor approach of potential reactants the probability of an encounter is changed from the average value for the whole solution. In the derivation of equation 25 an isotropic environment is assumed for the diffusing species and diffusion is considered to be a continuous process;

any distortion of the environment upon close approach could lead to deviations from the rate predicted by equation 25.

In the photochemical reactions under consideration here, the deviations of the shapes of the reactants from spheres is very considerable. Furthermore, some long-range interactions almost surely occur between donor and acceptor. If Noyes' explanation of the iodine in carbon tetrachloride experiment is correct, then there is no guarantee that any two diffusion-controlled reactions should have the same rate. In Table VI are given quenching constants measured by Herkstroeter (11), by Liu, Fry and Hammond (25), by Vesley and Hammond (26), by Caldwell and Hammond (27), and by other workers for various energy transfer processes in high energy sensitizer-substrate systems. As can be seen from the data in Table VI, the rates are not all the same; this is, of course, exactly what might be expected, even if reaction in every case occurs on the first encounter in solution.

Although it seems quite reasonable to explain the different rate constants observed for energy transfer from high energy sensitizers as being due to different rates of physical encounters between donor and acceptor pairs, the obvious extension of this argument to explain differences in k_{qt} and k_{qc} for various sensitizer-stilbene systems is far less convincing. From the observed photostationary states with acetophenone and benzophenone as sensitizers for stilbene isomerization, it may be concluded that the ratio k_{qt}/k_{qc} is 20% less for the higher energy sensitizer. If this change were to be ascribed solely to

TABLE VI

Reported Rates of Exothermic Electronic Energy Transfer in Solution

Donor	Acceptor	ΔE_T[a]	10^{-9} k_q (ℓ/m-sec.)	Source
Triphenylene	1,3-Cyclohexadiene	+12	4.3	Ref. 26
β-Acetonaphthone	1,3-Cyclohexadiene	+ 6	4.6	Ref. 26
α-Naphthylphenyl ketone	1,3-Cyclohexadiene	+ 5	4.1	Ref. 26
Triphenylene	Isoprene	+ 5	6.4	Ref. 25
Thioxanthone	3-Bromostilbene	+ 8	6.0	Ref. 27
Biacetyl	Pyrene	+ 7	7.6	b
	1,2-Benzpyrene	+ 5	6.0	b
	Fluoranthene	+ 3	5.2	b
Thioxanthone	<u>trans</u> α-Methylstilbene	+14?	5.0[c]	Ref. 11
β-Acetonaphthone	<u>trans</u> α-Methylstilbene	+ 8	1.2	Ref. 11
α-Naphthylphenyl ketone	<u>trans</u> α-Methylstilbene	+ 5?	0.8	Ref. 11

[a] Calculated using best estimates of triplet energies of involved species.

[b] See reference 11 for the sources of these values

[c] Values estimated using total quenching rates observed for <u>cis</u> and <u>trans</u> photostationary mixture.

differences in the rates of diffusion of the species involved, then necessarily the relative rates of physical encounters of acetophenone triplets with the two stilbene isomers must differ by 20% from the corresponding rates for benzophenone triplets and the stilbenes. This appears unlikely for two reasons. Considering first the data in Table VI we note, for example, the data for quenching of biacetyl include quenching constants for a number of quenchers of very different configurations, distributions of excitation and energy. Despite the differences in acceptors the quenching rates are all very similar. It seems unlikely that differences as relatively subtle as changing from acetophenone to benzophenone triplets could produce large enough changes in relative diffusion rates to account for the differences observed in k_{qt}/k_{qc}.

We conclude that the most plausible explanation of the changes observed in k_{qt}/k_{qc} is to be found not in terms of different numbers of encounters of the two stilbenes with sensitizer triplets but rather in terms of different probabilities of energy transfer to the two stilbenes in each single encounter. In other words, energy transfer from sensitizer to at least one of the stilbene isomers is not diffusion controlled. There are three basic possibilities. The least likely of these is that k_{qt} decreases as the energy of the sensitizer increases from 62 to 73 kcal/mole. This we reject as unlikely on the basis of the data in Table VI which show an opposite trend for a number of systems. It is, of course, very difficult *a priori* to imagine why k_{qt} should vary inversely with the sensitizer energy.

A possible explanation of variation in k_{qt}/k_{qc} which deserves somewhat more consideration is that highly exothermic triplet energy transfer to cis-stilbene may occur with reasonable probability over distances in excess of those established in encounters. In this case k_{qc} need not be limited to the rate of diffusion. Some experiments have been carried out to establish the critical radius factors other exothermic transfers of triplet energy (28, 29), however, and the results suggest that over distances in excess of those achieved in encounters, the probability of triplet energy transfer is quite low. Certainly that the longer-range transfer could be sufficiently different for the two classes of sensitizer to produce the 20% difference observed in the overall rates, is improbable. We believe long-range transfer of triplet energy to either stilbene is unlikely to contribute much to the observed rates for the overall processes.

We are left with the conclusion that the probability of energy transfer to cis-stilbene during any given encounter between the sensitizer and stilbene, is less than unity. The reasons for this inefficiency are at present uncertain, but any explanation proposed must take into account the remarkable insensitivity of the ratio k_{qt}/k_{qc} to factors others than the triplet energy of the sensitizer for high energy sensitizer-stilbene systems. A few exceptions to this strict dependence upon energy have been noted. It is possible, of course, that some of the data in Table IV which were previously discarded because of experimental uncertainties should have been retained. In addition, it has been reported that the highly hindered benzophenone, 2, 4, 6-

triisopropyl benzophenone, transfers energy to cis-stilbene at a significantly slower rate than the unhindered ketone (11, 32). A number of other hindered benzophenones was reported by Jones (32) to give about 60% cis in the photostationary mixture.

Specification of the sources, or even of the most probable sources of the inefficiency in energy transfer to cis-stilbene from high energy sensitizers is not possible at the present time. In view of the fact that the overall transfer process is substantially exothermic throughout the high energy region, it seems clear that some orientation process, even perhaps requiring some activation energy, must occur before energy transfer can take place. The effect of raising the temperature upon the observed photostationary states was investigated by Saltiel who found an effectively equal increase in the amount of cis-stilbene at the stationary state for several sensitizers. This increase, which was attributed to differences in $\left(\frac{\alpha}{1-\alpha}\right)$ is in the opposite direction from that expected if energy transfer to cis-stilbene from high energy sensitizers were an activated process. However, the activation energies required to produce the energy transfer effects we observed are sufficiently small that they would probably be masked by the decay effects. This point is discussed in more detail later.

It is possible in theory to design experiments whose careful execution permits determination not only of k_{qt}/k_{qc} but also, with less precision, k_{qt} and k_{qc}. The two stilbenes are allowed separately to compete with another substrate for the triplets of a sensitizer of interest. Quantum yields are determined for all processes involved;

the proper ratios of these quantum yields then permit determination of k_{qt}/k_{qc}. If the rate at which the competing substrate quenches the sensitizer triplets is known, the absolute magnitudes of k_{qt} and k_{qc} may be determined also. An example of the kind of information which may be obtained from this type of experiment was given in the first part of this Thesis. Unfortunately, in our case competition experiments are not sufficient to answer the question of most interest — whether the apparent differences in k_{qt} and k_{qc} are due to different numbers of encounters of sensitizer triplets with the two stilbenes or to different probabilities of the two isomers accepting excitation during an encounter with a sensitizer triplet. Nevertheless, a number of competition experiments were carried out in the hope of providing direct evidence for differences in k_{qt}/k_{qc}. As can be seen from the results given in Table VII, the precision of the various experiments is insufficient to permit any conclusions as to their significance. More work on this kind of experiment should be profitable.

Since there is obviously definite variation in the photostationary states obtained for stilbene-high energy sensitizer systems, it is not out of place to inquire whether there is any system solid evidence that constant rates of energy transfer are found in the high energy region. We have already considered some data relevant to this question — the quenching constants given in Table VI. These data, however, suffer the disadvantage of including experimental uncertainty almost always of the order of the effect which is under investigation. Although photostationary state data can only give the ratio of k_{qt}/k_{qc} the greater

TABLE VII

Measurement of k_{qt}/k_{qc} for Stilbene by Competition Experiments

Sensitizer	Competing Substrate	k_{qt}/k_{qc} [a]
Benzophenone	α-Methylstilbene	1.0 ± 0.2
	Piperylene	0.90 ± 0.10
	Diethyl fumarate	1.1 ± 0.2
Acetophenone	Piperylene	0.95 ± 0.15

[a] All determinations except for methylstilbene experiment were made using analysis for the stilbenes only.

accuracy of measurement possible makes them much more suitable for investigating small differences in rate constants. In Table VIII are presented photostationary state data gathered in these laboratories for a number of different substrates. All of these data were obtained with sensitizers having energies at least 5 kcal/mole greater than the triplet energy of any of the substrates involved.

Some of the data in Table VIII are presented only for completeness. The isoprene dimerization does not furnish a meaningful case to study because the results obtained depend upon the relative rates of energy transfer to the two ground state conformers of the diene (15). In both cases, the minor conformer is present in such small amounts that the experimental error in determining product ratios obtained would mask out rather considerable rate differences in energy transfer to the two conformers. The data for the piperylenes and the α-methyl stilbenes are not characterized by outstanding precision, but in both cases show a trend toward more nearly equal quenching constants for the two isomers involved as the sensitizer triplet energy increases. Whether the precision of the data justifies any conclusion is questionable, but certainly little support seems available for the argument that k_{qt}/k_{qc} becomes constant in the sensitizer energy range investigated. For the α, α' dimethylstilbene system, the data is very precise and it seems quite clear that no leveling off of k_{qt}/k_{qc} was observed in this case. To be sure, the triplet energy of <u>trans</u>-dimethylstilbene is not known; however, it seems unlikely to be higher than 59 to 62 kcal/mole, in which case at least some of the data in

TABLE VIII

High Energy Photostationary States for Various Photosensitized Reactions

Piperylene Isomerization (Reference 4)

Sensitizer	E_T[a] (kcal/mole)	Stationary State (% trans-Piperylene)
Acetophenone	74	54 ± 1.0
Benzaldehyde	72	54 ± 1.0
Benzophenone	69	57 ± 0.5
Ethyl pyruvate	65	57 ± 1.0

α-Methylstilbene Isomerization (Reference 4)

Sensitizer	E_T[a] (kcal/mole)	Stationary State (cis/trans)
Acetophenone	74	1.18
Benzophenone	69	1.24

α, α' Dimethylstilbene Isomerization (Reference 17)

Sensitizer	E_T[a] (kcal/mole)	Stationary State (trans/cis)
Propiophenone	74	2.26
Xanthone	70	1.54
Benzophenone	69	3.38
1, 3, 5-Triacetylbenzene	68(?)	1.92
Thioxanthone	66	2.51
Anthraquinone	62.5	2.01

Table VIII (continued)

<u>Dimerization of Isoprene</u> (Reference 16)

Sensitizer	E_T	Σ[b]
Cyclopropylphenyl ketone	74	92
Propiophenone	74	93
Acetophenone	74	92
Benzaldehyde	72	90
1, 3, 5-Triacetylbenzene	68[c]	92
o-Dibenzoylbenzene	69	92
Benzophenone	69	93
Thioxanthone	66	92

[a] Reference 19.

[b] Σ represents the % noncyclohexene products in the dimer mixture and is a measure of the relative rates of energy transfer to the *s*-*cis* and *s*-*trans* conformers of isoprene. See the Introduction to Part One.

[c] Estimated.

Table VIII are for high energy sensitizers (14). It is thus not obvious that the ratio k_{qt}/k_{qc} has in any system been demonstrated to achieve a limiting value as the sensitizer energy increases.

Quantum Yields for Sensitized Isomerization of the Stilbenes

The original intent of this work was to study and to remove, if possible, the apparent anomaly presented by the measurement of quantum yields for isomerization of the stilbenes effected by high energy sensitizers. In Table IX we present the quantum yields previously reported by Cowan, Saltiel and Hammond (4), Saltiel, et al. (5); and in Table X we give our own measurements of quantum yields for the isomerization reaction. Our experimental conditions for these measurements are described in the Experimental Section; in general, we believe our conditions to have been somewhat more carefully controlled than those of previous workers.

Saltiel's (5) analysis of the quantum yields has been briefly reviewed in the Introduction. His analysis will not be further considered here because we believe it was based on erroneous data. We have calculated in Table XI the ratios $\phi_{t \rightarrow c}/\phi_{c \rightarrow t}$ obtained by comparing our measurements of $\phi_{t \rightarrow c}$ with our measurements of $\phi_{c \rightarrow t}$ for six sensitizers; and also by comparing our $\phi_{t \rightarrow c}$ measurements with the values obtained for $\phi_{c \rightarrow t}$ for benzophenone and acetophenone by Hammond, Saltiel et al. (4) and Lamola and Hammond (13). We prefer the latter comparison because our $\phi_{c \rightarrow t}$ values tend to be about 10% lower than those measured by those authors. Our sample of cis-

TABLE IX

Previously Reported Quantum Yields for Sensitized Isomerization of the Stilbenes

Sensitizer	Conc.[a]	Stilbene Conc.	$\Phi^{b}_{t \to c}$	$\Phi^{b}_{c \to t}$
Benzophenone	0.05	0.05	0.44	0.37
			0.45	0.39
		0.025	0.43	
		0.001	0.48	
Acetophenone	1.0	0.05	0.39	0.37
			0.40	0.37
				0.40

[a] All measurements were in benzene solvent.

[b] Values from reference 4.

TABLE X

Quantum Yields for Sensitized Isomerization of the Stilbenes

Sensitizer	Conc.[a]	Stilbene Conc.	$\Phi_{t \to c}$	$\Phi_{c \to t}$
Benzophenone	0.05	0.05	0.55 ± 0.02[b] 0.55 ± 0.01[c] 0.57 ± 0.04[d]	0.38[e] ± 0.02
	0.05	0.016	0.57 ± 0.03	
1,4-Diacetylbenzene	0.05	0.05	0.52 ± 0.02	0.37 ± 0.03
Acetophenone	0.80	0.045	0.52[e] ± 0.03	0.37 ± 0.03
Propiophenone	0.80	0.045	0.52 ± 0.03	0.37 ± 0.03
Thioxanthone	0.005	0.05	0.49 ± 0.02	0.33 ± 0.02
9,10-Anthraquinone	0.05	0.05	0.51 ± 0.02	0.28 ± 0.02

[a] The solvent was benzene.

