THE EXCITED-STATE GEOMETRY OF CONJUGATED DIENES AND CHARACTERIZATION OF A QUANTUM CHAIN-TRANSFER MECHANISM OF ENERGY TRANSFER

Thesis by
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Ad majorem Dei gloriam

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ABSTRACT

An investigation has been carried out to determine whether the geometry corresponding to the lowest lying triplet state of conjugated dienes is in the form of a 1, 4-biradical system or an allyl-methylene system (a "1, 2-biradical"). This has been done by measuring the various quantum yields for cis-trans isomerization of these dienes and comparing the results with certain previously conceived empirical standards and to the criteria imposed by the proposed mechanism.

During the course of this investigation, a novel and very interesting phenomenon was uncovered. It appears that a quantum-chain mechanism, heretofore unreported for this type of system, is in operation in at least the early stages of the photoisomerization process. Characterization of such a mechanism and the chain propagating species has been carried out.

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INTRODUCTION

For a fuller knowledge of the photochemistry of unsaturated hydrocarbons, it is necessary to have a better understanding of the properties of their electronically excited states. Olson (1) has made a thorough theoretical study of the electronically excited states of cis and trans isomers of the substituted ethylenes, which is one of the first reported discussions of the nature of these species. In 1939, Lewis and Calvin (2) presented the "loose bolt" theory, which discusses the conversion of electronic oscillation to atomic vibrations and heat. In another paper, Lewis et al. (3) discuss further the conversion of electronic energy into rotational and vibrational energy. They state that if ordinary cis and trans molecules are given increasing torsional vibration about the ethylenic double bond, the distinction between the two isomers will persist until the torsional energy approaches $\Delta H^{\neq}$ for thermal isomerization, above which true rotation will occur, and that it seems certain that cis isomers and some trans isomers excited to the lowest excited states will, before they decay to the ground state, probably acquire enough torsional energy to lose their identity as cis or trans molecules.

As long ago as 1947, Mulliken and Roothan calculated (4) from molecular orbital considerations that the perpendicular form of the ethylene triplet should be more stable than the planar form by at least 20 kcal per mole. No experimental consideration of this matter was reported until 1963 when Hammond et al. (5, 6, 7) reported studies of the photochemical cis-trans isomerization of piperylene and stilbene. In this report, they invoked the use of a "phantom" triplet; that is, one which is twisted out of a planar configuration, although not necessarily into a perpendicular form, to explain the relatively high rates of triplet energy transfer to these olefins from sensitizers whose triplet energy was several kilocalories per mole less than that of the spectroscopic triplet energy of the olefin acceptors. This "phantom", or twisted triplet, was assumed to have an energy sufficiently lower than that of the spectroscopic, or planar, triplet to allow the observed rates of energy transfer to occur on an exothermic, or at least isoenergetic basis.

Since the foregoing seems to be the nature of the olefinic triplet state, it became a very interesting problem to extend those concepts to apply to the excited triplet states of conjugated diene systems. Among the possible structures of diene triplets, the two which are believed most probable are consistent with information about diene triplets obtained from photochemical studies. One such structure is with both methylene groups perpendicular to the plane formed by the π-electrons of the C_2-C_3 carbon atoms. The other possibility is one with only one end methylene in the perpendicular position, and the remaining end methylene group lying in the same plane as the π electrons of the central carbon atoms, thus forming an allyl radical.

These two cases can be represented as in Figure 1a and 1b.

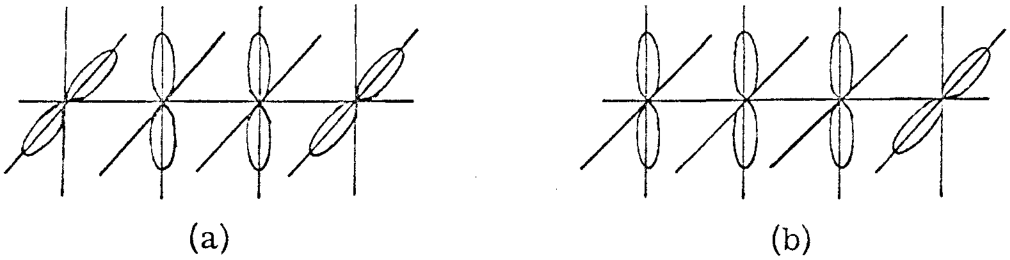
(a) (b)

Figure 1. Representation of two possible diene triplets.

In order to be more explicit, let us consider the following system. Suppose we have a diene (I) which, in case (a), gives a "1,4-biradical" in which the electronic repulsion caused by the now parallel electron spins and overlap of the various orbitals is minimized by twisting the methylene groups at the ends of the π-system out of the planar form with the resulting loss of the allyl resonance energy. On the other hand, we might suppose the diene forms an allyl-methylene type triplet which retains the allyl resonance energy but has more electronic repulsion in the adjacent p-orbitals. It can be seen immediately that in this case there are two different triplets for an unsymmetrical diene such as I. (Refer to Figure 2.) A very important and critical observation now is that, in case (a), a single quantum of energy can cause cis-trans isomerization at both double bonds whereas, in case (b), a single quantum can cause isomerization of only one of the double bonds. This observation, of course, assumes that there is no rapid interconversion of the excited states in the case (b) triplet, and leads to the conclusion that the sums of the various

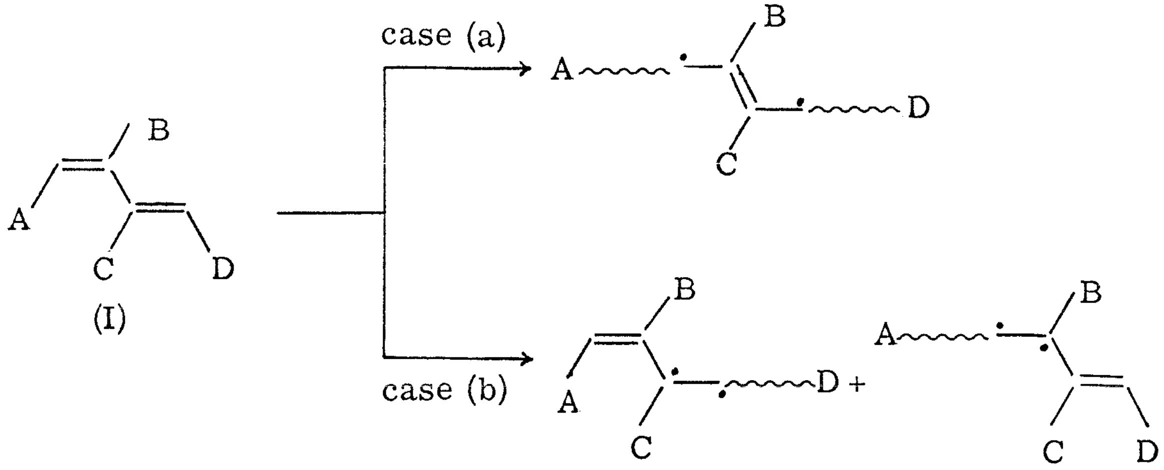

Figure 2. The possible excited geometries for conjugated dienes.

quantum yields for isomerization in each case will be different. These sums can be calculated as follows.

In the following derivations for the photosensitized isomerizations, three explicit assumptions are made about the sensitizer:

a. The sensitizer absorbs all the light.

b. The singlet-triplet intersystem crossing quantum yield for the sensitizer is unity.

c. The triplet energy of the sensitizer is high enough so that the rate of energy transfer to the diene substrate is diffusion controlled.

It may be mentioned here that benzophenone at 0.050 M concentration satisfies all three conditions. Now consider the following model system.

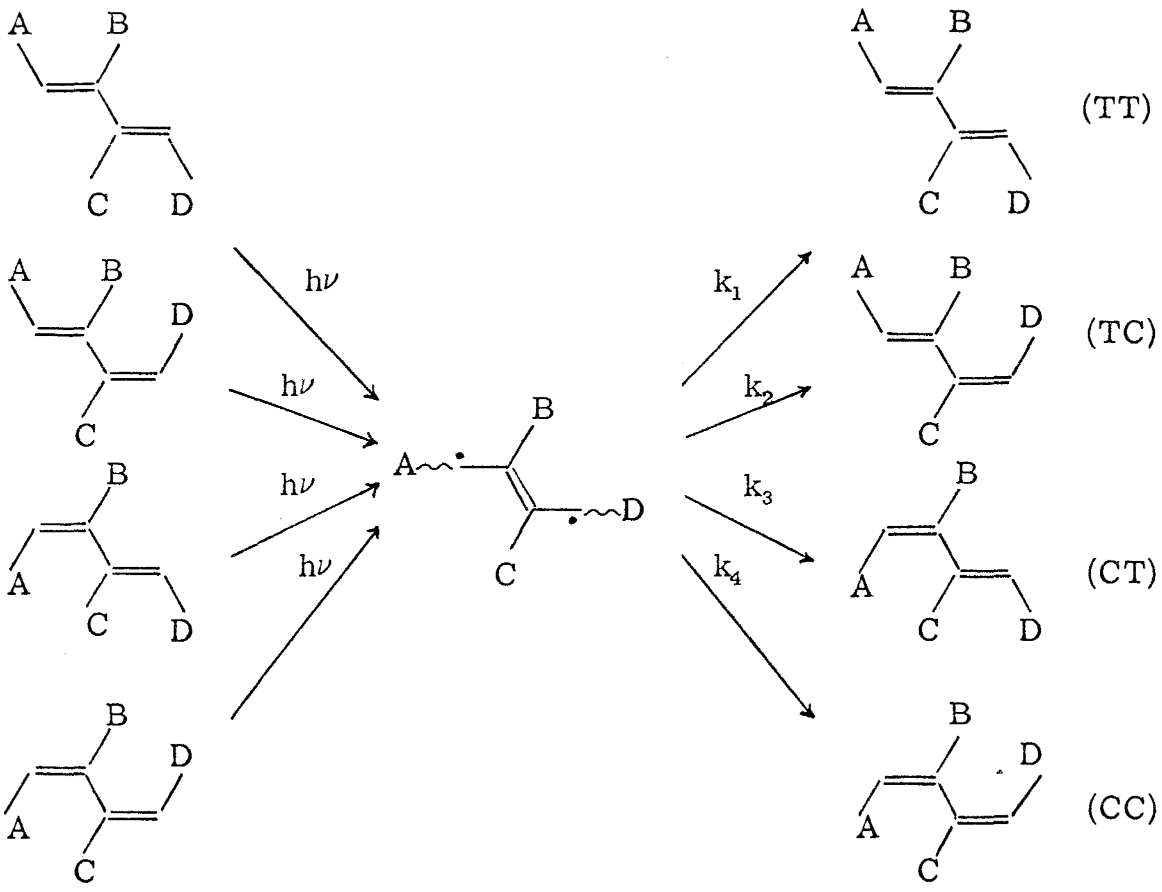

Figure 3. Model system, assuming a common [case (a)] triplet.