[b] Determined using potassium ferrioxalate actinometry.

[c] Determined using benzophenone sensitized dimerization of cyclohexadiene as an actinometer. The quantum yield for that process was assumed to be 0.88 ± 0.02.

[d] Determined using benzophenone sensitized isomerization of α-methyl stilbene as the actinometry system. The quantum yield of the isomerization reaction was taken as 0.44 ± 0.02.

[e] All other values determined relative to the quantum yield for isomerization of <u>trans</u>-stilbene sensitized by benzophenone.

TABLE XI

The Ratio $\phi_{t \to c}/\phi_{c \to t}$ for Stilbene Isomerization As Determined from Quantum Yield Measurements

Sensitizer	$\phi_{t \to c}/\phi_{c \to t}$[a]	$\phi_{t \to c}/\phi_{c \to t}$[b]
Acetophenone	1.39	1.25
Benzophenone	1.47	1.37
Propiophenone	1.39	1.25[c]

[a] Comparison of our quantum yields.

[b] Comparison of Cowan's (4, 33) and Lamola's value for cis-stilbene isomerization (0.40), the highest value yet recorded for isomerization of stilbene, with our quantum yields for the trans- to cis-isomerization.

[c] Estimated, using $\phi_{c \to t}$ for acetophenone.

stilbene was also known to contain impurities.*

Using the right-hand column in Table XI it is found that the average $\phi_{t \to c}/\phi_{c \to t}$ value is about 1.30, in good agreement with the photostationary state cis/trans ratio of 1.27 measured for acetophenone. As can be seen from inspection of equation 21, the ratio $\phi_{t \to c}/\phi_{c \to t}$ should be equal to the stationary state cis/trans ratio only if $k_{qc} = k_{qt}$. The fairly close agreement of the two ratios for acetophenone then, presumably means that for this sensitizer $k_{qt} \approx k_{qc}$. Of course the ratio of quantum yields has considerable uncertainty so conclusions of this nature are hazardous undertakings.

Some interest attaches to the use of equation 20 and our measured quantum yields to estimate the intersystem crossing yields of the various sensitizers employed. For benzophenone, the sum $\phi_{t \to c} + \phi_{c \to t} = 0.93 \pm 0.04$ if our measurement for $\phi_{c \to t}$ is used and 0.95 ± 0.03 if Cowan's (4) and Lamola's measurements are used. For acetophenone, the corresponding numbers are 0.86 ± 0.04 and 0.90 ± 0.03. For both acetophenone and benzophenone, Lamola reported unit efficiency of intersystem crossing, so the quantum yield measurements still indicate that a small fraction of the incident quanta is wasted. With benzophenone it is questionable whether the observed difference (1.00 vs. 0.95) lies outside the actual experimental error, and for both sensitizers the discrepancies might be due to impurity

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*It was also difficult to obtain good analyses for small amounts of trans-stilbene. See Experimental Section.

quenching processes. We cannot entirely discount either of these possibilities. Nevertheless, there remains the disturbing possibility that the failure of the quantum yields to sum to unity is due to the ability of some sensitizer triplets to interact inefficiently with either or both of the stilbenes in ways other than by simple failure to transfer energy in a given encounter. For example, one possibility might be reversible addition of sensitizer to stilbene. It is quite possible that this kind of process could occur sufficiently often to produce the observed quantum loss and still not be detected in the measurement of azulene effects. Another possibility is formation during the first encounter of a weak complex which later breaks up to give the stilbene triplets. If such a complex occasionally failed to yield stilbene triplets, giving instead both stilbene and sensitizer in their respective ground states, the observed quantum loss would be explained. It is of interest and perhaps significance that acetophenone and propiophenone which give trans-rich photostationary states relative to that obtained with benzophenone as sensitizer both give also lower $\phi_{t \rightarrow c}$ values in stilbene isomerization. This point is given more amplification in the next section.

Stilbene with Sensitizers Having Triplet Energies Below 62 Kcal/mole

Photostationary state data given in Figure I for the stilbenes with sensitizers having triplet energies below 62 kcal/mole present an incomplete and, as seen from Figure III and Table XII, very misleading

TABLE XII

Photostationary States for Stilbene Isomerization Sensitized by Compounds with Triplet Energies Below 62 Kcal/mole

Sensitizer Conc.	Total Stilbene Conc.	% *cis* Initially	Filter System	Temp. °C	Photo-stationary % *cis*
Naphthalene[a] (E_T = 60 kcal/mole)[b]					
0.13	0.0050	0	U[c]	27	72.2 ± 0.5
0.11	0.0050	100	U	27	70.6 ± 1.5
Phenanthrene[a] (E_T = 60 kcal/mole)					
0.09	0.0050	0	U	27	65.1 ± 0.5
0.09	0.0050	100	U	27	63.9 ± 0.9
Chrysene (E_T = 56.6 kcal/mole)					
0.01	0.050	0	U	29	76.5 ± 0.5
1,2,5,6-Dibenzanthracene (E_T = 52.3 kcal/mole)					
0.006	0.050	0	U	29	88.2 ± 0.1
0.006	0.050	100	U	29	88.3 ± 0.2
Fluoranthene (E_T = 52.9 kcal/mole)					
0.0093	0.050	0	U	29	88.3 ± 0.4
0.0087	0.050	100	U	29	89.2 ± 0.4
0.0060	0.050	0	U	29	89.2 ± 0.5
0.0060	0.050	100	U	29	91.5
0.0032	0.050	0	U	29	89.5 ± 0.1
0.0031	0.050	100	U	29	88.6 ± 0.8

Table XII (continued)

Sensitizer Conc.	Total Stilbene Conc.	% *cis* Initially	Filter System	Temp. °C	Photo-stationary % *cis*
		Pyrene (E_T = 48.7 kcal/mole)			
0.031	0.050	100	U	29	90.6 ± 0.1
0.031	0.050	86	U	29	91.0 ± 0.1
0.018	0.050	100	U	29	91.6 ± 0.2
0.018	0.050	86	U	29	91.3 ± 0.1
0.011	0.050	100	U	29	92.7 ± 0.05
0.050	0.050	100	P	28	91.5 ± 0.2[d]
0.050	0.050	80	P	28	91.5 ± 0.2[d]
0.020	0.050	100	P	28	91.3 ± 0.1[d]
0.020	0.050	80	P	28	90.8 ± 0.3[d]
0.010	0.050	100	P	28	88.2 ± 0.1[d]
0.010	0.050	80	P	28	87.5 ± 0.1[d]

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[a] Indirect technique used with benzophenone (see Table IV).

[b] All triplet energies are from reference 19.

[c] "U" means uranium glass filter, "P" means Pyrex glass filter was employed.

[d] All of these values are from Saltiel's Thesis (5).

picture of the behavior of these systems. As a result, much of the Hammond-Saltiel interpretation of the data in Figure I is, we believe, in need of revision. Most of the difficulty appears to have been due to Saltiel's two assumptions that: a) the triplet energy of the sensitizer was sufficient to determine the photostationary state it would effect in stilbene isomerization; and b) that all of the data in Figure I represented the results only of energy transfer processes compatible with the general mechanism given in the Introduction. We believe neither of these assumptions is justified. The significance of the photostationary states will be considered first.

Photostationary state data in Figure III are given in % _cis_-stilbene instead of as the _cis_/_trans_ ratio. While the latter quantity is that directly related to k_{qt}/k_{qc}, it is subject to considerable error in highly _cis_-rich photostationary states such as are encountered with sensitizers having energies below 62 kcal/mole. The use of % _cis_-stilbene also permits a convenient demonstration of the steady tendency toward less _cis_-rich photostationary states as the sensitizer triplet energy increases in the high energy region. Points given in Figure I for photostationary states obtained with _p_-benzoquinone, 1,4-naphthoquinone, 9,10-dibromoanthracene and eosin* are omitted in Figure III. The reasons for these omissions are given below. The solid points are calculated from flash photolytic measurements of k_{qt} and k_{qc}, assuming invariant α (11). It will be noted that the points for very low

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*2,3,5,7-Tetrabromofluorescin.

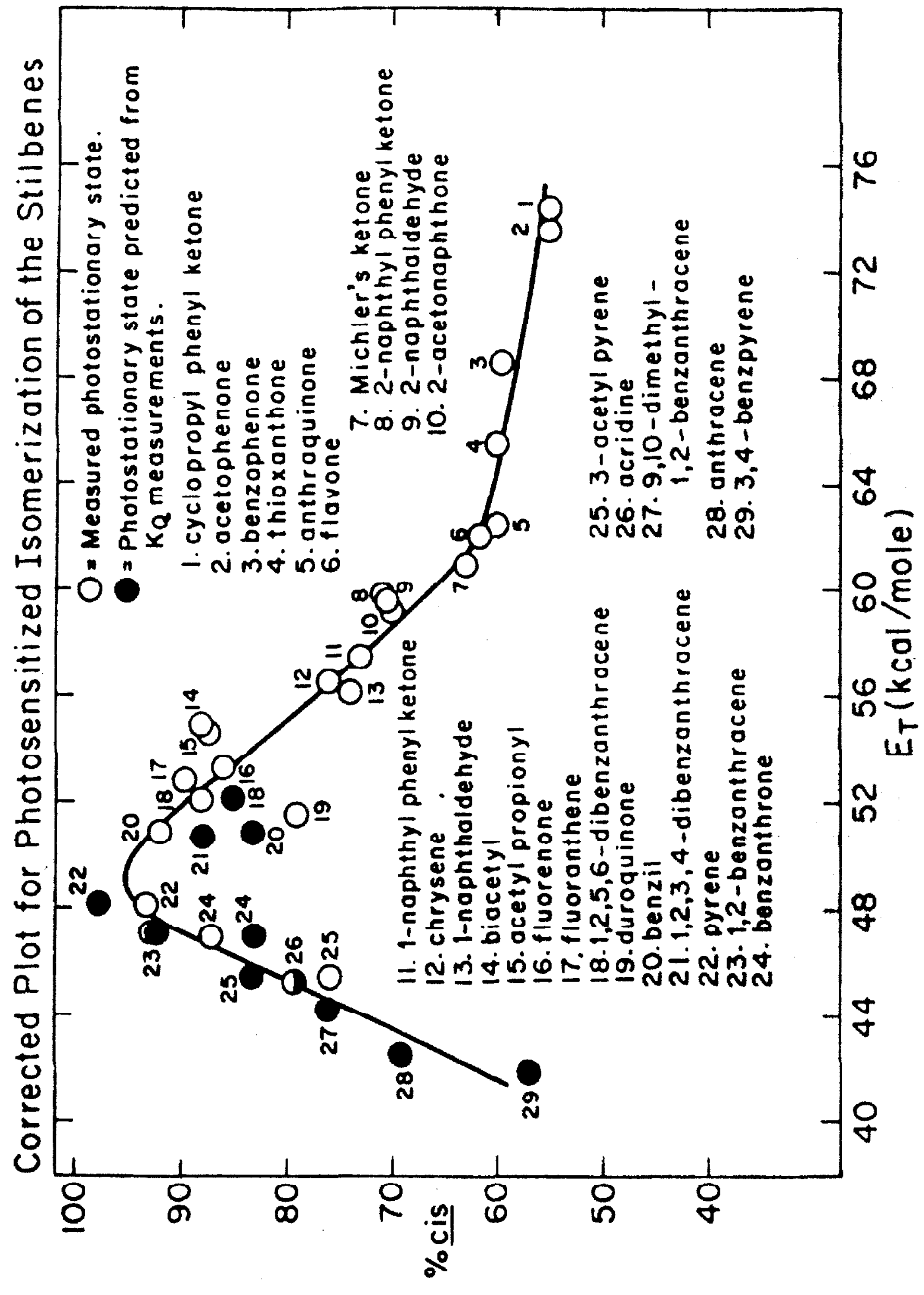
Corrected Plot for Photosensitized Isomerization of the Stilbenes
○ = Measured photostationary state.
● = Photostationary state predicted from K_Q measurements.
1. cyclopropyl phenyl ketone
2. acetophenone
3. benzophenone
4. thioxanthone
5. anthraquinone
6. flavone
7. Michler's ketone
8. 2-naphthyl phenyl ketone
9. 2-naphthaldehyde
10. 2-acetonaphthone
11. 1-naphthyl phenyl ketone
12. chrysene
13. 1-naphthaldehyde
14. biacetyl
15. acetyl propionyl
16. fluorenone
17. fluoranthene
18. 1,2,5,6-dibenzanthracene
19. duroquinone
20. benzil
21. 1,2,3,4-dibenzanthracene
22. pyrene
23. 1,2-benzanthracene
24. benzanthrone
25. 3-acetyl pyrene
26. acridine
27. 9,10-dimethyl-1,2-benzanthracene
28. anthracene
29. 3,4-benzpyrene
% cis
100
90
80
70
60
50
40
E_T (kcal/mole)
40
44
48
52
56
60
64
68
72
76

Figure III

energy sensitizers are only predicted values.

p-Naphthoquinone (E_T = 57 kcal/mole), duroquinone (E_T = 51.5 kcal/mole) and p-benzoquinone (E_T = 50 kcal/mole) were used by Saltiel to effect stilbene isomerization. The first and last of these quinones gave photostationary states which define the minima in the Saltiel plot given in Figure I. It is unfortunate that so much interpretation was based upon the results obtained with these compounds as their behavior as sensitizers appear now to be highly atypical due almost certainly to the ability of quinones to effect isomerization of the stilbenes by paths not described in the general mechanism given above.