In this system, there are four possible isomers, each being excited to the same triplet state which can then decay to any of the four ground states. Making the assumptions listed above (and the implicit assumption that only pure isomer is present initially in each case), the following quantum yields may be derived:

$$\phi_{TT \rightarrow TC} = \frac{k_2}{k_1 + k_2 + k_3 + k_4}$$

$$\phi_{TT \rightarrow CT} = \frac{k_3}{k_1 + k_2 + k_3 + k_4}$$

$$\phi_{TT \rightarrow CC} = \frac{k_4}{k_1 + k_2 + k_3 + k_4}$$

$$\phi_{TC \rightarrow TT} = \frac{k_1}{k_1 + k_2 + k_3 + k_4}$$

$$\phi_{TC \rightarrow CT} = \frac{k_3}{k_1 + k_2 + k_3 + k_4}$$

$$\phi_{TC \rightarrow CC} = \frac{k_4}{k_1 + k_2 + k_3 + k_4}$$

$$\phi_{CT \rightarrow TT} = \frac{k_1}{k_1 + k_2 + k_3 + k_4}$$

$$\phi_{CT \rightarrow TC} = \frac{k_2}{k_1 + k_2 + k_3 + k_4}$$

$$\phi_{CT \rightarrow CC} = \frac{k_4}{k_1 + k_2 + k_3 + k_4}$$

$$\phi_{CC\rightarrow TT} = \frac{k_1}{k_1 + k_2 + k_3 + k_4}$$

$$\phi_{CC\rightarrow TC} = \frac{k_2}{k_1 + k_2 + k_3 + k_4}$$

$$\phi_{CC\rightarrow CT} = \frac{k_3}{k_1 + k_2 + k_3 + k_4}$$

and it can be seen that

$$\Sigma_{\phi} = \frac{3k_1 + 3k_2 + 3k_3 + 3k_4}{k_1 + k_2 + k_3 + k_4} = 3.$$

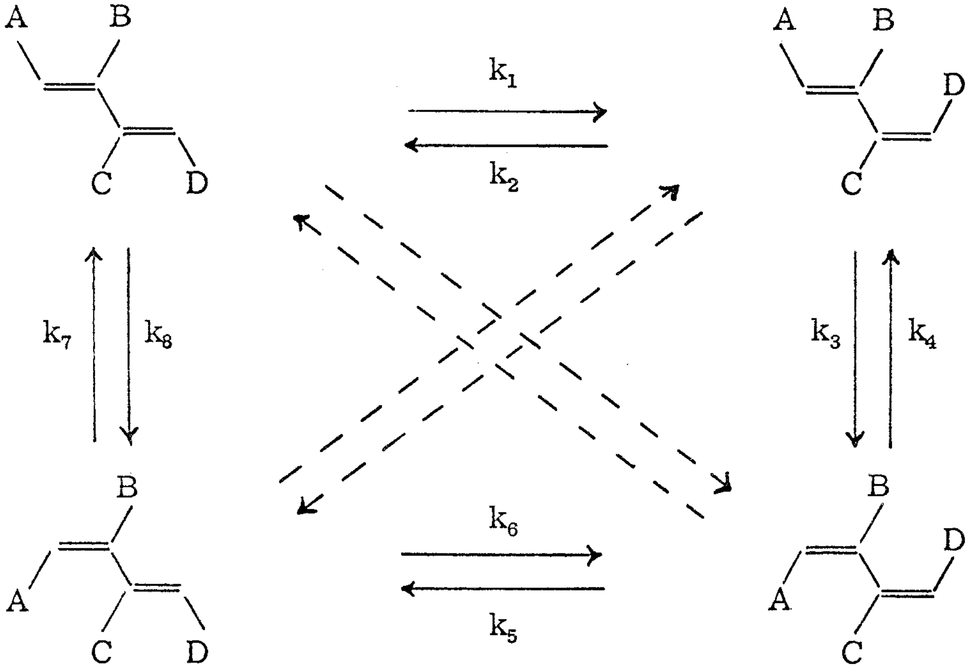

Figure 4. Model system, assuming a different [case (b)] triplet.

Referring to Figure 4, consider the same diene system where case (b) triplets are assumed. (At this point the problem can be stated by asking whether the two paths shown in dashed lines in Figure 4 do, in fact, exist.) Now one additional factor must be considered in deriving the quantum yields. That factor is the fraction of total energy transferred from the sensitizer that is transferred into the particular double bond of interest. The two double bonds are labelled AB and CD with rates of energy transfer from the sensitizer to the particular double bond of k_{AB} and k_{CD}, respectively. (We have assumed that k_{AB} and k_{CD} are independent of the exact <u>cis</u> or <u>trans</u> nature of the individual bond. This seems reasonable since we know that $[k_{AB} + k_{CD}]$ is diffusion controlled and therefore independent of the exact <u>cis</u> or <u>trans</u> nature of the system.) The eight possible quantum yields are as follows:

Sum of bracketed pairs

$$\left.\begin{aligned}\phi_{TT\rightarrow TC} &= \left(\frac{k_{CD}}{k_{AB}+k_{CD}}\right)\left(\frac{k_1}{k_1+k_2}\right)\\[2ex] \phi_{TC\rightarrow TT} &= \left(\frac{k_{CD}}{k_{AB}+k_{CD}}\right)\left(\frac{k_2}{k_1+k_2}\right)\end{aligned}\right\} \qquad \frac{k_{CD}}{k_{AB}+k_{CD}}$$

Sum of bracketed pairs

$$\left.\begin{aligned} \phi_{\mathrm{TC}\to\mathrm{CC}} &= \left(\frac{k_{AB}}{k_{AB}+k_{CD}}\right)\left(\frac{k_3}{k_3+k_4}\right) \\ \phi_{\mathrm{CC}\to\mathrm{TC}} &= \left(\frac{k_{AB}}{k_{AB}+k_{CD}}\right)\left(\frac{k_4}{k_3+k_4}\right) \end{aligned}\right\} \qquad \frac{k_{AB}}{k_{AB}+k_{CD}}$$

$$\left.\begin{aligned} \phi_{\mathrm{CC}\to\mathrm{CT}} &= \left(\frac{k_{CD}}{k_{AB}+k_{CD}}\right)\left(\frac{k_5}{k_5+k_6}\right) \\ \phi_{\mathrm{CT}\to\mathrm{CC}} &= \left(\frac{k_{CD}}{k_{AB}+k_{CD}}\right)\left(\frac{k_6}{k_5+k_6}\right) \end{aligned}\right\} \qquad \frac{k_{CD}}{k_{AB}+k_{CD}}$$

$$\left.\begin{aligned} \phi_{\mathrm{CT}\to\mathrm{TT}} &= \left(\frac{k_{AB}}{k_{AB}+k_{CD}}\right)\left(\frac{k_7}{k_7+k_8}\right) \\ \phi_{\mathrm{TT}\to\mathrm{CT}} &= \left(\frac{k_{AB}}{k_{AB}+k_{CD}}\right)\left(\frac{k_8}{k_7+k_8}\right) \end{aligned}\right\} \qquad \frac{k_{AB}}{k_{AB}+k_{CD}}$$

If these are paired and added as shown, and then the four sums are themselves added, it is obvious that

$$\Sigma_{\phi} = \frac{2k_{AB}+2k_{CD}}{k_{AB}+k_{CD}} = 2.$$

Thus the sums of the quantum yields are exactly 3 in the case (a) of a single triplet or exactly 2 in the case (b) of different triplets. It was hoped that the quantum yields for the photosensitized isomerization of some appropriate conjugated diene could be measured and added to distinguish between these two possible cases.

A further criterion for the nature of the triplet is imposed by the mechanism itself. That is, any mechanism (or proposed mechanism) which invokes a direct interconversion of the TT and CC pair or the TC and CT pair will necessarily require a common [case (a)] triplet.

EXPERIMENTAL

A. Materials

1. Benzene--Baker and Adamson reagent grade benzene was stirred over concentrated sulfuric acid for three two-day periods, the acid being changed each time. The benzene was then washed three times with dilute solution of sodium bicarbonate, dried over magnesium sulfate, and distilled from phosphorous pentoxide.
2. n-Hexane--Phillips reagent grade n-hexane was purified by the same method as for the benzene, except that the hexane was heated to reflux while stirring over the acid.
3. Benzophenone--Matheson, Coleman and Bell reagent grade benzophenone was recrystallized twice from ligroin (60/70). M.p. 49.0-49.5° C.
4. 2,4-Hexadiene--2,4-Hexadiene (cis,cis, cis,trans, and trans,trans) was obtained either from K & K Laboratories or Columbia Organic Chemicals Company, and was used without further purification. (Chemical purity $> 99.9\%$ by v.p.c. Isomeric purity $> 98\%$ by v.p.c.)

5. Triphenylene--Triphenylene was obtained from Dr. L. M. Coyne who had recrystallized reagent material twice from ethanol.

B. Measurement of Quantum Yields

Hexane solutions of diene and sensitizer were delivered by calibrated syringe into constricted Pyrex test tubes which had been cleaned by soaking overnight in alcoholic potassium hydroxide, rinsing in distilled water and oven-drying at approximately 110° C. The tubes were wrapped in aluminum foil just prior to introduction of the solution so as to exclude all stray light. The samples were then 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 the samples was carried out in a "merry-go-round" which insures equal amounts of radiation incident on each sample. The lamp used was a 450 watt Hanovia medium pressure mercury arc in a quartz immersion well for cooling. The filter system employed with benzophenone sensitizer consisted of Corning 737 and 052 filter plates. This sytem admits only a very narrow band of light of wavelengths of 3650 ± 50 Å. This system has been described elsewhere (8). For the few samples using triphenylene as sensitizer, two filter solutions in series were employed. One solution was 260 g. $CoSO_4 \cdot 7H_2O$ dissolved in 1 liter of distilled water. The other solution contained 127 mg. K_2CrO_4 in 250 ml. of 1% sodium bicarbonate solution.

These solutions have the spectral properties shown below (from Dr. G. F. Vesley).

	Wavelength	Absorbance
$CoSO_4 \cdot 7H_2O$	3130 Å	0.060
	4358	1.13
	5460	2
K_2CrO_4	3035	0.966
	3130	0.402
	3341	2.11
	4045	∞
	4358	0.801
	5460	0.002

These solutions, in series, will thus isolate the 3130 Å line of the mercury emission spectrum.

Analysis of the irradiated samples was carried out by vapor phase chromatography using an Aerograph Model 600 B instrument with a flame ionization detector and an integrating recorder. The column used consisted of (1) 15 ft. ($\frac{1}{4}$ in. O. D.) of 10% triethylene glycol saturated with $AgNO_3$ on Chromosorb P (60-80, acid-washed) and (2) 10 ft. ($\frac{1}{8}$ in. O. D.) of 25% β,β-oxydipropionitrile on Chromosorb P (80-100). At least three, and sometimes four, aliquots of each sample were analyzed.

Equimolar solutions of the three isomers of 2, 4-hexadiene showed equal response, and the percentage composition of the irradiated sample could be readily calculated by dividing the peak area of the product isomer by the total peak area.

For all measurements potassium ferrioxalate actinometry was used to determine the intensity in einsteins per minute of the particular wavelength of light being used. In general, the method was that of Hatchard and Parker (9) with some modifications. To prepare the potassium ferrioxalate, 3 ml. of 0.2000 M $Fe(NH_4)(SO_4)_2$ and 3 ml. of 0.6000 M $K_2C_2O_4$ were diluted in the dark to 100 ml. with 0.1 N H_2SO_4. Three samples of four milliliters each of this solution were irradiated for three minutes. Then 2 ml. aliquots of these irradiated samples (thoroughly mixed) and 1 ml. of the acetate/acetic acid buffer and 1 ml. of 0.1 % o-phenanthroline solution were diluted to 10 ml. with distilled water; these were left standing in the dark for 20-30 minutes for the Fe(II) complex to develop. The optical density was then measured at 5100 Å on a Beckman DU spectrophotometer.

The intensity was calculated from the following formula:

$$I = \frac{(OD) \times F \times (V)}{\phi \times A \times t}$$

where I = intensity in einsteins/minute

(OD) = optical density at 5100 Å

(V) = volume of $K_3Fe(C_2O_4)_3$ solution irradiated (in liters)

ϕ = quantum yield--1.21 at 3660 Å

1.24 at 3130 Å

A = amount of light absorbed (> .999)

t = time of irradiation (minutes)

$$F = \frac{\text{volume of dilution (in liters)} \times 10^{-3}}{\text{volume of aliquot (in liters)} \times \epsilon}$$

$\epsilon = 10{,}900$

Under the conditions described this reduces to

$$I = (OD) \times 5.055 \times 10^{-7}$$

This modification has also been described by Vesley (10).

Quantum yields were calculated from the following formula:

$$\phi = \frac{[D]_0 \times V \times \%\ \text{conv.}}{I \times t}$$

where $[D]_0$ = initial concentration of the starting isomer of the diene

V = volume sample irradiated

% conv. = percent conversion to the product isomer

I = lamp intensity as measured by the actinometer

t = time of irradiation

C. Measurement of Photostationary States

In the measurement of the photostationary states, samples were prepared in the same way as for the measurement of quantum yields, except that the tubes were not wrapped in aluminum foil. The irradiation was conducted in a stationary system immersed in a water bath. The lamp and immersion well have already been described (p. 12). A uranium glass filter sleeve (0. 25 cm thickness) was used to stop all irradiation of wavelength less than 3400 Å. Analysis was carried out as previously described (p. 13-14).

RESULTS AND DISCUSSION

The chemical system which was selected for this investigation was 2, 4-hexadiene. This system has the advantage over other systems which might be chosen of being easily obtainable and of being relatively easy to analyze using vapor phase chromatography as described in the previous section. However, because of the structural symmetry of the 2, 4-hexadiene molecule, it has only three geometrical isomers, and this in turn demands that some modifications be made to the quantum yield calculations for the ideal case described in a previous section.

In applying that model system to our specific case, we designate that A = D = CH_3 and B = C = H (refer to Figures 3 and 4). Now it becomes obvious that the isomers labelled "TC" and "CT" are in fact the same molecule, thus eliminating in effect one of the pathways shown in Figure 3 and one-half of the rectangle of paths shown in Figure 4. In the following paragraphs, the quantum yield calculations are applied to the specific case of 2, 4-hexadiene.

In the case of a common triplet capable of decaying to any of the three possible ground states, the six possible quantum yields can be written (assuming isomerically pure starting material and the assumptions previously mentioned concerning the sensitizer) as follows:

$$\phi_{TT \to CT} = \frac{k_3}{k_1 + k_3 + k_4}$$

$$\phi_{CT \to TT} = \frac{k_1}{k_1 + k_3 + k_4}$$

$$\phi_{CT \to CC} = \frac{k_4}{k_1 + k_3 + k_4}$$

$$\phi_{CC \to CT} = \frac{k_3}{k_1 + k_3 + k_4}$$

$$\phi_{TT \to CC} = \frac{k_4}{k_1 + k_3 + k_4}$$

$$\phi_{CC \to TT} = \frac{k_1}{k_1 + k_3 + k_4}$$

and, as before, these are added to give

$$\Sigma_{\phi} = \frac{2k_1 + 2k_3 + 2k_4}{k_1 + k_3 + k_4} = 2.$$

In the case of two individual triplets, the difficulties become somewhat more serious. Now the two double bonds in each of the TT and CC isomers become identical and the quantum yield for isomerization to CT becomes independent of the fraction of energy transferred to a particular double bond since excitation of either one can produce the desired isomerization. This results in unfortunate mathematical complications. The quantum yields may now be written as follows:

$$\phi_{TT\to CT} = \frac{k_8}{k_7 + k_8}$$

$$\phi_{CT\to TT} = \left(\frac{k_{AB}}{k_{AB} + k_{CD}}\right)\left(\frac{k_7}{k_7 + k_8}\right)$$

$$\phi_{CT\to CC} = \left(\frac{k_{CD}}{k_{AB} + k_{CD}}\right)\left(\frac{k_6}{k_5 + k_6}\right)$$

$$\phi_{CC\to CT} = \frac{k_5}{k_5 + k_6}$$

When these expressions are added, the following sum is obtained:

$$\Sigma_\phi = 1 + \frac{k_5k_7k_{AB} + k_5k_8k_{AB} + k_5k_8k_{CD} + k_6k_8k_{CD}}{(k_5 + k_6)(k_7 + k_8)(k_{AB} + k_{CD})}$$

Unfortunately, the individual rate constants in the second term are not available, nor are they likely to be as will be seen from the complexity of the proposed mechanism (discussed in detail later) for this case. However, it can be seen upon expansion of the denominator that this term must be less than unity, thus making the sum of the quantum yields less than two. It was estimated that this sum should be in the range of 1.2 to 1.5. Thus, in the specific case of 2,4-hexadiene, in order to identify which of the two possible geometries represents the excited triplet state, we must now attempt to distinguish between the sum of quantum yields of either exactly two or something in the 1.2 to 1.5 range.

With the foregoing idealized discussion, we measured the quantum yields for the photosensitized cis-trans isomerization of 2,4-hexadiene. The results are given in Table I.

Table I. Quantum Yields for Isomerization of 2,4-Hexadiene.[a,b]

$\phi_{TT \rightarrow CT} = 6.3$

$\phi_{CT \rightarrow TT} = 3.2$

$\phi_{CT \rightarrow CC} = 2.0$

$\phi_{CC \rightarrow CT} = 5.5$

$\phi_{TT \rightarrow CC} = 0.4$

$\phi_{CC \rightarrow TT} = 0.6$

[a] Initial concentration of the starting isomer was 0.10 M.

[b] Benzophenone sensitizer concentration was 0.050 M.

It should be noted that, although $\phi_{TT \rightarrow CC}$ and $\phi_{CC \rightarrow TT}$ have been written as one-step processes, they might well be two-step processes which could be more appropriately described as $\phi_{TT \rightarrow CT \rightarrow CC}$ and $\phi_{CC \rightarrow CT \rightarrow TT}$ respectively. In any case, the data in this and subsequent tables actually represent the rate of formation of the final product from the starting material.

From Table I it is apparent that $\Sigma_\phi = 18.0$ for a case (a) triplet or $\Sigma_\phi = 17.0$ for case (b) triplets (which require that $\phi_{TT \rightarrow CC}$ and $\phi_{CC \rightarrow TT}$ each equal zero). Of course, it is immediately apparent that in either case the sum is far greater than can be accounted for by the discussion of the results which were to be expected. At this point it became necessary to find an explanation for these very high initial quantum yields. Five possible causes of these high quantum yields are listed below.

1. Stray light, causing actinometrically unmeasured isomerization.
2. Isomerically impure starting materials.
3. Thermal catalysts present in the solvent, causing thermal isomerization.
4. Loss of starting material via dimerization or polymerization.
5. A chain mechanism of some sort.

Each of these possibilities was investigated further and four of the five were finally eliminated (as described below) as causes of this very unusual effect.

To demonstrate the actual effect of stray light from the room, an experiment was conducted in which samples of cis, cis diene were prepared, left out in the room light for 20 hours, and analyzed. These were compared with samples prepared in an identical manner, except that they were wrapped in aluminum foil during preparation and were wrapped in black cloth and stored in a cupboard until they were analyzed.

Table II. Effect of Stray Room Light [a]

Sample	Exposed to room light	% CT	%TT
1	yes	4.26	0.15
2	yes	4.30	0.18
3	no	2.82	-
4	no	2.87	-

[a] *cis, cis*-Hexadiene initial concentration = 0.20 M.
benzophenone sensitizer concentration = 0.050 M.

Thus it can be seen that approximately 1.6% conversion occurred after 20 hours exposure to room light. However, this small amount of conversion is not nearly enough, in itself, to account for the observed effect. Furthermore, in the quantum yield experiments the samples were never exposed to room light for more than about two or three hours and then only during the degassing stage. During this phase, they were wrapped in foil and for the most part in the solid state at 77° K. Since the diene has no significant ($\epsilon > \sim 1$) UV absorption at wavelengths greater than 280 millimicrons and since benzophenone does not transfer triplet energy at liquid nitrogen temperature, it can be assumed that no light energy is being put into the diene, either directly or indirectly during this phase. Therefore the possibility of stray room light was discarded as a reasonable explanation of the high quantum yields.

To check the effect of isomeric (geometrical, not structural) impurities in the starting material, the various samples of "pure" isomer were analyzed before sensitizer was added. Since this factor varied with each batch of purchased material, it is sufficient here to merely note that this variable was checked prior to each quantum yield experiment and the samples were seldom found to have more than 1.5 to 2.0 % total isomeric impurity. Here also, this small amount of impurity, while technically significant, is not sufficient to account for the large effect observed. Furthermore it was felt that energy transfer to this small amount of impurity was negligible and that the quantum yields could be (and, indeed, <u>must</u> be, in many cases) corrected by simply subtracting the initial percentage from the final percentage of isomer after photolysis in order to obtain the true percent conversion. Thus, this factor was eliminated as a possible cause.