Both naphthoquinone and benzoquinone undergo photoreactions with the stilbenes, the latter very rapidly. Benzoquinone forms ground state complexes with the stilbenes which in solutions of the concentrations used in determining photostationary states, probably absorbs most of the incident light. Duroquinone, however, neither forms ground state complexes with, nor consumes the stilbenes upon irradiation. It is probably significant, therefore, that the photostationary state achieved with duroquinone as sensitizer deviates much less from the apparent norm then do those for the other two quinones. Saltiel extrapolated the photostationary state obtained with benzoquinone to infinite dilution in both quinone and stilbene and assumed the "stationary state"* thus obtained resulted only from

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*Here "stationary state" means, of course, only the stilbene isomer ratio predicted by $(k_{qt}/k_{qc})\ (\alpha/1 - \alpha)$. The stationary state in the benzoquinone-stilbene system is, of course, probably all quinone-stilbene adduct.

energy transfer processes compatible with the general mechanism given above. This assignment has very little to recommend it: a) because there is no evidence that isomerization of stilbene occurs except in the complex and b) because the effects of consumption of the stilbenes during the photoreaction cannot be evaluated. Similar arguments can be seen to apply to the stationary state obtained with naphthoquinone.

A considerably more interesting and potentially more informative problem is presented by the behavior of the stilbenes with a number of α-diketones, namely biacetyl, 2, 3-pentandione and benzil (E_T = 53 kcal/mole).* All three diketones give photostationary states appreciably cis-rich with respect to those obtained with other sensitizers of apparently comparable energy. Photostationary states for both biacetyl and 2, 3-pentandione were obtained by Saltiel using Pyrex filters which would tend to increase the amount of cis at the stationary state relative to that obtained in the purely sensitized reaction; however, this error should be relatively small. Numerous and reliable data have been obtained for the system benzil-stilbene and we now consider this in some detail.

Benzil gives stationary states containing 93% cis-stilbene independent of the sensitizer concentration (vide infra) and does not form ground state complexes with the stilbenes (5). Conflicting data exist concerning the material balance obtained upon long irradiation of this

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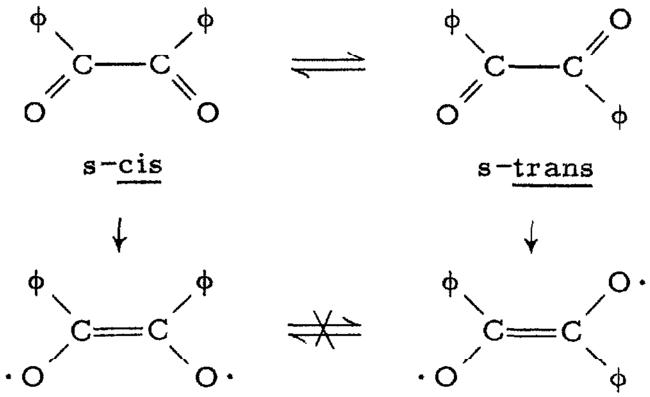
*Calculated from the phosphorescence spectrum.

system. Solutions containing 0.05 M benzil and 0.1 M stilbene degassed by the usual procedure employed for photostationary state determinations (see Experimental) showed upon prolonged irradiation no detectable loss of the stilbenes; in fact, these conditions were employed in this work in synthesis of <u>cis</u>-stilbene on a preparative scale. On the other hand, rigorously degassed solutions of 10^{-3} M benzil and 5×10^{-5} M stilbene used in flash experiments gave after prolonged irradiation and concentration in a nitrogen stream, evidence of a new product of retention time intermediate between those of the stilbenes on Apiezon J v.p.c. columns (31). Material balance under these conditions was poor. Whether the new product was produced photochemically or in the subsequent concentration of the solutions, is not known. Using the dilute solutions described above, Herkstroeter found k_{qt} and k_{qc} for benzil-stilbene which were both less than the corresponding rate constants obtained with stilbene and fluorenone, which is believed to have a lower triplet energy than benzil. This is the only instance (Table I) in which decrease in k_{qt} and k_{qc} does not accompany a decrease in the triplet energy of the sensitizer. Of course in view of the occurrence of a new product in the flash solutions, the significance of the measured quenching constants is uncertain.

Another complication in benzil-stilbene systems arises from the ability of benzil to exist in both s-<u>cis</u> and s-<u>trans</u> conformations. Excitation of either of these rapidly interconvertible forms provides a triplet which should have some degree of configurational stability.



The isomeric benzil triplets would be expected to have different energies (6). Phosphorescence observed from benzil fixes the energy of one of these triplets at 53 kcal/mole; however, there is no guarantee that it is this triplet which is observed in the flash photolysis experiments and which is responsible for stilbene isomerization. Discussion of the behavior of the α-diketones as sensitizers must then be hedged with the condition that the unusual effects observed may be due to our uncertainty about the triplet energies of these compounds. Herkstroeter (11) noted that benzil tends in many but not all systems to behave as though its triplet energy were about 51 kcal/mole. In Figure III, the photostationary state for benzil is plotted at 51 kcal/mole and the improvement in agreement of the stationary state with those obtained with other sensitizers of similar energy, is clear. We feel that this is not sufficient to justify the new assignment of triplet energy, especially in view of the fact that even if the lower energy is assigned, the measured values of k_{qt} and k_{qc} seem unusual (Figure III). We take the triplet energy of benzil to be 53 cal/mole, but acknowledge that a lower value is certainly possible.

We note finally that any peculiarities in the behavior of benzil and, by implication, other diketone sensitizers are restricted to the original energy transfer processes. The normal azulene effect observed with benzil implies that this sensitizer effects stilbene isomerization only by energy transfer to give the usual stilbene triplets (5). This observation lends strength to the supposition that the new product observed by Herkstroeter (11) arose in the concentration of his solutions following the photoreaction.

Before considering what factors may influence energy transfer from benzil to stilbene, we consider again the data of Figure III. These data make it clear that for many sensitizers, effects other than energy operate to determine the relative rates of triplet energy transfer to the two stilbenes, although the magnitude of the deviations caused is perhaps substantially less than for benzil and the other α-diketones. We believe there are strong qualitative though not quantitative similarities between the effects observed for benzil and other sensitizers.

We have already pointed out that benzil sensitized stilbene isomerization involves the usual, free stilbene triplets as intermediates. There is no reason to suppose that the same is not true of stilbene isomerization effected by the other sensitizers for which data is given in Figure III, and in the absence of contraindication we assume this to be the case. Discussion of the effects which determine photostationary states obtained with these sensitizers can then be centered only upon the original energy transfer process. It seems reasonable to suppose that the more exothermic energy transfer to trans-stilbene should, for sensitizers of energy greater than 50 kcal/mole or so, be less subject to special influences than transfer to cis-stilbene. We presume without proof that the major cause of variations in the excitation ratio is fluctuation of the rate constant k_{qc}. Of course most of the following discussion could apply also to energy transfer to trans-stilbene.

Definite limits can be placed on the ways in which k_{qc} can fluctuate. Flash spectroscopic measurements of k_{qc} and k_{qt} given in Table I show that both decrease monotonically with decreasing sensitizer energy. Although the data in Table I would not show up any small variations, they preclude large differences in k_{qc} not related to the sensitizer energy. Wherever it was possible in Table I to obtain separate measurements of k_{qc} and k_{qt} the agreement of the observed photostationary state with that calculated by taking the ratio k_{qt}/k_{qc} and multiplying it by $\alpha/1 - \alpha$, was good (Figure III) showing that quenching of sensitizer triplets by the stilbenes led in most cases to stilbene triplets and ruling out with these sensitizers at least, large scale effects of the type described in Part One of this Thesis, in which the stilbenes quench sensitizer triplets but are not themselves promoted to the triplet state.

Discussion of the factors which determine k_{qc} is rendered difficult by our ignorance about the relative contributions for any sensitizer of k_3 and k_4 to k_{qt}. It is not even certain whether reactions 3 and 4 represent different, competing processes or whether there is for any given sensitizer only one path by which energy is transferred to cis-stilbene. In our opinion the latter possibility is the more likely. We prefer to interpret the observed differences in k_{qc} in terms of a short-lived complex as shown in reaction 26. A similar complex is shown for trans-stilbene in reaction 27. Reactions 26 and 27 may be thought to supply details respectively of the mechanisms of reactions 3 plus 4 and 2.

$$(26)\quad S^3 + c \longrightarrow \text{Complex} \begin{array}{ll} \nearrow\ S + t^3 + p^3 & (a) \\ \rightarrow\ S + c & (b) \\ \searrow\ S^3 + t & (c) \end{array}$$

$$(27)\quad S^3 + t \longrightarrow \text{Complex} \begin{array}{ll} \nearrow\ S + t^3 + p^3 & (a) \\ \rightarrow\ S + t & (b) \\ \searrow\ S^3 + t & (c) \end{array}$$

There is little direct evidence to justify the formulation of the complex as in equations 26 and 27. Certainly the data given above for such sensitizers such as benzil indicate that the complex if formed, does not live long enough to undergo bimolecular reactions. This means that most of the effects we wish to explain must be attributed to the only process which can have a substantial activation energy, namely initial formation of the complex. It is not, therefore, surprising that attempts to detect emission from these complexes have met with failure. Writing the energy transfer to cis-stilbene in terms of reaction 26 would, in fact, have to be considered merely a superfluous method of reminding one that proper orientation was probably important to insure energy transfer were it not for the fact that there is evidence to indicate that reaction 26c is competitive with other possible processes for at least some sensitizer triplet-cis-stilbene systems. As was the case in the first part of this Thesis, where a similar mechanism was proposed for some sensitizer triplet-cyclohexadiene systems, the evidence in favor of 26c consists of quantum yield measurements. As can be seen from the data in Table XIII quantum yields ($\phi_{c \rightarrow t}$) for both 2-acetonaphthone and fluorenone sensitized stilbene isomerization are lower by a factor of two than predicted by equations 16 and 17 and the measured intersystem crossing efficiencies of these sensitizers (13). It is difficult to imagine how the spin-forbidden process 26c could be accomplished without intimate contact of sensitizer triplet and stilbene over a fairly long time interval; hence, the complex. Of course the above argument is based upon unexpectedly low quantum yields and must, therefore, be regarded as dubious. Obviously, further study of the quantum yields for sensitized isomerization of cis-stilbene is indicated.

As would be expected from the above discussion, isomerization of the α, α' dimethyl stilbenes sensitized by compounds with triplet energies below 62 kcal/mole leads to photostationary states which are not strongly dependent upon the sensitizer energy. The α-methyl stilbene system, for which a dependence of photostationary states upon sensitizer energy essentially identical to that given for stilbene in Figure I was reported (4), has not been reinvestigated but the structural features of that plot are again defined by stationary states

TABLE XIII

Quantum Yields for Stilbene Isomerization
Sensitized by 2-Acetonaphthone and 9-Fluorenone

Sensitizer Conc.	Stilbene Conc.	$\phi_{t \to c}$	$\phi_{c \to t}$
	2-Acetonaphthone[d] (E_T = 59.3 kcal/mole)[a]		
0.05	0.050	–	0.17[b]
	9-Fluorenone[d] (E_T = 53 kcal/mole)		
0.05	0.050	0.41[b]	
0.05	0.050	0.48[c]	
0.05	0.050		0.23[b]
0.05	0.050		0.19[c]

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[a] Reference 19.

[b] Reference 33.

[c] This work.

[d] For 2-acetonaphthone, a is reported to be 0.84 (13); hence, $a\alpha$ = 0.32. For 9-fluorenone, a is reported to be 0.93 (13); hence, $a\alpha$ = 0.37.

obtained with quinones as sensitizers.

Having presented the currently available data concerning the behavior of the stilbenes with sensitizers of energy between 50 and 62 kcal/mole, it is perhaps worthwhile to indicate explicitly which parts of the Hammond-Saltiel interpretation of the data in Figure I must be revised or discarded. That the photostationary state for sensitized stilbene isomerization cannot be predicted from the triplet energy of the sensitizer alone is obvious. It will also be obvious from photostationary state data and the quenching constants given in Table I, that there is no evidence at all for resonance energy transfer at the diffusion-controlled rate to either <u>cis</u>- or <u>trans</u>-stilbene. There is, therefore, no evidence either that the 50 kcal/mole triplet energy obtained by Evans (7) for <u>trans</u>-stilbene is in reality the energy of the 0-1 and not the 0-0 band.

Concluding our investigation of the dependence of the excitation ratio k_{qt}/k_{qc} for the stilbenes upon the properties of various sensitizers we review briefly the behavior of the stilbenes with sensitizers having triplet energies less than 50 kcal/mole. For these sensitizers energy transfer to either stilbene to produce the corresponding planar triplet is endothermic. As the data in Table I show, the rate of energy transfer from sensitizer to <u>trans</u>-stilbene drops off quite rapidly as the sensitizer triplet energy falls below 50 kcal/mole. The rate of drop-off is that expected if only energy transfer to produce the planar triplet is involved and has been taken as evidence for this (11). As was indicated in the Introduction, this finding is consistent with the type of triplet state potential energy surface drawn in Figure II. The rate of energy transfer to cis-stilbene on the other hand drops off more slowly with decreasing energy of the sensitizer. This is due to the nonvertical energy transfer process (reaction 4) which was first postulated by Saltiel (5) to account for the behavior of the stilbenes with sensitizers having very low triplet energies. For a variety of reasons nonvertical energy transfer is not easily studied in the stilbene system and has been investigated thoroughly only in other systems (3). There is, however, no apparent reason to doubt that nonvertical energy transfer is not an important means of exciting cis-stilbene by low energy sensitizers.

Photostationary states containing only 0.02% cis-stilbene were reported by Saltiel (5) for the very low energy sensitizers ($E_T \sim 40$ kcal/mole) eosin and 9, 10-dibromoanthracene. The preponderance of trans-stilbene was taken as evidence that k_4 dominated the excitation ratio. Herkstroeter (11), however, found that k_{qc} and k_{qt} for anthracene and 9, 10-dimethyl-1, 2-benzanthracene, which also have triplet energies around 40 kcal/mole, were approximately equal. The predicted photostationary states for these sensitizers are shown in Figure III. The discrepancy could be accommodated by postulating for trans-stilbene occurrence of reaction 27c. However, we believe that the sensitizers containing bromine cause stilbene isomerization by light induced ejection of bromine atoms which subsequently add reversibly to the stilbenes. Evidence to favor this assertion will now be presented.