The factor of thermal catalysts (especially, H^+) being present in the solvent and causing thermal isomerization, which was being attributed to photoisomerization in the calculation of quantum yields, was considered chemically possible, since the solvents were purified over sulfuric acid, although not very probable physically. This consideration was easily checked in the following experiment. Samples were prepared for photostationary state measurements using the same batch of purified solvent as the samples for the quantum yields reported in Table I and were irradiated under the conditions described earlier for one week. They were then left sitting for nearly three weeks awaiting analysis. It was felt that if any thermal catalyst was present it would have brought the solutions to a thermal equilibrium rather than a photochemical equilibrium. This feeling is supported in several ways by the report of Döring and Hauthal (11) who made a careful study of the thermal isomerization of 2, 4-hexadiene, using iodine (approximately 10^{-3} M) as the catalyst and heptane as the solvent. First, they report a thermal stationary state which is significantly different from the measured photostationary state. Second, they found that the thermal stationary state is reached within a maximum of 30-36 hours, so that three weeks should certainly be sufficient to bring the aforementioned samples to the thermal stationary state. Table 3 shows the comparison of the analysis of these samples, presumably at photostationary state, with the thermal stationary state as reported by Döring and Hauthal.

Table III. Comparison of Thermal and Photo-Stationary States

Stationary State	%TT	%CT	%CC
photo-	33.5	50.3	16.2
thermal-[a]	65.5	30.7	3.8

[a] At a temperature of 20.2° C.

Based on the comparison in Table III and on the other considerations discussed above, it was concluded that the presence of thermal catalysts was not an important factor and, again, insufficient in itself to explain the observed high quantum yields.

Probably the most important consideration that must be made in attempting to identify the cause of this unusual effect is that of loss of starting material. Loss of starting material, caused by dimerization or more extensive polymerization, would make the size of the peak of the predominant isomer in the vapor phase chromatogram smaller than expected, thereby making the peak of the product isomer seem relatively larger. Photosensitized dimerization of conjugated dienes has been extensively investigated by Hammond <u>et al.</u> (12-17 and references cited therein). Polymerization of butadiene is a well-known reaction and could be particularly important in this case if free radicals were present. It should be mentioned here that benzophenone triplet does behave like a free radical in some cases such as hydrogen abstraction from alcohols and various hydrocarbons (18-20). This consideration was carefully studied in two ways.

The first obvious observation that was made was that samples of relatively high diene concentration (1.0 M) irradiated for approximately one week (to photostationary state) showed no physical evidence of polymerization. The samples remained colorless and no solid deposits were formed. The first way in which this problem was investigated was to analyze solutions for loss of diene monomer. Samples were prepared and the total integrated peak areas from the v.p.c.

trace of the diene isomers from irradiated and unirradiated solutions were compared using carefully controlled sample sizes (10 microliter syringe with a Cheney adapter).

Table IV. Total Peak Areas of Irradiated and Unirradiated Diene Solutions

	Total area[a]	Average
Unirradiated	10143	10189 ± 45
	10234	
Irradiated	9928	10054 ± 126
	10180	

[a] In arbitrary units.

From the data in Table IV, it is apparent that no diene is lost within experimental error (approximately 1.25%).

The second way in which this matter was investigated was by looking specifically for the presence of diene dimers in solution. In this experiment, various solutions of diene were injected onto a 20% Carbowax 20 M v.p.c. column used by G. F. Vesley (10) to separate cyclohexadiene dimers. By comparison of retention times with those of pure materials, the various peaks were identified. With the injection block at 220° C, a 1.0 M solution of diene was analyzed and a new peak appeared. As the temperature of the injection block was lowered to room temperature, this peak decreased and disappeared with the injection block at 30° C. In addition, the retention time of this new peak is approximately the same as that observed under the same condition by Vesley for the cyclohexadiene dimers. It was concluded that the new peak could be attributed to hexadiene dimers formed thermally on the injection block. Now a 1.0 M solution of diene which had been irradiated to photostationary state (conditions which would have allowed the most extensive dimerization) was analyzed (with the injection block at 30° C). No peak was observed at the retention time attributed above to hexadiene dimers. Thus, with the data from these two experiments and the original observation, it was concluded that loss of material was unable to account for the quantum yields observed. It might be further noted that, since Σ_{ϕ} was nearly a factor of ten "too high", 90% of the starting material would have to be lost to account for the effect solely on this basis. Clearly, no such thing was happening.

It should be mentioned here that all quantum yields (including those in Table I) have been corrected for the effect of isomeric impurities and precautions were taken to minimize the effect of stray room light.

Thus we were left with the possibility of a chain process accounting for these rather high cis-trans isomerization quantum yields. On the face of the matter, this might have seemed the rather obvious answer; yet, considering the chemical system, conditions used, and the type of reaction involved, it was not immediately clear that it was a likely explanation at all. However, having apparently eliminated all other explanations, we proceeded on the basis that a chain process of some sort was in operation.

In an effort to obtain some more positive evidence of a chain process, we reasoned that, if such a process was in operation, then there must be some sort of chain—propagation step, such as

$$X + CC \longrightarrow CT + X$$

in the mechanism. Inclusion of such a step in the mechanism, however, implies that in the overall kinetics quantum yield should show a very pronounced dependence on the concentration of diene. It was this concentration effect that was investigated next and for which data are reported in Table V. These data are shown graphically in Figures 5-10.

A comment or two about Table V is in order. First, the data are given as averages of several (at least, three) analyses plus or minus the standard deviation from that average. Second, the data represent the best values obtained, since they were not as precise or reproducible as one might like. These faults, it is felt, can be explained by the magnitude of the quantum yields themselves (noting that the percent errors are not much greater than in the studies on stilbene and piperylene) and the fact that the quantum yield also depends on the time of irradiation. This second factor will be discussed in detail later in connection with the suggested mechanism. At any rate, it is evident that there is a very pronounced concentration effect on the quantum yield, and a chain process of some sort seems confirmed since the previously reported (5) "classical" mechanism for

Table V. Quantum Yields as a Function of Diene Concentration

[Diene]	$\phi_{TT\rightarrow CT}$	$\phi_{CT\rightarrow TT}$	$\phi_{CT\rightarrow CC}$	$\phi_{CC\rightarrow CT}$	$\phi_{TT\rightarrow CC}$*	$\phi_{CC\rightarrow TT}$*
.005	1.05 ± 0.02	0.69 ± .00	0.14 ± .00	0.85 ± 0.01	0.28 ± 0.05	0.55 ± 0.12
.010	1.47 ± 0.02	0.50 ± .09	0.20 ± .00	1.5 ± 0.05	0.40 ± 0.07	0.30 ± 0.03
.050	3.69 ± 0.03	2.4 ± 0.1	0.52 ± .05	5.2 ± 0.1	0.36 ± 0.15	0.5 ± 0.1
.100	6.30 ± 0.19	3.2 ± 0.1	2.0 ± .0	5.5 ± 0.2	0.44 ± 0.10	0.6 ± 0.1
.150	8.77 ± 0.23				0.44 ± 0.15	
.250	14.53 ± 0.25				0.52 ± 0.06	
.500	32.34 ± 0.62	11.5 ± 0.6	3.0 ± 0.3	31.8 ± 0.6	0.87 ± 0.06	0.3 ± 0.1
.750	40.17 ± 0.19	10.5 ± 0.5	2.3 ± 0.1	44.5 ± 0.9	0.85 ± 0.19	0.9 ± 0.2
1.00	48.69 ± 1.11	9.0 ± 1.67	-	56.3 ± 3.9	0.87 ± 0.12	-

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* See the bottom of page 20.

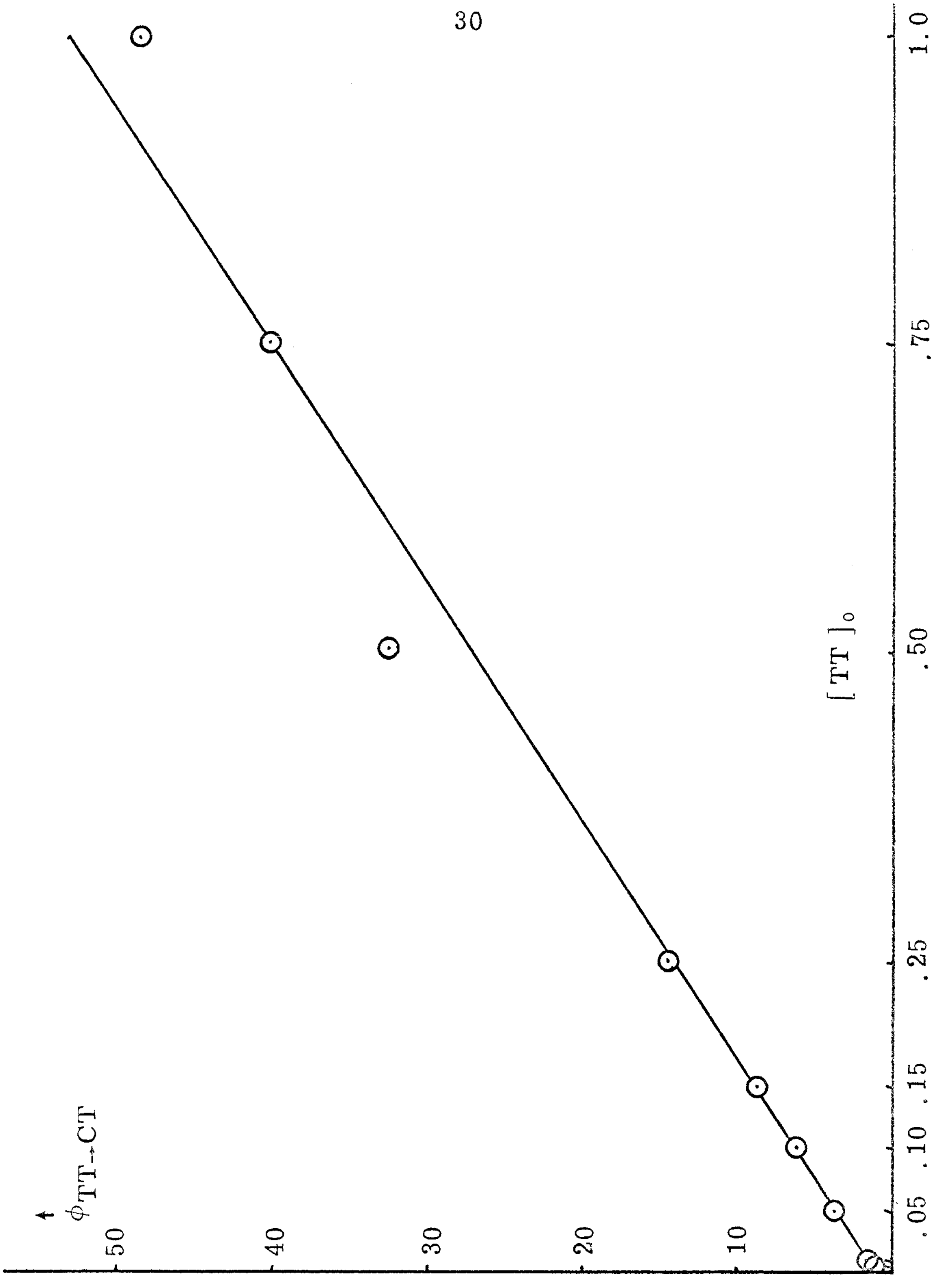


Figure 5. $\phi_{TT\rightarrow CT}$ as a function of initial trans, trans-hexadiene concentration.