Approximate quantum yields were determined for isomerization of cis-stilbene sensitized by 4-bromobenzophenone, 9,10-dibromoanthracene and eosin, both with and without added 1,4-diazabicyclo-[2.2.2]öctane, a strong organic base. The results are given in Table XIV. The results with eosin are probably not meaningful because diazabicycloöctane appeared to form an addition compound with eosin in a dark reaction. The intended function of the diazobicycloöctane was to scavenge hydrogen bromide or bromine atoms and prevent these substances from catalysing isomerization of the stilbenes. If either of the substances were the agent responsible for stilbene isomerization then the presence of the amine should lead to decreases in the quantum yield, $\phi_{c \rightarrow t}$, obtained with these sensitizers. This expectation was realized as shown by the data in Table XIV.

A number of apparently contradictory quantum yield measurements has been reported for 4-bromobenzophenone as a sensitizer in different systems. These data are given in Table XV. Cowan (33) found $\phi_{c \rightarrow t} = 0.050$ and $\phi_{t \rightarrow c} = 0.04$ for stilbene isomerization photosensitized by 4-bromobenzophenone. Our measurements were made at higher conversions so as to allow time for the build-up of a sizeable concentration of bromine atoms. This probably explains why the quantum yield we measured is so much higher than that reported by Cowan. Lamola (13) reported a quantum yield $\phi_{t \rightarrow c} = 0.45$ for bromobenzophenone sensitized piperylene isomerization, indicating an intersystem crossing ratio for the sensitizer of 1.00. This result is somewhat puzzling but may be due to capture of bromine atoms or HBr

TABLE XIV

Approximate Quantum Yields for Stilbene Isomerization Sensitized by Compounds Having Bromine Substituents

Sensitizer Conc.	Stilbene Conc.	Diazabicycloöctane Conc.	% Conc.	$\phi_{c \to t}$[a]
		4-Bromobenzophenone		
0.02[a]	0.05	0	52.0 ± 0.2	0.98
0.02	0.05	0.20	~3	0.07
		Eosin[b]		
0.0029	0.050	0	2	0.04
0.0029	0.050	0.20	2	0.04
		9,10-Dibromoanthracene		
0.0032	0.050	0	2.5	0.05
0.0032	0.050	0.20	0	0

[a] The actinometer was the benzophenone sensitized isomerization of trans-stilbene for which process the quantum yield was assumed to be 0.5.

[b] Eosin formed a red salt with diazobicyclooöctane upon standing in the dark.

TABLE XV

Quantum Yields Reported for Various
Processes Sensitized by 4-Bromobenzophenone

Substrate	$\phi_{t \rightarrow c}$	$\phi_{c \rightarrow t}$	Source
trans-Stilbene	< 0.05		Ref. 33
	0.98		This work
cis-Stilbene		0.04	Ref. 33
cis-Piperylene		0.55	Ref. 11

by the piperylenes.

To add weight to the assertions made previously about bromine as an active agent for effecting stilbene isomerization, an 0.05 M solution of *cis*-stilbene in benzene was refluxed one hour in the presence of 0.025 M N-bromosuccinimide. At the end of this time the *cis*-stilbene was about 80% converted to *trans*-stilbene. Since N-bromosuccinimide is known to produce bromine atoms (35), this result would seem to demonstrate that bromine atoms can effect stilbene isomerization. In the above experiment material balance appeared to be excellent and no side products were observed. In conclusion, it should be emphasized that the above results do not prove, although they do strongly suggest, that the isomerization of the stilbenes produced by eosin and 9, 10-dibromoanthracene is effected by bromine atoms.

The Stilbene Triplets

The Hammond-Saltiel description (4, 5) of the properties and reactions of the stilbene triplets was based primarily upon observation of the ways in which the decay processes of the stilbene triplets were affected by the controlled addition of selected substances believed capable of quenching triplet states and by other changes in the experimental conditions. Several presumptions were involved in this treatment; these have been considered in detail elsewhere (4, 5) and do not seem to be open to question. Saltiel's description of the stilbene intermediates is qualitatively in accord with all data presently available but the results of this work indicate that some quantitative revisions of the theory are in order.

Plotting the trans/cis ratio at the stationary state against sensitizer concentration or the concentration of added azulene was found by Saltiel to give good fits to the linear curves demanded by equation 12. These results appear to demand the existence of one triplet which is quenched preferentially or exclusively to give trans-stilbene; for reasons given above this triplet is believed to have a transoid configuration. Kinetic analyses of the azulene and sensitizer concentration effects were given by Saltiel. The slope of a plot of trans/cis at the stationary state divided by the intercept of this plot ($[S] = 0$) can be seen from equation 12 to give k_{-2}/k_9. In Table XVI are tabulated k_{-2} values obtained with a number of different sensitizers. Because of the short lifetime of the stilbene triplets, energy transfer to the sensitizer can compete with unimolecular decay of the sensitizer only if the rate k_{-2} is high; for all sensitizers with energies greater than 53 kcal/mole $k_{-2}[S] \ll k_9$ and no sensitizer concentration effect is observed. As can be seen from Table XVI, k_{-2} is not correlated satisfactorily by sensitizer (here, acceptor) energy alone; in fact, the data in Table XVI present an interesting study of the effects which the structure of an acceptor may have upon the rate of energy transfer. That such effects should be important is, of course, exactly what would be expected in terms of the discussion given in the previous section.

Referring again to equation 12, it is clear that for sensitizers for which $k_{-2}[S] \ll k_9$, the slope of a plot of the stationary trans/cis

TABLE XVI

Rates of Reverse Energy Transfer from Stilbene Triplets to Various Sensitizers

Sensitizer	E_T	$k_{-2}/K_6k_8 \times 10^{-2}$	Source
Acetophenone	74	0	This work
Propiophenone	74	0	This work
Isobutyrophenone	74	0	This work
Benzophenone	69	0	This work
Thioxanthone	67	0	This work
β-Acetonaphthone	59	0	Ref. 5
Benzil	53(?)[a]	0	This work; Ref. 5
9-Fluorenone	53	0	Ref. 5
Fluoranthene	52.2	0	This work
Duroquinone	51.7	0.07[b]	Ref. 5
Pyrene	45.5	0.09[c]	This work
1,2-Benzanthracene	47.3	0.35[b]	Ref. 5
Benzanthrone	47(?)[d]	1.7	Ref. 5
Acridine	45.3	0.87	Ref. 5
3-Acetyl pyrene	45.3(?)	0.88	Ref. 5

[a] See text.

[b] All numbers taken from reference 5 are divided by 1.5 to correct a computational error made by Saltiel. This error was pointed out by Dr. R. A. Caldwell.

[c] Saltiel's determination (5) of pyrene stationary states was in error so his reported value for k_{-2}/K_8k_6 is erroneous.

[d] Estimated value. See reference 11.

ratio against the concentration of added azulene, divided by the intercept of such a plot, will give k_{10}/k_9. We have previously shown that the ratio k_{10}/k_9 is a constant for all sensitizers for which the azulene effect was determined. It should be noted, however, that k_{10}/k_9 can be determined as described above only if $k_{-2}[S] \ll k_9$. It is, therefore, not possible to use azulene effects to draw conclusions about the stilbene intermediates obtained with sensitizers showing sensitizer concentration effects.

Saltiel assumed that the rate of quenching of the transoid triplet by azulene was diffusion controlled and assigned it a value of $k_{10} = 1.0 \times 10^{10}$ ℓ/m-sec. This assignment permitted in turn assignment of upper limits for k_9 and k_{-2}; for k_9 the upper limit was estimated to be about 5×10^7 sec.$^{-1}$, implying that the lifetime of the stilbene triplets was almost two orders of magnitude shorter than any reported previously. We believe that the upper limits are probably not good estimates of the actual values of k_9 and k_{-2}. First, it seems unlikely that diffusion-controlled rates are, as Saltiel assumed, satisfactorily estimated by equation 25 or its analogues. Second, it has already been shown (15) that energy transfer from the nonplanar triplets of isoprene to azulene occurs at less than the diffusion-controlled rate. If the transoid triplet configuration is significantly nonplanar, it would be expected to transfer energy to azulene at less than the diffusion-controlled rate. Consequently, it would not be surprising if the lifetime of the stilbene triplets was significantly longer than that postulated by Saltiel.

A comparison of k_{-2} with k_{10} was used by Saltiel to determine the rate for transfer of energy from the transoid triplet to sensitizer. As can be seen from Table XVI, the rate constant k_{-2} achieves its maximum value with benzanthrone as sensitizer when $k_{-2} \approx k_{10}$ and, by the argument given by Saltiel, k_{-2} is diffusion controlled. That k_{-2} for benzanthrone appeared to be diffusion controlled was assumed to be the result of resonance transfer of triplet energy, and taken to mean that the energy of the relaxed transoid triplet was 47 kcal/mole (see Figure II). This assignment cannot, of course, be substantiated. There is no way at present of estimating with any accuracy the energy of the relaxed transoid triplet.

The general shape of the potential energy curve of the stilbene triplets given in Figure II was inferred from the observation that increasing the reaction temperature led to increased production of cis-stilbene in the sensitized reaction. Since the increase was very nearly independent of the sensitizer employed, Saltiel (5) concluded that: a) inefficiencies in energy transfer to cis-stilbene did not appear as an activation energy, and b) the increased production of cis-stilbene at higher temperatures was due solely to perturbation of the equilibrium between t^3 and the slightly more energetic triplet p^3. It has been argued by Herkstroeter* that these conclusions cannot be valid, because for the sensitizers used in studying the temperature effects, energy transfer to trans-stilbene is diffusion controlled while transfer

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*Private communication.

to *cis*-stilbene sometimes is and sometimes is not diffusion controlled. Changes in the viscosity of the solvent occasioned by changes in the temperature then will have an effect upon the diffusion-controlled transfer to *trans*, but not the slower transfer to *cis*-stilbene. What this argument ignores, however, is the activation energy for transfer to *cis*-stilbene which will cause the rate of transfer to *cis*-stilbene to increase as the temperature is increased. There are, then, three effects which must be taken into account in discussing the temperature dependence of stilbene isomerization: increases in the rate of transfer to *trans*-stilbene due to changes in the viscosity; increases in the rate of transfer to *cis*-stilbene, an activated process; and differences in α. According to equation 25, the rate of transfer to *trans*-stilbene should increase by a factor of 2 over the 30° temperature range investigated by Saltiel. It is not clear how much the rate of transfer to *cis*-stilbene might be expected to increase although we suspect the increase will probably be at least a factor of 2. These two effects should then lead to increased production of *trans*-stilbene. Since more *cis*-stilbene is produced it is evident that the decay of stilbene triplets gives substantially more *cis*-stilbene at the higher temperature. This problem deserves further study, but Saltiel's conclusions — shown schematically in Figure II — seem generally correct.

The only process postulated in the Saltiel mechanism which is not included in the mechanism we have given is self-quenching of the *transoid* triplet by *trans*-stilbene.

(10) $t^3 + \underline{t} \longrightarrow 2\underline{t}$

TABLE XVII

Stilbene Concentration Effect upon Photostationary States in the Benzophenone Sensitized Isomerization

Stilbene Conc.	Initial % *cis*	Photostationary State in % *cis*	Source
0.1	?	59.6	Ref. 4
0.05	0	59.6 ± 0.3	This work
	100	59.7 ± 0.3	This work
0.01	0	59.4 ± 0.1	This work
	100	59.6 ± 0.2	This work
0.005	0	60.1 ± 0.3	This work
	100	59.8 ± 0.6	This work
0.001	?	61.6	Ref. 4

Reaction 10 was included in the Saltiel mechansim to account for a small but definite increase in the cis/trans ratio at the stationary state obtained upon lowering the concentration of the stilbenes below 0.01 M. Some data for acetophenone and benzophenone sensitized stilbene isomerizations are given in Tables III and XVII. Although the process(es) responsible for the observed increase in the stationary cis/trans ratio are not known and the data are not sufficient to permit identification of the functional dependence of the photostationary state upon the stilbene concentration, it appears that reaction 10 does not represent the required process. It is possible to obtain an explicit solution for the trans/cis ratio at the stationary state as a function of total stilbene concentration when reaction 10 is included in the mechanism for stilbene isomerization. The equation to be solved (assuming $k_{-2}[S] = 0$) is

$$(28) \quad \left(\frac{\underline{\text{trans}}}{\underline{\text{cis}}}\right)_{\text{stat.}} = \left(\frac{k_3 + k_4}{k_2}\right) \left(\frac{K_6 k_7 + k_9 + k_{-2}[\underline{\text{trans}}]}{K_6 k_8}\right)$$

And the solution is:

$$(29) \quad \left(\frac{\underline{\text{trans}}}{\underline{\text{cis}}}\right)_{\text{stat.}} = \left(\frac{k_3 + k_4}{k_2}\right) \left(\frac{u}{T - u}\right)$$

where T represents the total stilbene concentration and u is given by:

$$(30) \quad u = \frac{k_{10}T - K_6(k_7 + k_8) - k_9 + \sqrt{(k_{10}T - K_6(k_7 + k_8) - k_9)^2 + 4k_{10}T}}{k_{10}}$$

The variation in the stationary trans/cis ratio with T is of approximate order one-half; hence, reaction 10 does not offer a sufficient explanation of the data in Table III showing changes in trans/cis ratio with stilbene concentration only for low stilbene concentrations. Omission of reaction 10 from consideration earlier was not intended to deny the observed data but merely to indicate that their explanation is unknown.

Summary

We now summarize briefly the general conclusions which appear to follow from our study of the photosensitized cis-trans isomerization of the stilbenes. Detailed study of the behavior of high energy sensitizer-stilbene systems reveals that the rates of energy transfer from these sensitizer to cis- and trans-stilbene are not the same. The less exothermic transfer to cis-stilbene appears to proceed at a slower rate than transfer to trans-stilbene. Although other possibilities exist it seems most likely that the lower rate of transfer to cis-stilbene reflects a nonunit probability of energy transfer during the first encounter in solution. This is the first example of substantially exothermic electronic energy transfer which apparently does not occur at the diffusion-controlled rate. What factors lead to failure to transfer energy during the first encounter is unknown. The strong dependence of the photostationary states upon the sensitizer triplet energy suggests the general unimportance of steric effects although at least one documented steric effect has been reported. Quantum yield measurements tend to support the above conclusions. It is found that the quantum yields predict the photostationary state observed for acetophenone. There is no evidence of extensive quantum wastage in isomerization of trans-stilbene sensitized by benzophenone.

For sensitizers with triplet energies below 62 kcal/mole, sensitizer triplet energy is not a sufficient parameter to determine stilbene photostationary states. Saltiel's postulate to the contrary is wrong. There is no evidence which indicates that resonance transfer of triplet energy occurs in the stilbene system. Several of the sensitizers used by Saltiel are apparently capable of affecting stilbene isomerization by processes other than energy transfer. Quinones and sensitizers containing bromine comprise this class.

The mechanistic puzzle presented by the variations of the excitation ratio k_{qt}/k_{qc} admits no obvious solutions. For sensitizers having triplet energies greater than 50 kcal/mole we presume that most of the variation in the excitation ratio is due to changes in k_{qc}. Energy transfer to cis-stilbene from sensitizers having energies lower than 57 kcal/mole probably involves both vertical and nonvertical excitation processes. It is not known, unfortunately, whether these processes actually involve different mechanisms. There is evidence in other systems, however, which suggests that nonvertical excitation of cis-stilbene should require very intimate contact and precise orientation of the donor-acceptor pair. A likely possibility is that the energy transfer takes place through a short-lived complex which breaks up to give the normal stilbene triplets. It is also possible that the postulated complex can break up to yield both the sensitizer and cis-stilbene in their respective ground states. This unprecedented type of reaction offers an intriguing explanation of some unusually low quantum yields observed for isomerization of cis-stilbene, but there is no evidence which demands such a process. Rather little is known about the behavior of the stilbenes with sensitizers having triplet energies below 50 kcal/mole. Flash spectroscopic studies show that k_{qt} drops rapidly with decreasing sensitizer energy and for sensitizers of about 42 kcal/mole energy is once again roughly equal to k_{qc}. The flash data indicate that only classical energy transfer to trans-stilbene is important. Only nonvertical energy transfer processes should be important sources of excitation of cis-stilbene for low energy sensitizers. It is not possible to measure unambiguously the effect of azulene on these systems but the same stilbene triplets are being produced by low as by high energy sensitizers as can be seen from the fact that the rate constants k_{qc} and k_{qt} obtained by flash spectroscopy serve to predict the photostationary state with reasonable accuracy. There are not enough photostationary state data available to permit any estimation of the importance of nonenergy dependent parameters for sensitizers of very low energy. The two lowest energy sensitizers used by Saltiel, eosin and 9, 10-dibromoanthracene, appear to effect isomerization of the stilbenes by liberating bromine atoms.

With regard to the stilbene triplets, later work has tended only to confirm the Hammond-Saltiel picture of a two minimum potential energy curve for the stilbene triplets as shown in Figure II. Quenching of stilbene triplets by azulene offers the strongest evidence that the same stilbene triplets are produced by most sensitizers and that the use of photostationary state measurements to determine k_{qt} and k_{qc} is justified. Transfer of energy from the <u>transoid</u> triplet to various sensitizers depends upon nonenergetic factors as would be expected. There is no evidence that resonance energy transfer occurs in this process and consequently there can be no justification for assigning the relaxed <u>transoid</u> triplet an energy of 46 kcal/mole. What the energy of this species is, is uncertain, but the temperature effects clearly indicate that it is less energetic than the twisted triplet p^3.

EXPERIMENTAL

Materials

trans-Stilbene. — trans-Stilbene used in photostationary state determinations was MCB scintillation grade which was twice recrystallized from ethanol and sublimed under vacuum at about 80° (1 mm.). The melting point of this sample was 125.6–125.8°.

trans-Stilbene used in quantum yield determinations was zone refined by Dr. J. Hinton, Valparaiso, Florida and used as received. It contained 0.08% cis-stilbene and melted at 125.9–126.0°.

cis-Stilbene. — cis-Stilbene for use in most of the experiments described in this work was prepared and purified by Dr. K. R. Kopecky. It contained 0.09% trans-stilbene.

A few experiments were carried out using cis-stilbene prepared from trans-stilbene as follows. Solutions of 0.1 M trans-stilbene and 0.05 M benzil in benzene were irradiated until the photostationary state was reached. Evaporation of the benzene and chromatography of the residue on neutral, activity one alumina using hexane as element, gave after evaporation a mixture of 97% cis- and 3% trans-stilbene. Vacuum distillation gave a middle fraction of 99.5% pure cis-stilbene which was again vacuum distilled giving 55% overall yields of cis-stilbene containing 0.5% trans-stilbene.

cis and trans-α-Methyl Stilbene. — Both cis- and trans-α-methyl stilbene were kindly supplied by Dr. D. J. Cram and were used as received.

Benzene. — Benzene (MCB analytical reagent) was stirred over sulfuric acid layers until the acid layer was not discolored, washed with distilled water, dried over potassium carbonate and distilled from phosphorous pentoxide through a column packed with glass helices. A middle fraction, b.p. 79.9°-80.0° was collected. The benzene was redistilled if the phosphorous pentoxide layer was discolored during the distillation. Benzene prepared in this way was satisfactory for use in flash photolysis and was used throughout this work.

n-Hexane. — Technical grade *n*-hexane was washed with sulfuric acid until the acid layer was no longer discolored, washed with dilute aqueous sodium bicarbonate and water, dried over magnesium sulfate and distilled from sodium, b.p. (of the middle fraction) 68.7-68.9°. Hexane so prepared was transparent above 2100 Å.

Ethanol. — Absolute ethanol from stock was distilled before use as a recrystallizing solvent; the middle fraction, b.p. 78°, was collected. Ethanol so prepared was transparent to u.v. above 2100 Å.

Methanol. — Spectroquality methanol was used as received.

1,3-Cyclohexadiene. — Cyclohexadiene (Aldrich Chemical Company) was washed with aqueous sodium bisulfite and with water, dried over potassium carbonate, distilled from sodium, b.p. 78-79°, and finally bulb-to-bulb distilled and stored at 0° under vacuum.

Isoprene. — Isoprene (MCB Chemical) was distilled before use.

***cis*-Piperylene.** — *cis*-Piperylene was obtained from Mr. L. M. Stephenson. It contained 1.0% *trans*-piperylene.

1,4-Diazabicycloöctane. — Diazabicycloöctane was obtained from K and K Laboratories and used as received.

Acetophenone. — Acetophenone (MCB Chemical) was twice recrystallized from ethanol and vacuum distilled. It was placed over potassium carbonate for 30 minutes then again vacuum distilled. It was stored at 0° and redistilled prior to each use.

Propiophenone. — Propiophenone (Aldrich Chemical Company) was vacuum distilled through a packed column placed over potassium carbonate for 30 minutes and redistilled. It was stored at 0° and vacuum distilled prior to each use.

Isobutyrophenone. — Isobutyrophenone (Aldrich Chemical Company) was distilled under vacuum through an efficient column, placed over potassium carbonate for 30 minutes and redistilled. It was stored at 0° and vacuum distilled before each use. V.p.c. analysis on Apiezon L revealed about 2% impurity, probably an isomeric ketone.

Cyclopropyl Phenyl Ketone. — Aldrich cyclopropyl phenyl ketone was vacuum distilled before use and stored at 0°. It contained two impurities and appeared to give a photoproduct upon irradiation, even in the presence of stilbene. The identity of this product is unknown.

_p_-Biacetylbenzene. — Biacetylbenzene used in determining photostationary states for stilbene isomerization was prepared by treating Aldrich biacetylbenzene with Norite in ethanol and recrystallizing several times from the same solvent. The tan crystals resulting were sublimed to give white cubes. Substantially the same results were obtained by simply subliming Eastman White Label biacetylbenzene to give white crystals. This latter material was used in quantum yield determinations.

_o_-Dibenzoylbenzene. — *o*-Dibenzoylbenzene obtained from Dr. A. A. Lamola was sublimed before use.

Deoxybenzoin. — MCB reagent grade deoxybenzoin was used as received, m.p. 54-56°.

Benzophenone. — Benzophenone used in stationary state and some quantum yield determinations was MCB reagent grade recrystallized three times from ethanol, m.p. 45.8-46.0°. For quantum yield determinations for the sensitized isomerization, zone-refined benzophenone, m.p. 45.9-46.0° was used.

Thioxanthone. — Thioxanthone (Aldrich Chemical Company) was treated with Norite in boiling ethanol and recrystallized from the same solvent. Four repetitions of this procedure gave slightly yellow crystals, m.p. 213-214°. Sublimation then gave at first white crystals, m.p. 216.0-216.5°, and later yellow crystals, m.p. 214° and lower. The white crystals were used in making all measurements reported here. Irradiation of the yellow crystals in deoxygenated solutions resulted in bleaching as reported by Saltiel (5). The yellow impurity was produced by heating thioxanthone in the presence of oxygen. Its nature is unknown.

_p_-Bromobenzophenone. — _p_-Bromobenzophenone (Cal Biochem) was twice treated with Norite in ethanol and crystallized from the same solvent. The resulting tan crystals were sublimed under vacuum to give white crystals.

_p_-Cyanobenzophenone. — _p_-Cyanobenzophenone (Aldrich Chemical Company) was treated with Norite in ethanol and recrystallized from the same solvent. Sublimation of the resulting crystals gave white crystals.

1, 3, 5-Triacetylbenzene. — 1, 3, 5-Triacetylbenzene was treated with Norite in ethanol and crystallized from the same solvent. Sublimation then gave white crystals.

Triphenylene. — Triphenylene used was obtained from Mr. C. D. DeBoer and was zone refined, m.p. 198-199°.

Diphenylene Oxide (1, 2, 4, 5-Dibenzofurane). — Diphenylene oxide was obtained from Dr. W. G. Herkstroeter. It had been recrystallized from hexane, m.p. 85-86° (reported: 87°).

Fluorene. — Fluorene (MCB Chemical) was recrystallized twice from ethanol giving colorless plates, m.p. 114.7-115.1°.

Fluoranthene. — Fluoranthene (Aldrich Chemical Company) was treated with Norite in ethanol and recrystallized three times from the same solvent to give white crystals, m.p. 109-110°.

Carbazole. — Carbazole (MCB Chemical) was treated with Norite in methanol and recrystallized four times from that solvent, giving fluffy white crystals, m.p. 244-246° (reported: 246°).

9, 10-Anthraquinone. — 9, 10-Anthraquinone (Aldrich Chemical Company) was recrystallized twice from glacial acetic acid and sublimed under vacuum at about 110°, 0.1 mm., to give beautiful, light-yellow crystals, m.p. 284-285° (sealed capillary).

9-Fluorenone. — 9-Fluorenone was zone-refined material obtained from Dr. W. G. Herkstroeter, m.p. 84.5-84.6°.

2-Acetylfluorene. — 2-Acetylfluorene was obtained from Mr. C. D. DeBoer. It had been sublimed under vacuum and was used without further purification.

Flavone. — Flavone was obtained from Dr. A. A. Lamola and used as received, m.p. 95-96° (reported: 97°).

Diphenylenesulfide (1, 2, 4, 5-Dibenzthiophene). — Dibenzthiophene was recrystallized twice from *n*-hexane and gave white crystals.

9-Benzoylfluorene. — Aldrich Chemical Company 9-benzoylfluorene was treated with Norite in ethanol and recrystallized four times from that solvent. Sublimation then gave white crystals.

1, 2, 5, 6-Dibenzanthracene. — Dibenzanthracene was obtained from Dr. J. Fox. It had been crystallized from glacial acetic acid and sublimed under vacuum, m.p. 266.5-267.2° (sealed capillary).

Chrysene. — Chrysene was obtained from Dr. W. Herkstroeter and used as received. It had been recrystallized from benzene and sublimed under vacuum, m.p. 251.5-252.6° (reported: 254°).

Pyrene. — Pyrene was obtained from Dr. J. Saltiel. It had been recrystallized from ethanol and sublimed under vacuum, m.p. 147-148°.

Phenanthrene. — MCB reagent grade phenanthrene was sublimed under vacuum, m.p. 98.6-99.3°.

Eosin. — Eosin used was a student preparation recrystallized from acetone before use.

9,10-Dibromoanthracene. — To a stirred solution of anthracene (Eastman Red Label) (11.0 g.) in 350 ml. of carbon disulfide was added 6 ml. of bromine over a 20 minute period. After stirring the solution for 6 hours at room temperature, it was cooled in a dry ice-acetone bath whereupon there precipitated 13 g. of dibromoanthracene. After separation of the crystals, the CS_2 layer was washed with water and again cooled, yielding an additional 4 g. of dibromoanthracene. The product was washed with water, dried in a vacuum desiccator, recrystallized three times from carbon tetrachloride and finally sublimed under vacuum, giving beautiful yellow needles, m.p. 219.5-219.8°.

Extinction Coefficients of Sensitizers. — Approximate extinction coefficients were measured for all the sensitizers employed to effect stilbene isomerization. The values given (Table XVIII) are for

TABLE XVIII

Approximate Extinction Coefficients of Various Sensitizers

Sensitizer	Extinction Coefficient for $\lambda = n$ Å							
$n =$	3650	3600	3350	3200	3150	3100	3050	3000
Acetophenone	3	7	46	58	57	53	50	65
Propiophenone	2	4	37	49	48	46	42	50
Isobutyrophenone	5	10	59	70	66	59	54	58
1,4-Diacetylbenzene	39	67	193	350	> 750	> 750	> 750	> 750
1,3,5-Triacetylbenzene	15	26	113	152	166	225	331	425
Deoxybenzoin	21	29	109	113	101	93	87	117
9-Benzoylfluorene	28	43	190	300	450	1000	>2500	>2500
Benzophenone	66	91	122	85	70	62	86	271
p-Bromobenzophenone	88	122	164	118	99	89	125	390
p-Cyanobenzophenone	98	121	132	113	108	252	697	1450
2-Acetylfluorene	29	56	> 700	> 700	> 700	> 700	> 700	
o-Dibenzoylbenzene	135	190	296	327	357	448	2072	
Thioxanthone	>5700	>5700	1800	360	420	465	>5700	
Carbazole	23	29	3000	3550	3000	2900	3800	
Flavone	37	56	611	> 700	> 700	> 700	> 700	
Diphenylenesulfide	0.9	1.4	15	—	—	—	—	
Diphenyleneoxide	0	0	0	—	—	—	—	
Fluorene	0	0.4	2.4	48	66	280	8900	
Fluoranthene	2200	4000	5500	4800	4000	3600	2000	

solutions in methanol vs. methanol and were measured on a Cary 11 recording spectrophotometer.