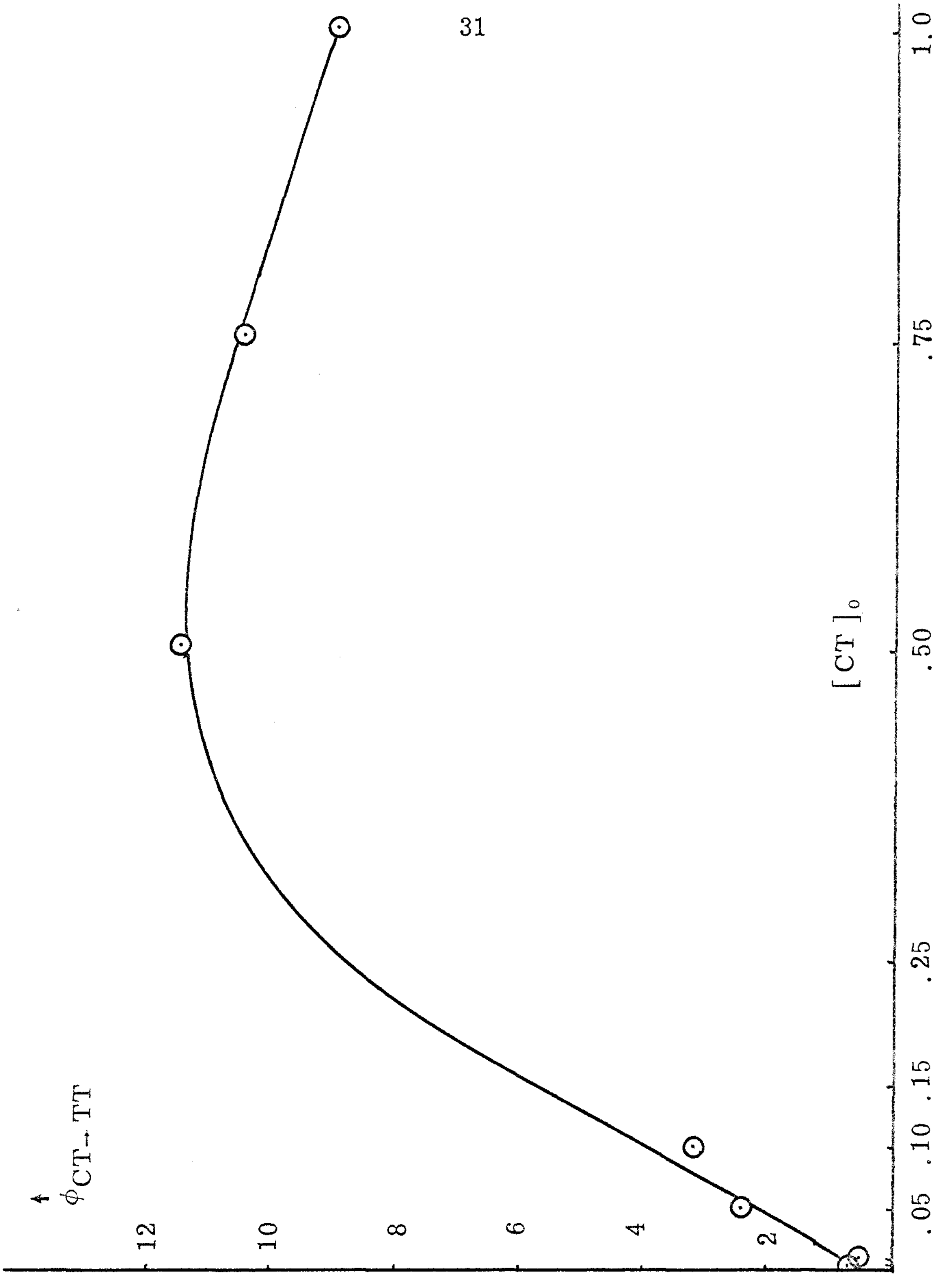


Figure 6. $\phi_{CT\rightarrow TT}$ as a function of initial cis, trans-hexadiene concentration.

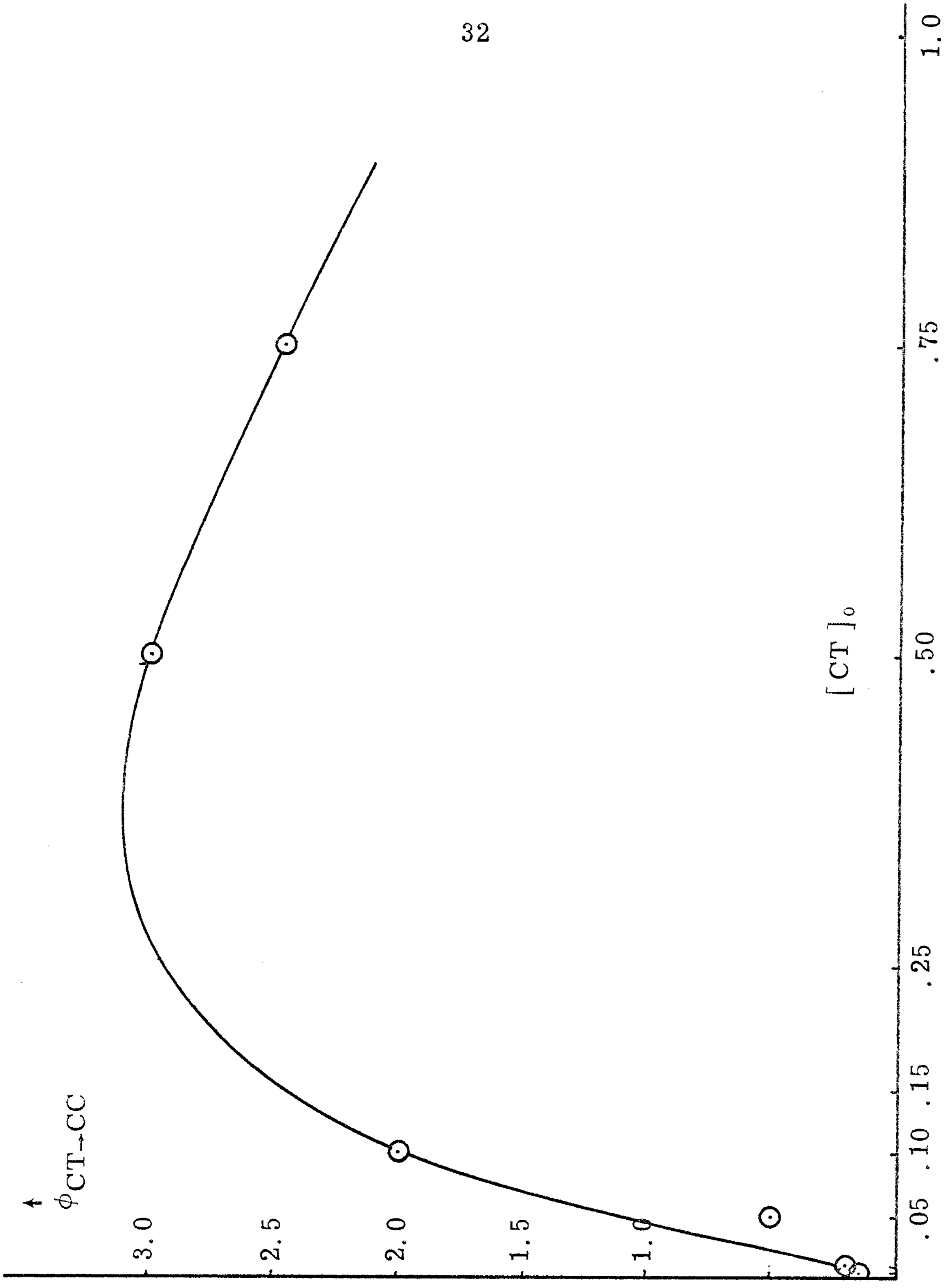


Figure 7. $\phi_{CT\rightarrow CC}$ as a function of initial <u>cis, trans</u>-hexadiene concentration.