Determination of Photostationary States for Stilbene Isomerizations. — Several procedures were used to determine photostationary states the sensitized isomerization of the stilbenes.

The general method was to introduce benzene solutions of the stilbenes and sensitizers in the proper concentrations into clean Pyrex tubes constricted near the top. The solutions were then degassed, sealed under vacuum and irradiated with a 450 watt Hanovia lamp housed in a quartz immersion well. A number of different filter systems was employed. Analysis of the photostationary compositions was carried out using standard v. p. c. techniques.

Test tubes for stationary state determinations were washed with aqueous solutions of orvus, scrubbed carefully with a test tube brush, rinsed many times with distilled water and dried several hours in the oven at 110°. Tubes prepared in this way were wet entirely by a single drop of water. The outsides of sealed tubes were washed previous to irradiation.

All samples were degassed using a vacuum line which achieved a pressure of $< 5 \times 10^{-4}$ mm. Three freeze-thaw cycles were used with cooling in liquid nitrogen.

Irradiation of samples was carried out either in the "merry-go-round" which has been amply described elsewhere or in a stationary irradiation system described on the following page concomitantly with the 3130 Å filter system.

Several different filter systems were employed:

a) 3660 filter: This was a Corning filter which transmitted about 20% of the incident irradiation at 3650 Å (band width ~ 100 Å) and effectively no irradiation at other wavelengths.

b) Uranium glass filter: This filter was constructed of 0.25 cm. thick uranium glass and transmitted only wavelengths longer than 3400 Å. Its use was equivalent to using the 3660 Å filter.

c) Pyrex filter: This filter was a 0.25 cm. thick sheet of Pyrex and transmitted about 1% of the light at 2800 Å, 40% at 3100 Å, 75% at 3340 Å and > 90% at 3660 Å.

Determination of isomer compositions at the stilbene photostationary states was by v.p.c. analysis using either a Loenco model 15 B v.p.c. with a thermal conductivity detector or a Loenco model 70B with dual flame ionization detectors. In both cases equimolar solutions of the stilbenes gave peaks with relative areas 1:1 and results obtained with either v.p.c. agreed with those obtained by Saltiel using spectroscopic analysis. Periodic checks were run to insure that the detector responses were invariant with time and linear for all attenuations. The system used for this purpose was the photostationary state mixture obtained with 0.05 M stilbene and 0.05 M benzophenone. In every case the photostationary states were approached from both sides and duplicate samples were measured at one day intervals in the irradiation to insure that the actual stationary composition had been reached.

The uncertainties given in the % cis represent only the precision of the v. p. c. analysis (average of 3 or more determinations) and obviously do not measure the real errors in the determinations. Because of this fact several of the stationary states were redetermined; in these cases duplicate values are reported. In every case investigated the average values of two determinations differed by less than the measured uncertainty in either value.

In cases where the sensitizer, because of retention time comparable to that of the stilbenes, interfered with analysis of the stationary state, the reaction mixtures were chromatographed on alumina with benzene as eluent. Since the offending sensitizers were generally ketones it was usually sufficient to continue the chromatography until no more stilbene was eluted, and then analyse the combined fractions containing stilbene. This procedure was tried on several sensitizers for which the sensitizer did not interfere with v. p. c. analysis and the same stationary states were obtained before and after the alumina chromatography.

Indirect Determination of Photostationary States. - To permit measurement of stilbene photostationary states for sensitizers which did not absorb sufficiently well at long wavelengths (> 3400 Å), the following indirect technique was employed. Solutions in benzene were prepared to be 0.05 M in benzophenone (or 1.0 M in acetophenone) 0.1 to 0.2 M in the intended sensitizer and 0.005 M in total stilbenes. Preparation, irradiation and analysis of these solutions were then accomplished as described in the previous section.

Determination of Quantum Yields. — A. Preparation of Samples. Benzene solutions of the stilbene and appropriate sensitizer were delivered by calibrated syringe into constricted Pyrex test tubes surmounted by a grease trap and ground glass joint by which the tube was attached to the vacuum line. The grease trap consisted of a glass partition broken only by a small opening in the center.

Three degassing procedures were used to deoxygenate the solutions. The first method consisted simply of the procedure previously described for degassing solutions prior to stationary state determinations. It was employed only with tubes not possessing the grease traps or ground joints. The second method employed the ground glass joints and traps but used the same vacuum line as method one. In this case the ultimate vacuum was invariably 1.2×10^{-4} mm. The third method was the best. A vacuum line was used which had an oil diffusion pump capable of giving ultimate vacuums of 0.5 to 1.0×10^{-6} mm. Three freeze-thaw cycles were used with the diffusion pump operating.

B. Irradiation of Samples. Considerable care was taken to insure that the solutions for quantum yield measurements were not exposed to light except during the desired period of irradiation. For measurement of quantum yields for the sensitized reaction alone, irradiation was with a 450 watt Hanovia medium pressure mercury arc through Corning 737 and 052 filters. This filter system admits only a narrow band of light of wavelengths equal to 3650 ± 50 Å. It has been described elsewhere (11).

The irradiations were carried out in the "quantum yield merry-go-round," which insures equal amounts of radiation incident on each solution. To simplify calculations and permit accurate, direct comparisons of results as many determinations as possible were carried out at one time. Checks were run to insure that the values so obtained allowed repetition.

Actinometry for Quantum Yields. — For all measurements potassium ferrioxalate actinometry (4) was used to determine the quantum yield for the isomerization of *trans*-stilbene sensitized by benzophenone; then all the other measurements were made by comparison with this system.

Analysis of Quantum Yield Data. — Two aliquots of each solution for a particular determination, occasionally three, were analysed on a Loenco Dual Flame v.p.c. with integrating recorder as described earlier. Corrections were made for back reaction using the equation derived by Lamola (11). The errors reported represent precision limits of the analysis of the stilbene solutions by v.p.c. and do not, therefore, necessarily represent the actual errors in the measurements.

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PROPOSITION I

Excimer formation by 1, 2, 7, 8-dibenzanthracene offers a means of explaining the unusual sensitizer concentration effect observed with this sensitizer in stilbene isomerization.

* * * * * * * * *

In photosensitized isomerization of stilbene, sensitizers having triplet energies of less than 53 kcal/mole produce stationary *trans*/*cis* isomer ratios which increase linearly with increasing concentration of the sensitizer. This effect is believed due to quenching by the sensitizer of the *transoid* stilbene triplet (1).

$$(1) \quad t^3 + S \longrightarrow t + S^3$$

Interpretation of the sensitizer concentration effect in terms of reaction 1 is supported by the similar effect of azulene, a good triplet quencher, upon the stationary *trans*/*cis* ratio. That the triplet being quenched has *transoid* geometry is implied by the preponderance of *trans*-stilbene produced by quenching it. No evidence for any species quenched preferentially to give *cis*-stilbene has been found.

Until recently, all observed sensitizer concentration effects were in the direction predicted by equation 1; a recent report (2), however, describes a linear *decrease* in the stationary *trans*/*cis* isomer ratio with increasing concentration of 1,2,7,8-dibenzanthracene (1278) as sensitizer. Since there do not appear to be stilbene triplets which can be quenched to give preferentially *cis*-stilbene, the explanation for this effect must be found in the excitation processes. There is no evidence that 1, 2, 7, 8-dibenzanthracene forms ground state complexes with the stilbenes; hence, the only plausible explanation of the observed concentration effect is to be found in preliminary formation of a 1, 2, 7, 8-dibenzanthracene excimer which transfers triplet energy to the stilbenes in competition with the triplet state of the monomeric hydrocarbon.* The triplet energy of such an excimer would be lower than the triplet energy of the monomer and should, therefore, lead to a more preferential excitation of trans-stilbene than that effected by the monomer triplet.** Whether the excimer is the result of interaction of an excited singlet or triplet of the monomer with monomer ground state, the same dependence upon sensitizer concentration should be observed. From estimates of the rate constants for quenching of sensitizer monomer by cis- and trans-stilbene, it appears that if the excimer is formed from the triplet sensitizer then its rate of formation must be essentially diffusion controlled, but it does not appear possible to draw any other conclusions a priori.

Unfortunately, few good tests exist for excimer formation. What are probably the most promising approaches in this situation are

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*Evidence for excimer formation by a number of hydrocarbons is reviewed by Murrell, reference 3.

**It must be admitted, however, that in this case if the triplet energy of the excimer were very much less than the monomer triplet energy a very small normal concentration effect should be observed. Beyond the qualitative prediction that the triplet energy of the excimer should be lower, there isn't much to justify a priori predictions of the excimer energy.

measurements of the fluorescence and phosphorescence spectra of 1278 as a function of its concentration. The observation of a change in the fluorescence spectrum with concentration will provide evidence for excimer formation involving 1278 excited singlets (3); failure to observe any change is, of course, an ambiguous result. Phosphorescence of 1278 has been observed at 77°K in EPA glass; whether sufficient concentrations of 1278 can be obtained to study excimer formation at 77° is problematical. Once again only observation of a change in the phosphorescence can be interpreted. Information about the formation of the excimer can be obtained from study of the stilbene concentration effect upon the *trans*/*cis* ratio. If all of the excimers are formed from 1278 singlets then the usual stilbene concentration effect (1) ought to be observed; if part of the excimers are formed from 1278 triplets, then the *trans*/*cis* ratio ought to depend also upon the stilbene/1278 ratio.

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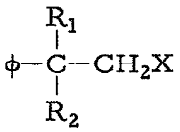
PROPOSITION II

Experiments are proposed to test the possible role of bridged radicals in the neophyl rearrangement.

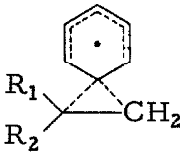
* * * * * * * *

Recent reports of delayed formation of bridged free radicals (1) raise the question of the importance of bridged intermediates in the homolytic rearrangement of neophyl type compounds 1. To determine the importance of such bridged intermediates as 2, investigation of the decarbonylation of the optically active aldehydes 3a and 3b is proposed.

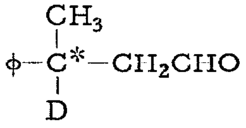


$\phi-\underset{R_2}{\overset{R_1}{C}}-CH_2X$

1

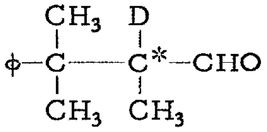


2



$\phi-\underset{D}{\overset{CH_3}{C^*}}-CH_2CHO$

3a



$\phi-\underset{CH_3}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{D}{C^*}}-CHO$

3b

X = CHO, $-N=N-$, CO_3tBu, etc.

R_1, R_2 = phenyl, aryl, alkyl, H, etc.

Skeletal rearrangements of 1 during homolytic substitution for X have been the object of intensive investigation mostly devoted to examination of Winstein's suggestion (2) that phenyl participation might occur in the homolytic as in the heterolytic reactions of neophyl type compounds. A typical example of the neophyl rearrangement is afforded by the peroxide induced decarbonylation of 4 at 130°C which yields a 1:1 mixture of rearranged and unrearranged product (3).

$$\phi C(CH_3)_2CH_2CHO \longrightarrow \phi C(CH_3)_2{-}CH_3 + \phi CH_2{-}CH(CH_3)_2$$

4

The products can be accounted for as arising from either the corresponding classical radicals or from the bridged species 2, $R_1{=}R_2{=}CH_3$. Many examples of the rearrangement are known, its homolytic character is well documented, and it is known that the migrating group is always phenyl or aryl. The nature of R_1 and R_2 and not the nature of X determine the extent of rearrangement.*

With a given substrate, the amount of rearrangement observed depends upon the reaction conditions. The presence of hydrogen donors or high aldehyde concentrations during decarbonylations suppresses rearrangements. The extent of rearrangement during decarbonylations increases with temperature, implying that the rearrangement is an activated process. In one case, the extent of rearrangement increases with time. There is no correlation between the rate of reaction and the extent of rearrangement.

With regard to the rate of decomposition or substitution reactions of 1, no correlation of rate with substituents on R = phenyl is found although the extent of rearrangement does correlate strongly with substituents on phenyl. If X = CO_3tBu and R_1 = CH_3, then R_2 = phenyl and R_2 = cyclohexyl decompose with fairly similar rates. In at least

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*Except, of course, in the sense that a particular X may require a different reaction temperature, in which case the extent of rearrangement may be different (vide infra).

one low temperature decarbonylation reaction, acyl radicals are observed.