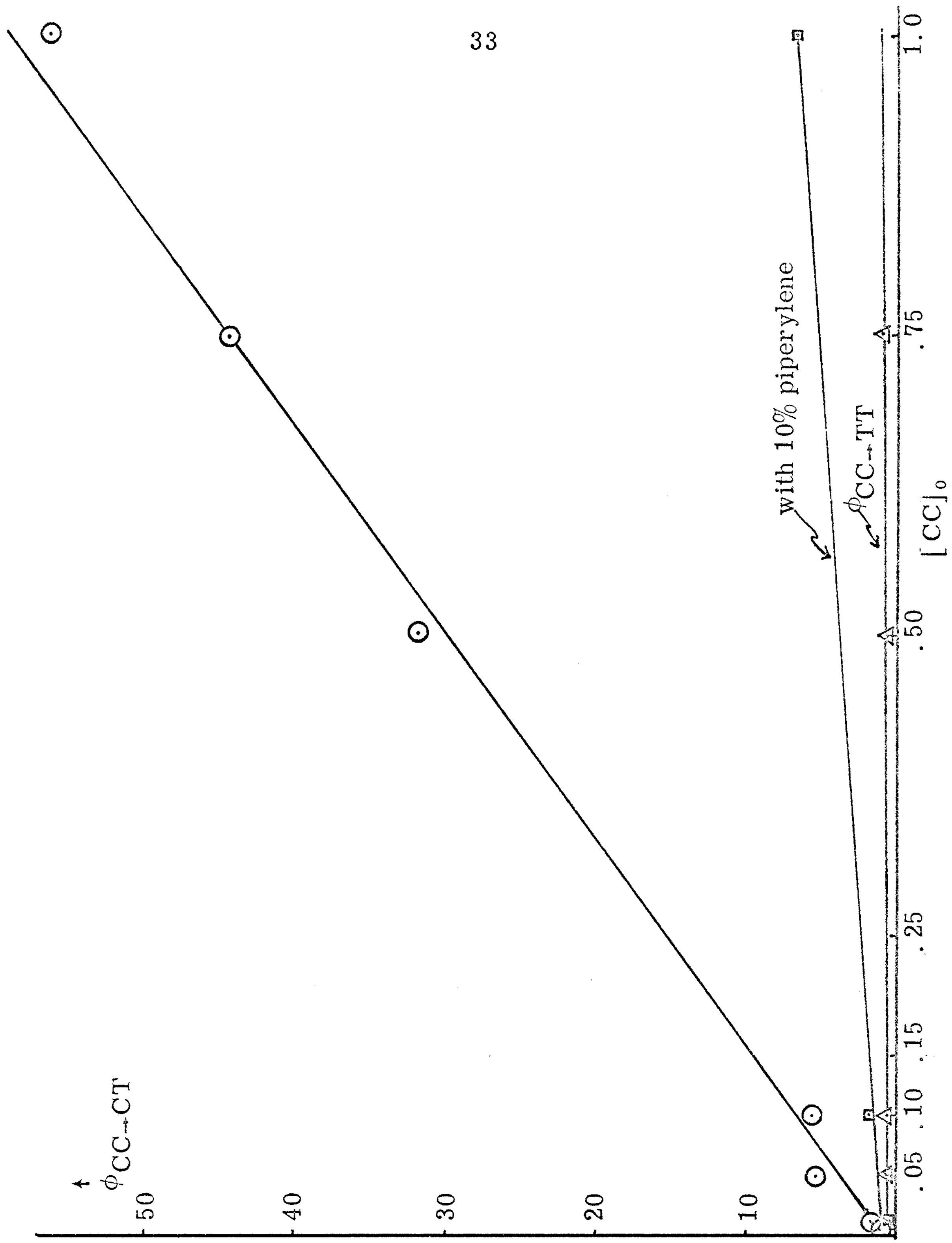


Figure 8. $\phi_{CC \to CT}$ as a function of initial *cis, cis*-hexadiene concentration.

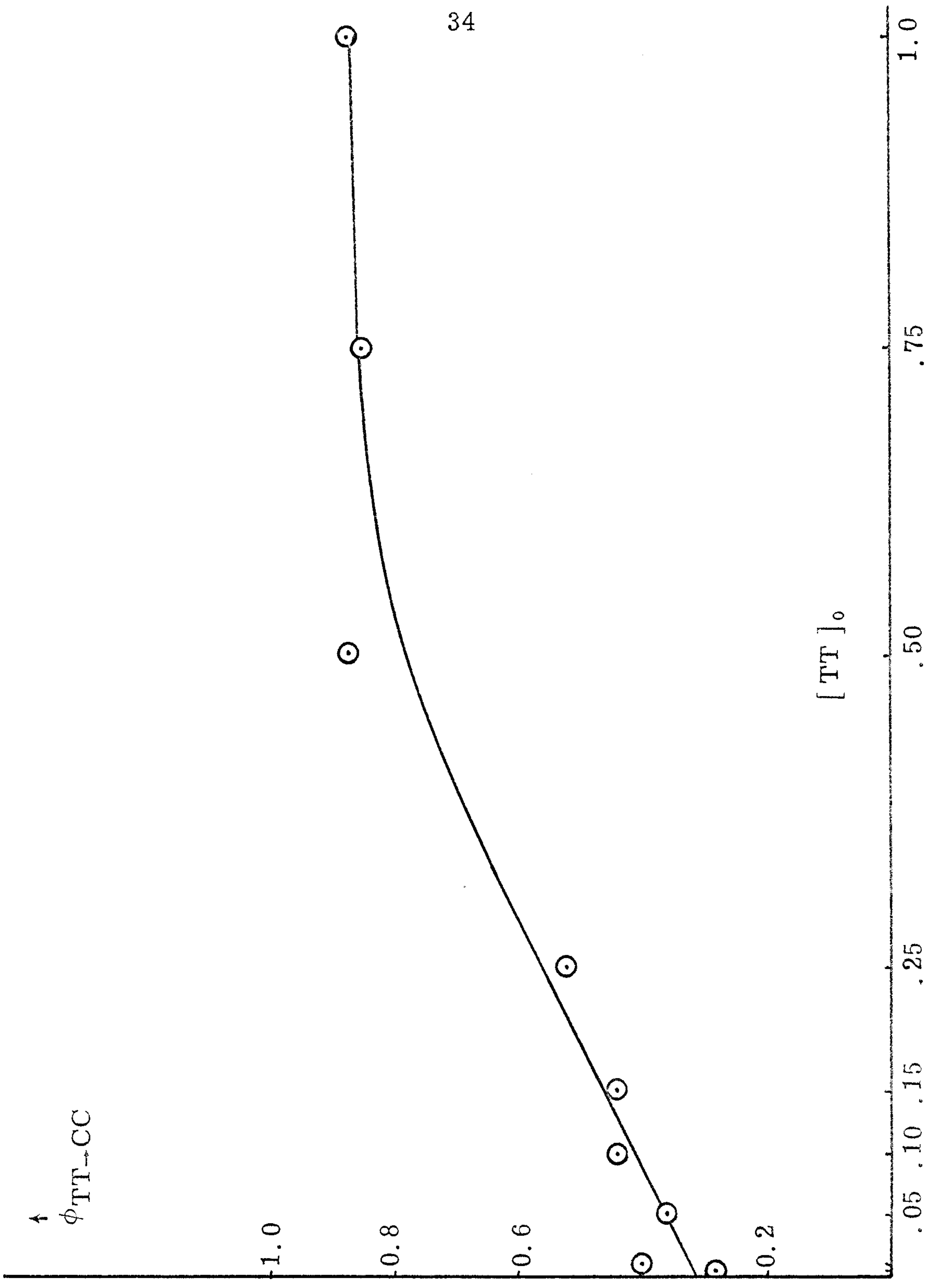


Figure 9. $\phi_{TT\to CC}$ as a function of initial *trans, trans*-hexadiene concentration.

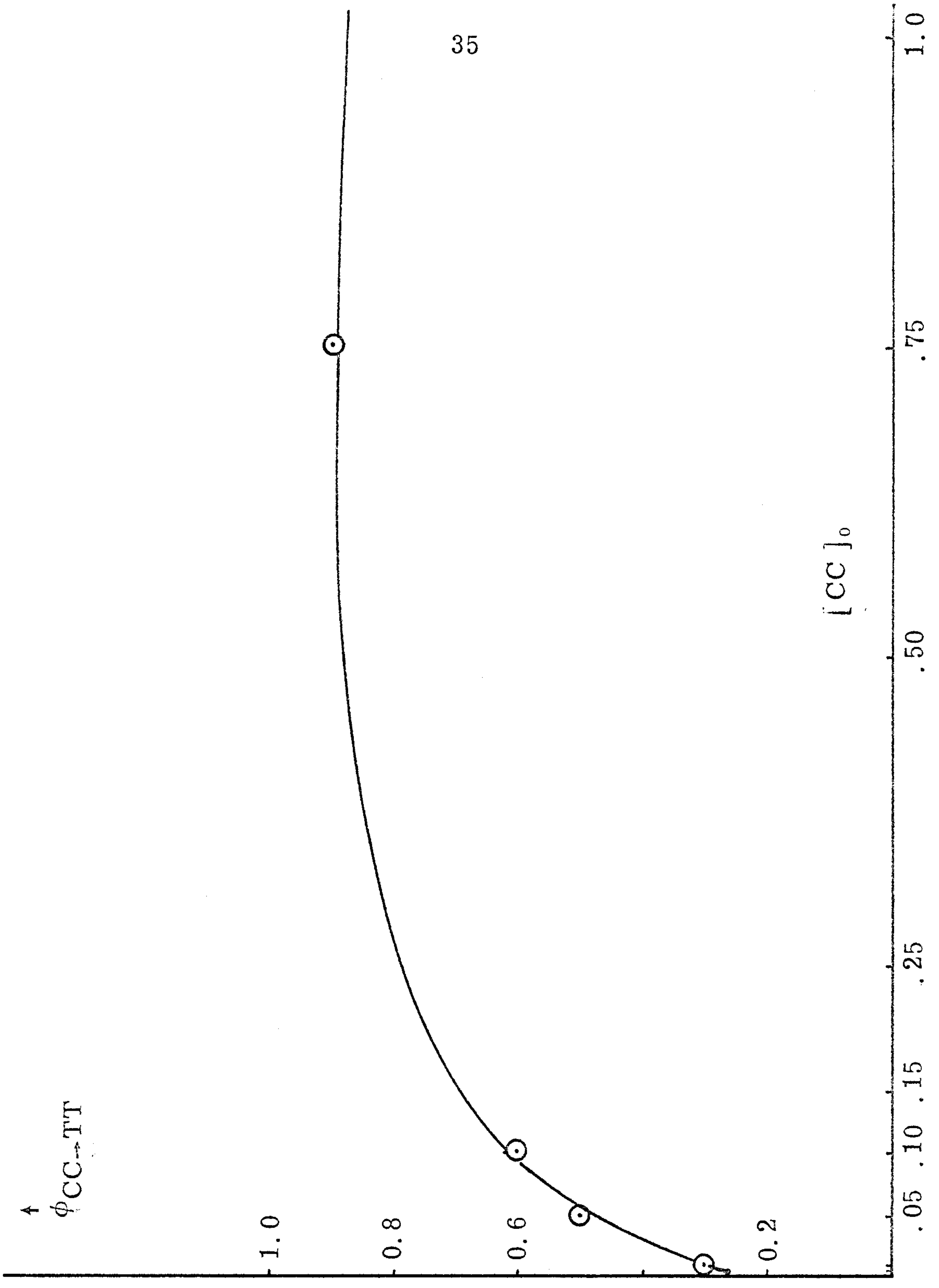


Figure 10. $\phi_{CC \rightarrow TT}$ as a function of initial cis,cis-hexadiene concentration.

the cis-trans isomerization of the stilbenes does not predict a significant dependence of the quantum yield on diene concentration (nor has it been observed in previously reported cases!).

Another interesting result is provided by an experiment in which piperylene was added to the reaction mixture. In this experiment, trans-piperylene was present in a 1:10 ratio with cis, cis-hexadiene and the quantum yields for isomerization of the hexadiene were measured. The results are given in Table VI and shown in Figure 8.