Data given above are consistent with but do not demand the classical radical sequence given by Seubold (4).

$$(2)\quad R_1CO\cdot \xrightarrow{k_1} R_1\cdot + CO$$

$$(3)\quad R_1\cdot + R_1CHO \xrightarrow{k_3} R_1H + R_1CO\cdot$$

$$(4)\quad R_1\cdot \xrightarrow{k_4} R_2\cdot$$

$$(5)\quad R_2\cdot + R_1CHO \xrightarrow{k_5} R_2H + R_1CO\cdot$$

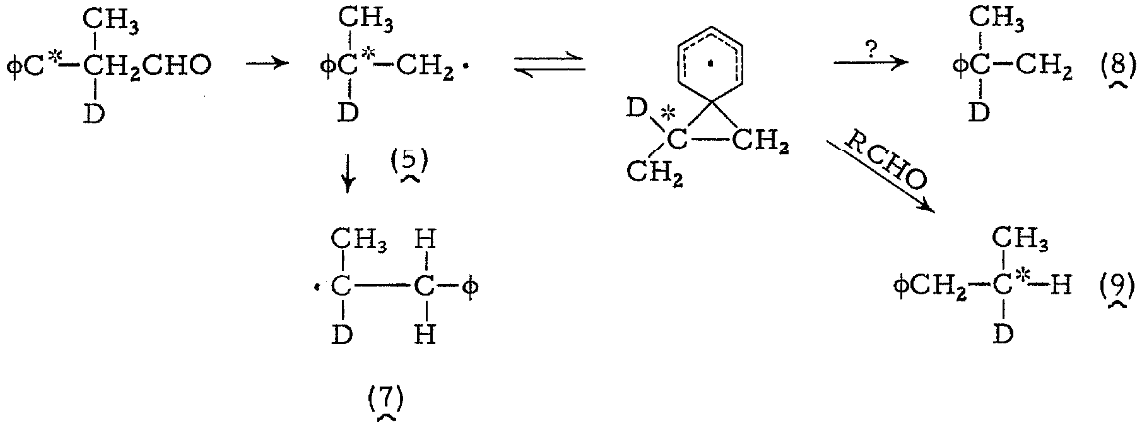
whence: $R_2[H] / R_1[H] \propto 1/[R_1CHO]$

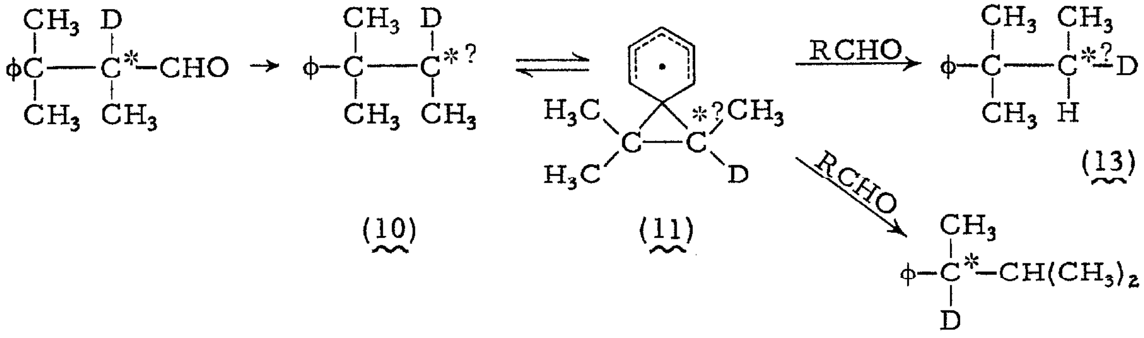
Phenyl participation in the original homolysis seems unlikely in view of the insensitivity of decomposition rate to the nature of R and substituents on phenyl. None of the studies provide information about the further course of the reaction.

To investigate the later course of the reaction, an extension of Cram's stereochemical work in solvolyses is proposed (5). Studies of the peroxide initiated decarbonylations of 3a and 3b at 130°C are proposed. These studies will show whether rearranged and unrearranged products are wholly or in part derived directly from attack of hydrogen donor on the bridged radical species 6 and 10, but will not give information about the possibility of bridged radical species 6 and 10 which give only unrearranged or rearranged radicals and never lead directly to products.

Decarbonylation of 3a will lead to either radical 5 or to the bridged species 6. If, as seems likely, 5 is formed initially, it can either abstract H from aldehyde to give 8 or rearrange to give either of the radicals 7 and 6. If 7 is formed, then, in sufficiently dilute solution at 130° (6), only racemic rearranged product will be obtained. If 6 is formed either in the initial homolysis or subsequently from 5, rearranged product 9 derived from it directly will show retention of configuration. Optically active rearranged product under these conditions will indicate the presence of bridged radical species (7).

In similar fashion, study of the decomposition of 3b in sufficiently dilute solution (6), will show whether any of the unrearranged product is derived directly from a bridged radical species (8). Neither study will afford information about intermediate bridged species which do not lead to products directly (8).





$\xrightarrow{?}$ indicates possible reaction.

$\xrightarrow{*?}$ indicates can be either active or inactive.

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(6) The corresponding cyclohexyl compound which should show similar or greater tendencies to retain configuration relative to the phenyl compound could be used to determine conditions of sufficient dilution to racemize 7 (decompose 2-cyclohexyl-1-methyl-1-deutero ethanal) and 10 (decompose 2-cyclohexyl-1, 2, 2-trimethyl-1-deuteroethanal). Running the reaction at higher temperatures will tend to minimize the tendency to retain a particular configuration.

(7) Even totally racemic products, however, are not inconsistent with the intervention of bridged species which decay only to rearranged or unrearranged radical. It is possible that such bridged species might give active product, but, subject to the footnoted conditions of (6), active product must mean intermediacy at some stage of bridged species.

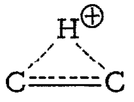
(8) The activation energies for rearrangement are known to be about 10 kcal/mole. If the racemization process in 10 has an activation energy of less than this then the data suggest that inactive unrearranged product will be obtained no matter the origin of all or part of the material.

PROPOSITION III

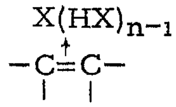
An experiment is proposed to test the nature of the intermediates in the polar addition of hydrogen halides to olefins.

* * * * * * * *

Until recently trans-addition of hydrogen halide to olefins under polar conditions was believed a general phenomenon (1). The studies of Hammond and co-workers (2, 3) showed that polar addition of HBr to 1, 2-dimethylcyclohexene and 1, 2-dimethylcyclopentene gave predominantly and perhaps exclusively trans-1, 2-dimethylcycloalkyl bromides. These studies were complicated by the lability of the products under the reaction conditions but were consistent only with preferential trans-addition. The stereospecifity of these and many similar reactions (1) was explained by Hammond in terms of π complexes of the types 1 and 2.



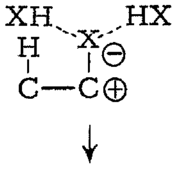
1



$$\overset{X(HX)_{n-1}}{\uparrow} \\ -C{=}C-$$

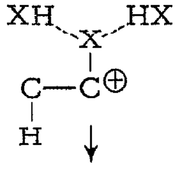
2

A recent study by Dewar and Fahey (4, 5) of the polar addition of DBr to acenaphthylene and indene, however, showed that these systems added DBr almost exclusively to give the cis-addition products. With both acenaphthylene and indene, the classical carbonium ions are aryl carbinyl and the intermediates in the addition reaction might but would not necessarily have to resemble more the classical ion than the π complex. Dewar postulated that the observed *cis*-addition resulted from collapse of the ion pair 3. The alternative reaction possibility for 3, rearrangement to 4 which would lead to *trans*-addition, was believed to be slow relative to collapse of 3 to product. This formulation allows accommodation of the observation that in a number of instances the rate of addition of hydrogen halide to olefin depends approximately upon the third power of HX concentration, and permits explanation of observation of *cis*- or *trans*-addition simply in terms of the relative rates of the various reaction paths open to 3 and 4.



3

cis adduct



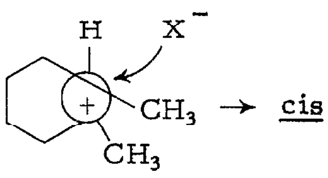
4

trans-adduct

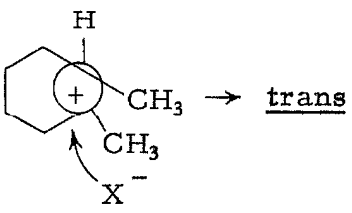
Dewar (5) applied his classical carbonium concept to the systems studied by Hammond (2, 3) and concluded that the ions 5 and 6, shown in Newman projection below were sufficient to account for the observed *trans*-addition provided it was assumed that the collapse to product was fast relative to ring inversion. The predominating *trans*-addition was ascribed to the necessity for eclipsing the methyl groups in the transition state. This argument allows the prediction that the addition of HBr to cyclohexene ought to give more *cis*-adduct, a prediction which is not confirmed; addition of HBr to cyclohexene was reported by Fahey (6) to give predominantly the *trans*-addition product.

Whether the observed course of addition to cyclohexene means that Dewar's theory is wrong is problematical. To be sure, there is no real reason to expect that the behavior of simple olefins and aryl carbinyl systems should be similar in the addition reaction. Nevertheless, it is not entirely obvious from examination of **5** and **6** (without the methyl groups) that _trans_-addition should not, because of the conformational preference of the ring, be the favored course of reaction of cyclohexene through this kind of intermediate.

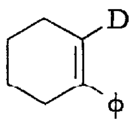
To provide more information about the course of this type of addition reaction we propose that addition of HBr to 1-phenylcyclohexene-d2, **7**, be investigated. The addition reaction in this system should proceed through a classical carbonium ion pair of the types **3** and **4**. We do not expect that the reaction pathways open to this ion pair will be altered significantly, by conformational preferences of the cyclohexyl system, from those available to ions **5** and **6** or their dimethylated analogues. The course of this addition reaction should then provide a test of the preferred course of the carbonium ion reaction. Specifically, observation of preferential _trans_-addition will imply that the carbonium ion pair can give rise to the products observed by Hammond for additions to 1,2-dimethylcycloalkenes. This



5



6



7

would lend support to Dewar's hypothesis although, of course, it will not constitute a proof of its accuracy. On the other hand, observation of *cis*-addition will indicate that the preferred course of addition to cyclohexene and its alkyl derivatives is probably not capable of explanation in terms of classical ions such as **5** and **6**.

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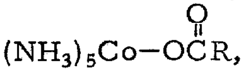
PROPOSITION IV

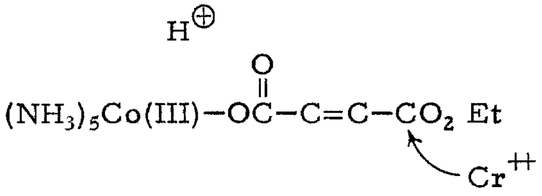
Investigation of the photoredox reactions of a pentammine cobalt(III) complex containing a conjugated organic ligand will supply information about the possibilities for electron transfer through conjugated systems during reduction of Co(III).

* * * * * * * *

A number of studies have been made of the reactions of Cr^{++} with complex ions of the class $(NH_3)_5Co(III)-L$ where L is an organic ion containing one or more carboxylate groups. The net changes in most of the systems studied are represented by

$$(1)\quad (NH_3)_5CoL^{++} + Cr^{++} + 5H^{+} = Co^{++} + CrL^{++} + 5NH_4^{+}$$

The stoichiometry of this reaction has been investigated carefully and seems to be established. A popular L group is carboxylate, for example  $(NH_3)_5Co-O\overset{\overset{O}{\|}}{C}R$, in which the usual course of reaction is attack upon the carbonyl by Cr^{++} resulting in the transfer of an electron to $(NH_3)_5Co^{III}L$ giving attachment of Cr^{+++} to L and liberation of Co^{++}. Considerable recent interest has attached to the study of systems in which R is a conjugated organic system; for example, fumarato, maleato and their half esters have all been used as ligands. It was reported that with these systems the rate of reduction by Cr^{++} was increased considerably over that observed when L was acetato, and that in addition to the usual term in the rate law, first order in reducing and in oxidizing agent, another, faster term appeared which included a first order dependence upon acid concentration. Further, it was observed that the half esters were hydrolysed during reduction of the complex and that isomerization of the conjugated double bond occurred during the reaction. These facts were explained as being due to competition with the usual adjacent attack of attack upon the remote end of the conjugated system by Cr^{++}, followed by transmission of an electron through the conjugated system to $(NH_3)_5Co(III)$ – thereby affecting reduction of Co^{+++} and leading to formation of CrL^{++}. The function of the proton was uncertain although it was speculated that it might serve to make transmission of the electron easier by protonating the carbonyl group adjacent to cobalt, for example

(2) 

$$(NH_3)_5Co(III){-}O\overset{\overset{H^{\oplus}\;O}{\|}}{C}{-}C{=}C{-}\underset{\nwarrow Cr^{++}}{CO_2}\,Et$$

etc.

Recently, however, some of these results, especially those upon which the remote attack postulate was based, have been called into question. It is no longer certain whether remote attack by Cr^{++} can effect reduction of $(NH_3)_5Co(III){-}L$. This proposal relates to the possibility of observing long range transfer of electrons in another type of redox reaction undergone by complex ions of Co(III).

Irradiation of aqueous solutions of Co(III) complexes with ultraviolet light leads in some cases to photoaquation of the complex and/or to photoreduction of cobalt (3). The net changes may be summarized as

$$(3)\quad \mathrm{Co(III)A_5X^{++}} \xrightarrow{h\nu} \begin{array}{l} \mathrm{Co(III)A_5H_2O}\ \ \text{(a)}\ \ \text{(aquation)} \\ \mathrm{Co^{++}} + 5\mathrm{A} + \mathrm{X}\ \ \text{(b)}\ \ \text{(reduction)} \end{array}$$

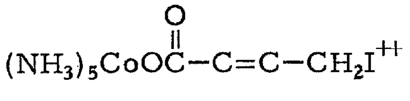
The crucial step in the reaction is believed to be transfer of an electron from X, which is usually an easily oxidized species, to cobalt, followed at some later (but perhaps not very much later) time by bond fission, for example

$$(4)\quad \mathrm{Co(III)A_5X} \xrightarrow{h\nu} \longrightarrow \mathrm{Co(II)A_5 \cdot X}$$

The species on the right of equation 4 is the crucial intermediate which can, depending upon the energetics, react either to acquire water and suffer electron return to give aquation (reaction 5), or break up according to 3b.

$$(5)\quad \mathrm{Co(II)A_5 \cdot X\ H_2O} \rightarrow \mathrm{Co(II)A_5 \cdot H_2O\ X^-} \rightarrow \mathrm{Co(III)A_5 \cdot H_2O}$$

We propose a study of the photochemistry of **1** in aqueous solution.

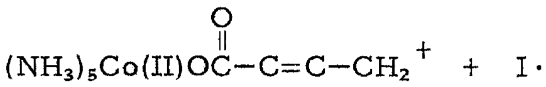


$$\mathrm{(NH_3)_5CoO\overset{\overset{\displaystyle O}{\|}}{C}{-}C{=}C{-}CH_2I^{++}}$$

cis or trans

1

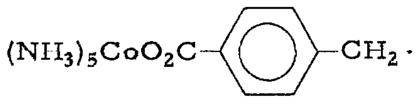
Previous studies with pentammine and hexammine Co(III) complexes show that the photoreduction of these species is very slow or nonexistent in the absence of an easily oxidized ligand, unless irradiation with very short wavelength light is employed. By using long wavelength light, therefore, it should be possible to insure that electron transfer in reaction 4 can occur only from the conjugated organic ligand. This system is, of course, analogous to that employed by Taube (1) in studies of the process of remote attack by Cr^{++} during reduction of Co(III) complexes. If electron transfer of the type postulated by Taube is possible, then there is an excellent chance that photoreduction of 1 will involve fragmentation of the conjugated ligand; that is, liberation of iodine leaving the carbonium ion 2.



$$(NH_3)_5Co(II)O\overset{\overset{\displaystyle O}{\|}}{C}-C{=}C-CH_2^{\,+} \quad + \quad I\cdot$$

2

Although there is little precedent for this specific type of cleavage reaction, the following considerations appear to favor its occurring. In the first place the formation of 2 during or subsequent to reaction 4 should be highly favored energetically. It is also already known that the presence of a Co(III) center coordinated to a conjugated system such as 3 has a strong tendency to remove electrons from the radical



3

system to form the carbonium ion (2). Further it has been suggested by Taube that the (possible) failure of Co(III) complexes with maleato, fumarato, etc., as ligands to give remote transfer reactions might be due simply to the difficulty of achieving the necessary conjugation between the carboxylato and cobalt orbitals (2). If this is the case, the transfer process here ought to be more favorable because of the better conjugation between excited cobalt and the carboxylate (1, 2).