Table VI. Quantum Yields Measured in the Presence of Piperylene

[CC], M	[t-piperylene], M	$\phi_{CC\rightarrow CT}$	$\phi_{CC\rightarrow TT}$
0.010	0.001	0.51 ± 0.01	0.33 ± 0.06
0.100	0.011	1.7 ± 0.0	0.33 ± 0.01
1.004	0.111	6.7 ± 0.0	0.95 ± 0.03

Based on the relative concentrations of piperylene and hexadiene, one would expect approximately 10% quenching of sensitizer triplets by piperylene, which, in a classical decay mechanism, should result in 10% quenching of the hexadiene isomerization. However, by comparison with the results given in Table V, one can see that this isomerization is about 90% quenched by the piperylene. Also azulene in 0.5% relative concentration with hexadiene completely quenches the diene isomerization. (In this case, azulene absorbs only about 1.5% of the light directly.) Apparently the species X in the chain mechanism must be destroyed (or deactivated) by interaction with piperylene and azulene.

Before continuing the investigation into the exact nature of diene triplet state, we conducted several experiments which were intended to identify the chain-carrying species in the reaction. First of all, as a result of an experiment previously described, in which it was concluded that there was no thermal catalysis occurring, it was now considered that the chain-carrying species must be generated photochemically. The first possibility which was considered was that of the photochemical formation of free radicals in the solution. On the face of the matter, this did not seem too likely since any free radicals should initiate extensive polymerization of the "substituted butadiene" substrate. This effect, as described before, was not observed. Nevertheless, the following experiments were designed either to detect the presence of free radicals or to eliminate the possibility of their formation.

The ability of benzophenone triplet to undergo free radical reactions, especially hydrogen abstraction, has been studied by several workers (18-20) as mentioned before, and it was felt that this could be a source of free radicals. The examination by electron spin resonance of various solutions of diene and sensitizer in hexane provided interesting results on this point. A 0.050 M benzophenone solution in hexane did, indeed, exhibit a weak e.s.r. signal. Although the signal was so weak under these conditions that no hyperfine analysis was possible, it seems safe to conclude that the signal observed was that of the benzophenone ketyl radical, especially as benzpinacol formation was also observed. When a similar solution which was also 1.00 M in cis, cis-hexadiene was analyzed, no signal whatsoever was observed. Apparently the diene quenches the formation of benzophenone ketyl radical, formed by the abstraction of a hydrogen atom from hexane by the benzophenone triplet. The quantum yield for hydrogen abstraction from hexane, in the absence of quenchers, has been reported (20) to be 0.55.

An additional experiment was carried out in which benzene was used as the solvent. The quantum yield for hydrogen abstraction by benzophenone triplet from benzene has been reported to be zero (20), so that no radicals should be possible under these conditions. Also triphenylene was used as a sensitizer since its triplet is a $\pi-\pi^*$ triplet and not capable of hydrogen abstraction. The results of these experiments are given in Table VII.

Although these data may vary somewhat from similar data in Table V, it is apparent that the very high quantum yields are not quenched by removing any free radicals present. From the results of the foregoing observations and experiments, it was concluded that there were no free radicals present in solution to act as the chain-carrying species.

The possibility of an ionic species could also be considered although the formation of ions or radical ions would be very difficult

Table VII. Quantum Yields as a Function of Diene Concentration in Benzene Solution

$[CC]_0$	ϕ_{CC-CT}	
	ϕ_2CO	triphenylene[a]
0.005	1.52 ± 0.10	0.58 ± 0.08
0.010	0.72 ± 0.06	2.38 ± 0.00
0.050	3.86 ± 0.06	7.17 ± 0.06
0.100		9.13 ± 0.13
0.150	9.79 ± 0.13	22.74 ± 0.08
0.200	9.12 ± 0.32	28.81 ± 0.23
0.750	24.04 ± 0.09	77.95 ± 0.78
1.000		93.90 ± 0.93

[a] In this case, wavelength of incident light was 3130 Å.

to rationalize under the conditions employed in these quantum yield measurements. Nevertheless, one could rationalize that, if this were the case, the quantum yield should be strongly dependent on solvent polarity. It is already apparent that the change of solvent from hexane to benzene produces little or no effect on the quantum yield. A few data were taken using acetonitrile as solvent. It is apparent from Table VIII that the quantum yields are certainly no larger than in any other solvent. Although these last results are perhaps not very conclusive in themselves, neither is it very reasonable to expect an ionic

Table VIII. Quantum Yields as a Function of Diene Concentration using Acetonitrile as Solvent

$[CC]_0$	$\phi_{CC\rightarrow CT}$
.005	0.40 ± 0.05
.050	1.79 ± 0.02
.500	3.10 ± 0.03

species to have sufficient lifetime under these conditions to exhibit this type of behavior.

One other possibility which has not yet been mentioned is that of homogeneity of the reaction. Thus far, it has been assumed that all reactions occur homogeneously, despite the fact that the glass-liquid interface is a possible site for occurrence of surface catalytic effects. It was felt that if catalytic sites were formed photochemically on the surface of the glass by one means or another, they might be formed by a prior irradiation and used to increase the quantum yield in a subsequent measured irradiation. This experiment was carried out by using specially constructed Pyrex tubes which could be used more than once. Two of these tubes were prepared as usual and irradiated for 44 hours under conditions described for photostationary state measurements. The tubes were rotated by hand periodically in an attempt to get equal irradiation on all the glass surfaces. They were then opened, emptied, refilled, degassed, sealed, and then exposed to measured irradiation for quantum yield measurement. The results are given in Table IX.

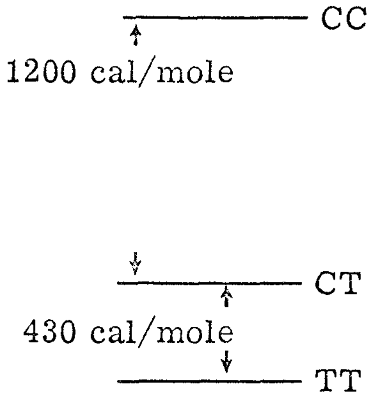
Table IX. Effect of Pre-Irradiated Tubes on the Quantum Yields [a]

Pre-irradiated tubes	$\phi_{CC \rightarrow CT}$	Average
yes	30.78	30.56
yes	30.35	
no	32.22	30.33
no	28.45	

[a] $[CC]_0 = 1.80$ M, $[\phi_2CO] = 0.050$ M in hexane.

The results here are nearly identical and it was concluded that catalytic sites on the surface of the Pyrex tube most likely do not play any part in causing the high quantum yields.

As a result of the foregoing experiments, it was then felt that the only species, being generated photochemically and having a sufficient lifetime to have multiple interaction with ground state diene, was the diene triplet. Examination of the thermodynamics of the 2,4-hexadiene system (11) shows that this type of interaction is, indeed, capable of producing a chain process. Döring and Hauthal report the following relative free-energy relationships for the ground states of the three 2,4-hexadiene isomers (11).



So, it is apparent that, when the triplet of the *cis, cis* isomer decays to the *cis, trans* ground state, there is 1200 cal/mole more energy released in that decay process than is needed to excite another *cis, cis* ground state isomer to the triplet state. This, of course, also applies to the other possible "downhill" processes. A more difficult rationalization to make is that the "uphill" processes also exhibit, at least to a degree, the high quantum yields attributed to a chain process. Here, however, it should be noted that the energy discrepancy in the *trans, trans* to *cis, trans* isomerization is only 430 cal/mole whereas the amount of thermal energy available at room temperature is 600 cal/mole. Therefore, this energy discrepancy could be made up from that source. The explanation in the case of the *cis, trans* to *cis, cis* isomerization is even more difficult, except to note that the quantum yields in this case are lower at a given concentration than the others. Indeed, it can be seen from Table V that the quantum yields for the "uphill" processes are lower in general than those for the "downhill" processes. This, of course, is as would be expected from the foregoing considerations.

Having reached these preceding conclusions, we are in a position to consider more or less specific mechanisms for the isomerization process. Basically, two mechanisms will be discussed--the first employing a single common [case (a)] triplet, the second and more complex mechanism employing two triplets [case (b)].

The first mechanism, assuming a common triplet capable of decaying to any of the ground states, is discussed from the point of view of starting with pure cis, cis-hexadiene and in terms of $\phi_{CC \rightarrow CT}$ and $\phi_{CC \rightarrow TT}$, both of which are energetically "downhill" processes. The scheme is shown in Figure 11. In this Figure, S represents the sensitizer with the superscripts denoting the excited states, and T^3 represents the diene triplet. Steps (1), (2), and (3) are the ordinary excitation and energy transfer steps. Steps (4) and (5) represent the unusual energy transfer interaction between the excited and ground state diene. (It was not considered necessary at this point to include similar interactions between T^3 and CT and T^3 and TT). Steps (6), (7), and (8) are the ordinary unimolecular decay processes of the diene triplet. From this mechanism, making the assumptions discussed previously about the sensitizer, the following quantum yields may be derived.

$$\phi_{CC \rightarrow CT} = \frac{k_1}{k_1' + k_2' + k_d'}[CC] + \frac{k_1'}{k_1' + k_2' + k_d'}$$

$$\phi_{CC \rightarrow TT} = \frac{k_2}{k_1' + k_2' + k_d'}[CC] + \frac{k_2'}{k_1' + k_2' + k_d'}$$

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

$$S^3 + CC \xrightarrow{k_t} T^3 + S \tag{2}$$

$$S^3 \xrightarrow{k_d} S \tag{3}$$

$$T^3 + CC \xrightarrow{k_1} CT + T^3 \tag{4}$$

$$T^3 + CC \xrightarrow{k_2} TT + T^3 \tag{5}$$

$$T^3 \xrightarrow{k_1'} CT \tag{6}$$

$$T^3 \xrightarrow{k_2'} TT \tag{7}$$

$$T^3 \xrightarrow{k_d'} CC \tag{8}$$

Figure 11. Mechanism for isomerization; assuming a common [case (a)] triplet.

These expressions predict, in the plot of quantum yield as a function of concentration (refer to Figures 8 and 10), a linear function with an intercept of less than unity. Both of these predictions seem to be reasonably well fulfilled. However, one further prediction is also made and must be considered in detail because of its extremely crucial implications. This prediction concerns the slopes of these linear plots.

The above mechanism predicts that, when $\phi_{CC \rightarrow CT}$ and $\phi_{CC \rightarrow TT}$ are plotted against concentration, the slopes of those two plots will be different only to the same extent that k_1 and k_2 are different. Now let us consider what differences one might expect between k_1 and k_2 in order to predict what difference is expected between the slopes of the plots.