It is, of course, obvious that this experiment is speculative in nature and that failure to observe the expected course of reaction will not disprove or discredit the possibility of remote attack and/or electron transfer through a conjugated system for any molecule but this one. On the other hand, it is worthwhile to consider in some detail just what significance a positive result will have. The details of reaction 4 are unknown, and in fact, there is not positive evidence that the mechanistic sequence given above is accurate. It is possible, therefore, that the cleavage of the ligand to give **2** might take place at a time when it was not associated with the cobalt center. There does not appear to be any way to test this possibility but its occurrence would not really vitiate the conclusions that the remote transfer process can occur. There is reason to believe from studies of photoreduction reactions of other Co(III) complexes that some complexes at least possess metastable excited states with lifetimes of perhaps 10^{-6} to 10^{-8} seconds. An example would be the metastable state formed during photoreduction of $Co(III)(en)_3^{+++}$ (4). No information is available about the possibility of metastable excited states of **1**, but is not unreasonable to expect that an excited state might survive long enough for the postulated fragmentation to occur in the complex.

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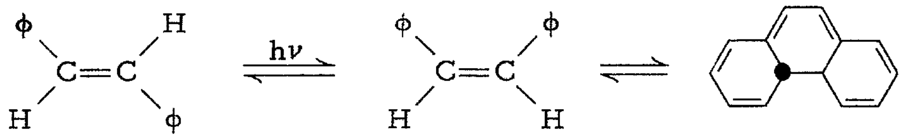
PROPOSITION V

Bimolecular reactions of the excited singlets of the stilbenes are implicated in the direct photoisomerization reaction.

* * * * * * * *

Direct photoisomerization of the stilbenes has been the object of intensive study (1). There are at the stationary state at least three substances in photoequilibrium, the two stilbenes and an orange transient, dihydrophenanthrene, (DHP), **3**. The transient is produced from excited singlets of *cis*-stilbene (2).



1 **2** **3**

Modern discussions (1, 3-8) of this reaction presume that the triplet states of the stilbenes are the principal isomerization pathway although it cannot be proven unequivocally that triplets are involved or that other pathways are not. Study of the fluorescence spectrum of *trans*-stilbene led Dyck and McClure (3) to conclude that the ethylenic double bond was preserved intact in the excited singlet; consequently this state cannot be directly responsible for the isomerization. Fluorescence is observed from *cis*-stilbene at 77°K but not at room temperature; the spectrum is diffuse and has not been analysed (9). The brief study of this problem by Hammond *et al.* (9) permits the interesting conclusion that radiationless decay of the excited singlet must include paths having significant activation energies, one of these paths being production of 3. The possibility of conversion of cis-stilbene excited singlets to trans-stilbene excited singlets has not been ruled out unequivocally.

An isomerization pathway which cannot be eliminated from consideration is isomerization in vibrationally excited ground states following internal conversion from excited singlets or intersystem crossing from triplets of the stilbenes. Hammond (8) carried out an interesting experiment which sheds some light upon this possibility. It is easy to derive the following equation for the photostationary state obtained upon long irradiation of the stilbenes, provided one assumes that 3 plays no role in the isomerization. That assumption will be justified below for Hammond's experimental conditions.

$$(2)\quad \left(\frac{c}{t}\right)_s = \left(\frac{\phi_{ic(t)}}{\phi_{ic(c)}}\right)\left(\frac{\epsilon_t}{\epsilon_c}\right)\left(\frac{\alpha}{1-\alpha}\right)$$

Here ϕ_{icx} represents the intersystem crossing yield of x, ϵ_x the appropriate extinction coefficient for x, and $(\alpha/1 - \alpha)$, as in Part Two of this Thesis, gives the fraction of stilbene triplets which decay to cis-stilbene. Assuming that $\phi_{ic(t)} = \phi_{ic(c)}$, Hammond found that equation 2 gave good predictions of the experimentally observed stationary states. This result was interpreted as evidence that the same reactive intermediate was involved in the direct as in the sensitized isomerization of the stilbenes. A conclusion of this type was, of course, recognized to be dependent upon the assumption that the intersystem crossing yields of the two isomers were, in fact, equal which is by no means necessarily the case. The significance of this result is now further clouded by the fact that the value of α used was off by about 20-30% (10). Nevertheless, it is likely that the intersystem crossing yields of the stilbenes are not appreciably different and the close agreement of prediction with experiment argues that if ground state isomerization is occurring the behavior of this state must be nearly independent of the multiplicity of the excited state from which it is produced. In view of the probable configurations of the stilbene excited singlets (*vide supra*) and the relaxed triplets (1, 8, 10) we regard this possibility as unlikely.

If it is accepted that the stilbene triplets are the *stilbene* intermediates which are important as isomerization pathways, there still remain two factors which complicate the reaction. The first is the decay processes by which 3 is destroyed. In the presence of oxygen or other oxidizing agents, 3 is converted irreversibly to phenanthrene (2, 10). In deoxygenated solutions in the dark, however, the thermal decay of the transient to *cis*-stilbene has a first order rate constant of 9.0×10^{-5} sec.$^{-1}$ (1); consequently, the rate of DHP production in the photoreaction exceeds that of its thermal decay (12), and the low steady concentrations of this species observed in the photoreaction imply that there must exist photochemical pathways for its destruction. That these pathways lead to appreciable amounts of *trans*-stilbene is rendered unlikely by the report of Fischer (5) that the course of the isomerization reaction is not affected by raising the temperature to limits at which thermal decay of DHP to *cis*-stilbene ought to be as fast as its photochemical production. The significance of Fischer's results is not, however, entirely clear, the problem being that Saltiel found over part of the temperature range for which Fischer reports temperature independent quantum yields, a dependence of photostationary states in the sensitized reaction upon the temperature. As we pointed out in Part Two of this Thesis it is reasonable to interpret Saltiel's result in terms of a change in α for stilbene triplets as the temperature is changed. An obvious conclusion from Saltiel's work is that the unsensitized isomerization ought also to exhibit a similar temperature dependence at temperatures for which the intersystem crossing yields of the stilbenes have become essentially constant. Clearly at high temperatures α might become constant as the population of transoid and twisted triplets become essentially equal, but in view of the apparently large changes in α over the 30° temperature range employed by Saltiel, it seems unlikely that any high energy plateau should be reached in the temperature interval under consideration. We believe this work deserves repetition, as does also Fischer's work indicating that the benzophenone sensitized isomerization of stilbene proceeds with temperature independent quantum efficiency over a wide range of temperatures all below 20°C. The latter result and Saltiel's study (1) of the temperature dependence of the same reaction seem definitely inconsistent.

The observed temperature dependence of the unsensitized reaction below room temperature, however, makes considerably more sense. For both isomers the quantum yields for conversion to the other isomer drop as the temperature is decreased. On the basis of Saltiel's work, it would be predicted that α should decrease with decreasing temperature. This would tend to increase $\phi_{c \to t}$ and decrease $\phi_{t \to c}$. Of course activated reactions of the singlets of both isomers are also important, especially in the case of trans-stilbene which fluoresces at room temperature. It is observed, as predicted by both these effects, that $\phi_{t \to c}$ drops more rapidly than $\phi_{c \to t}$ (6).

Of more interest to the study of the possible intermediates in direct photoreactions of the stilbenes is investigation of the concentration effects upon the photostationary states obtained at room temperature. For the stilbenes, Saltiel (1) found that the stationary trans/cis ratio increased by a factor of 2, upon going from 10^{-3} to 5×10^{-2} M stilbene. Although the functional dependence of this variation with concentration is not known for stilbene, study of the same effect in the m-nitro stilbenes systems gave a nearly linear plot at least at concentrations greater than 10^{-3} M. Saltiel interpreted these changes in terms of two processes, the first being quenching of transoid triplets by trans-stilbene (reaction 3).

$$(3) \quad t^3 + t \longrightarrow 2t$$

This interpretation is untenable because, as was pointed out in Part Two of this Thesis, the magnitude of the quenching effect is too small to account for the observed results. In fact, the observation of a linear concentration dependence with the nitro stilbenes suggests that some process other than reaction 3 is responsible for that effect. A more likely explanation is afforded by the various possible ways in which DHP can react with excited states of the stilbenes. Because of the low steady state concentration of DP which is probably due at least partially to reaction 4, it is unlikely that reactions 5 or 6 are important.

$$(4) \quad t^3 + \text{DHP} \longrightarrow \text{DHP}^3 \longrightarrow \text{c and/or t}$$

$$(5) \quad t^1 + \text{DHP} \longrightarrow \text{DHP}^1 \longrightarrow \longrightarrow \text{c and/or t}$$

$$(6) \quad c^1 + \text{DHP} \longrightarrow \text{DHP}^1 \longrightarrow \longrightarrow \text{c and/or t}$$

Clearly, however, the higher the stilbene concentration the greater the effect of DHP, since although the total rate of production of DHP in the photoreaction depends only upon the intensity of the light source for all stilbene concentrations under consideration here, the local concentration of this intermediate will depend upon the stilbene concentration. Thus the macroscopic observed concentration of $\sim 10^{-3}$ M may not accurately reflect the ability of DHP to center in the reaction. This could lead to the observed changes in the trans/cis ratio by the intervention of reaction 4. With respect to reactions 5 and 6, however, it is known that singlet energy from the stilbenes requires acceptor concentrations of the order of $10 - 20 \times 10^{-3}$ M and we feel these reactions are unlikely candidates for possible explanations of the observed concentration dependence.

More insight into the nature of the concentration dependence of the photostationary states is afforded by the fragmentary quantum yield measurements available which show clearly that both $\phi_{t \to c}$ and

$\phi_{c \to t}$ decrease as the stilbene concentration is increased (1, 7, 10). Thus, for stilbene $\phi_{t \to c} = 0.44$ at 4×10^{-5} M stilbene and 0.34 at 5×10^{-2} M, while $\phi_{c \to t} = 0.37$ at 4×10^{-5} M and 0.19 at 5×10^{-2} M stilbene (10, 12). For nitro stilbene isomerization, $\phi_{t \to c}$ drops with increasing nitro stilbene concentration. The most significant aspect of the results at 5×10^{-2} M that very low conversions were employed so that even the local concentrations of DHP should be very low (~ 10^{-4} M) throughout the reaction. When trans-stilbene is the starting material, there should also be negligible involvement of DHP. The possibility of a second transient formed unimolecularly from trans-stilbene we consider unlikely for the following reason. The sum for 4×10^{-5} M stilbene of $\phi_{t \to c} + \phi_{\text{fluorescence}}$ is 0.52, not significantly different from the quantum yield for the sensitized reaction (10). Consequently, any transient formed must decay to the same mixture of the stilbenes as do the stilbene triplets. Formation of a second transient by unimolecular reactions of excited cis-stilbene is shown to be unlikely by a similar argument; that is, the sum of the quantum yields for formation of stilbene and DHP is 0.41, or that measured for the sensitized reaction (8). Consequently, it appears necessary to conclude that bimolecular reactions of stilbene singlets can occur at higher stilbene concentrations and are a second complicating factor in direct isomerization; reactions 7 and 8 represent likely possibilities.

$$(7) \quad c' + c \longrightarrow \text{excimer} \longrightarrow 2c$$

$$(8) \quad t' + t \longrightarrow \text{excimer} \longrightarrow 2t$$

Occurrence of either of these reactions could lead to the linear dependence of $1/\phi$ upon substrate concentration observed by Schulte-Frohlinde (6) for nitro stilbene isomerization. We propose to study the functional form of the concentration dependence of $\phi_{t \rightarrow c}$ and $\phi_{c \rightarrow t}$ and the concentration dependence of the shape and quantum efficiency of the fluorescence of trans-stilbene. Occurrence of reaction 7 should be revealed by these experiments while reaction 8 can be made a plausible but not a required process owing to the failure of cis-stilbene to fluoresce at room temperature. The advantage of dealing with quantum yields is the absence of transients which may influence the decay processes of the stilbene intermediates.

It will have been noted by the reader that in order for reactions 7 and 8 to account for the observed photostationary state changes, it is apparently necessary to require that reaction 7 be more important than reaction 8, whereas the data given above apparently indicate the reverse to be true. In this connection three points may be made. First, all quantum yields measured previously for stilbene isomerization, except those at 0.05 M were measured in such a way as to include effects (probably small because of the low stilbene concentrations) of the transients, and must, therefore, be regarded as only roughly accurate. Second, there is, as might be expected, considerable scatter in the observed quantum yields at low stilbene concentrations. And third, there is, of course, no reason to expect that the quantum yields for the unsensitized isomerization should (naturally after correction for relative ϵ's) predict the photostationary states, due to the other effects we we have mentioned involving the various possible transients.

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ABSTRACTS OF PROPOSITIONS

I. Excimer formation by 1, 2, 7, 8-dibenzanthracene offers a means of explaining the unusual sensitizer concentration effect observed with this sensitizer in stilbene isomerization.

II. Experiments are proposed to test the possible role of bridged radicals in the neophyl rearrangement.

III. An experiment is proposed to test the nature of the intermediates in the polar addition of hydrogen halides to olefins.

IV. Investigation of the photoredox reactions of a pentammine cobalt (III) complex containing a conjugated organic ligand will supply information about the possibilities for electron transfer through conjugated systems during reduction of Co(III).

V. Bimolecular reactions of the excited singlets of the stilbenes are implicated in the direct photoisomerization reaction.