First of all, the reactants in steps (4) and (5) are the same so that difference in rates for those steps must be attributed to something that occurs after the "transition state" involved in these interactions. The assumption has been made that the same "transition state" (i. e., the common triplet) is involved regardless of the product formed. The only thing that occurs after that point is decay of a triplet to an isomerized ground state. Now we might ask what difference is expected in the rates of decay from the triplet to the ground state cis, trans or the ground state trans, trans isomers. Here we must consider two factors--energy differences in the ground state and steric effects. As mentioned before, the energy difference between cis, trans and trans, trans hexadiene in the ground state is only 430 cal/mole (less than RT at room temperature). Furthermore, this difference appears even less significant when one considers that, in order to get to either ground state, the triplet must lose 50,000-60,000 cal/mole. It seems difficult to believe that the loss of an additional 430 cal/mole could be a very significant factor in the rate. As far as steric effects are concerned, it can be said that these should favor the formation of the trans isomer over the cis isomer by a (very probably) negligibly small amount. In addition, we may compare this case to that of piperylene which seems fairly well understood. For the piperylene system, the decay ratio of $k_2 : k_1 = 1.25$ (5), favoring formation of trans-piperylene. It is perhaps noteworthy also that here the energy difference of the ground states is larger (2-3 kcal vice 430 cal) and more significant than in the hexadiene case. Nevertheless, the difference in decay rates is only 25%. Therefore, we have concluded a priori that k_1 and k_2 (and thus the slopes of the plots of quantum yields against concentration) should be very similar.

However, when $\phi_{CC \rightarrow CT}$ and $\phi_{CC \rightarrow TT}$ are plotted as a function of diene concentration (as in Figure 8), it is apparent that the formation of cis, trans is favored by nearly two orders of magnitude! Clearly, this result cannot be explained by the mechanism presented in Figure 11. Most importantly, that mechanism is based on the explicit assumption of a single common triplet. Therefore this assumption must also be wrong. Thus we have the first real evidence that a common triplet, as pictured in Figure 1a, probably does not correctly represent the geometrical structure of the lowest excited triplet state of conjugated dienes.

As further evidence now for the existence of two triplets as in Figure 1b, we considered a second mechanism as presented in Figure 12. The reaction scheme has become considerably more complex because of the introduction of a second triplet with all of its possible interactions. It is much easier to consider three separate cases in this mechanism--each of which begins with one of the three pure

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

$$S^3 + CC \xrightarrow{k_1} T_1 + S \qquad (2)$$

$$S^3 + CT \xrightarrow{k_2} T_1 + S \qquad (3)$$

$$S^3 + CT \xrightarrow{k_3} T_2 + S \qquad (4)$$

$$S^3 + TT \xrightarrow{k_4} T_2 + S \qquad (5)$$

$$S^3 \xrightarrow{kd} S \qquad (6)$$

$$T_1 + CC \xrightarrow{k_5} T_1 + CT \qquad (7)$$

$$T_1 + CT \xrightarrow{k_6} T_2 + CT \qquad (8)$$

$$T_1 + CT \xrightarrow{k_7} T_2 + CC \qquad (9)$$

$$T_1 + CT \xrightarrow{k_8} T_1 + CC \qquad (10)$$

$$T_1 + TT \xrightarrow{k_9} T_2 + CC \qquad (11)$$

$$T_1 + TT \xrightarrow{k_{10}} T_2 + CT \qquad (12)$$

$$T_2 + CC \xrightarrow{k_{11}} T_1 + CT \qquad (13)$$

$$T_2 + CC \xrightarrow{k_{12}} T_1 + TT \qquad (14)$$

$$T_2 + CT \xrightarrow{k_{13}} T_1 + CT \qquad (15)$$

$$T_2 + CT \xrightarrow{k_{14}} T_1 + TT \qquad (16)$$

$$T_2 + CT \xrightarrow{k_{15}} T_2 + TT \qquad (17)$$

$$T_2 + TT \xrightarrow{k_{16}} T_2 + CT \qquad (18)$$

$$T_1 \xrightarrow{k_{17}} CC \qquad (19)$$

$$T_1 \xrightarrow{k_{18}} CT \qquad (20)$$

$$T_2 \xrightarrow{k_{19}} CT \qquad (21)$$

$$T_2 \xrightarrow{k_{20}} TT \qquad (22)$$

Figure 12. Mechanism for isomerization, assuming different [case (b)] triplets.

isomers-- by making some assumptions about relative concentrations of the ground state isomers and the relative importance of various interactions. These simplifications are given in Figures 13-15, in which all reaction steps and rate constants may correlate with the overall mechanism in Figure 12, and are primarily concerned with the steps of energy transfer between sensitizer and diene. In Figure 12 are listed all the possible interactions of sensitizer triplet with ground state dienes, diene triplets with ground state dienes, and the unimolecular decay processes in the same general pattern as for Figure 11. The notation is also the same as in Figure 11, except that the different diene triplets have been denoted here as T_1 (formed from CC and CT) and T_2 (formed from CT and TT).

In Figure 13, the mechanism makes the assumptions that the sensitizer triplet lives only long enough to interact with the most predominant diene isomer (in this case, cis, cis), that the initially formed diene triplet (T_1) will interact with all three diene isomers, and that the diene triplet formed secondarily (T_2) and in lower concentration than the first will interact only with the predominant isomer. Steps (10) and (11) must be included to explain the concentration dependence, however slight, of $\phi_{CC-CT-TT}$*. Steps (8) and (9) are included since they can account for the curvature of the plot in Figure 10. Entirely analogous comments can be made concerning Figures 14 and 15.

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*This notation will be used hereafter since it seems certain that a single step process is not possible for this isomerization.

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

$$S^3 \xrightarrow{k_d} S \tag{2}$$

$$S^3 + CC \xrightarrow{k_1} T_1 + S \tag{3}$$

$$T_1 + CC \xrightarrow{k_5} T_1 + CT \tag{4}$$

$$T_1 + CT \xrightarrow{k_6} T_2 + CT \tag{5}$$

$$T_1 + CT \xrightarrow{k_7} T_2 + CC \tag{6}$$

$$T_1 + CT \xrightarrow{k_8} T_1 + CC \tag{7}$$

$$T_1 + TT \xrightarrow{k_9} T_2 + CC \tag{8}$$

$$T_1 + TT \xrightarrow{k_{10}} T_2 + CT \tag{9}$$

$$T_2 + CC \xrightarrow{k_{11}} T_1 + CT \tag{10}$$

$$T_2 + CC \xrightarrow{k_{12}} T_1 + TT \tag{11}$$

$$T_1 \xrightarrow{k_{17}} CC \tag{12}$$

$$T_1 \xrightarrow{k_{18}} CT \tag{13}$$

$$T_2 \xrightarrow{k_{19}} CT \tag{14}$$

$$T_2 \xrightarrow{k_{20}} TT \tag{15}$$

Figure 13. Mechanism for isomerization of *cis, cis*-hexadiene assuming two triplets.

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

$$S \xrightarrow{k_d} S \tag{2}$$

$$S^3 + CT \xrightarrow{k_2} T_1 + S \tag{3}$$

$$S^3 + CT \xrightarrow{k_3} T_2 + S \tag{4}$$

$$T_1 + CT \xrightarrow{k_6} T_2 + CT \tag{5}$$

$$T_1 + CT \xrightarrow{k_7} T_2 + CC \tag{6}$$

$$T_1 + CT \xrightarrow{k_8} T_1 + CC \tag{7}$$

$$T_1 + TT \xrightarrow{k_9} T_2 + CC \tag{8}$$

$$T_1 + TT \xrightarrow{k_{10}} T_2 + CT \tag{9}$$

$$T_1 + CC \xrightarrow{k_5} T_1 + CT \tag{10}$$

$$T_2 + CT \xrightarrow{k_{13}} T_1 + CT \tag{11}$$

$$T_2 + CT \xrightarrow{k_{14}} T_1 + TT \tag{12}$$

$$T_2 + CT \xrightarrow{k_{15}} T_2 + TT \tag{13}$$

$$T_2 + CC \xrightarrow{k_{11}} T_1 + CT \tag{14}$$

$$T_2 + CC \xrightarrow{k_{12}} T_1 + TT \tag{15}$$

$$T_2 + TT \xrightarrow{k_{16}} T_2 + CT \tag{16}$$

$$T_1 \xrightarrow{k_{17}} CC \tag{17}$$

$$T_1 \xrightarrow{k_{18}} CT \tag{18}$$

$$T_2 \xrightarrow{k_{19}} CT \tag{19}$$

$$T_2 \xrightarrow{k_{20}} TT \tag{20}$$

Figure 14. Mechanism for isomerization of *cis, trans*-hexadiene, assuming two triplets.

In Figure 14, it should be noted that cis, trans isomer can, of course, produce either diene triplet (with nearly equal probability) upon interaction with sensitizer triplet.

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

$$S^3 \xrightarrow{k_d} S \tag{2}$$

$$S^3 + TT \xrightarrow{k_4} T_2 + S \tag{3}$$

$$T_2 + TT \xrightarrow{k_{16}} T_2 + CT \tag{4}$$

$$T_2 + CT \xrightarrow{k_{13}} T_1 + CT \tag{5}$$

$$T_2 + CT \xrightarrow{k_{14}} T_1 + TT \tag{6}$$

$$T_2 + CT \xrightarrow{k_{15}} T_2 + TT \tag{7}$$

$$T_2 + CC \xrightarrow{k_{11}} T_1 + CT \tag{8}$$

$$T_2 + CC \xrightarrow{k_{12}} T_1 + TT \tag{9}$$

$$T_1 + TT \xrightarrow{k_9} T_2 + CC \tag{10}$$

$$T_1 + TT \xrightarrow{k_{10}} T_2 + CT \tag{11}$$

$$T_1 \xrightarrow{k_{17}} CC \tag{12}$$

$$T_1 \xrightarrow{k_{18}} CT \tag{13}$$

$$T_2 \xrightarrow{k_{19}} CT \tag{14}$$

$$T_2 \xrightarrow{k_{20}} TT \tag{15}$$

Figure 15. Mechanism for isomerization of trans, trans-hexadiene, assuming two triplets.

Collected in Figure 16 are the quantum yields derived from the respective mechanisms presented in Figures 13-15.

$$\phi_{CC \to CT} = \frac{(k_5 + k_{11})(CC) + k_{10}(TT) - (k_7 + k_8)(CT) + k_{18} + k_{19}}{k_{17} + k_{18} + k_{19} + k_{20}}$$

$$\phi_{CC \to CT \to TT} = \frac{k_{12}(CC) - (k_9 + k_{10})(TT) + k_{20}}{k_{17} + k_{18} + k_{19} + k_{20}}$$

$$\phi_{CT \to CC} = \frac{(k_7 + k_8)(CT) + k_9(TT) - (k_5 + k_{11} + k_{12})(CC) + k_{17}}{k_{17} + k_{18} + k_{19} + k_{20}}$$

$$\phi_{CT \to TT} = \frac{(k_{14} + k_{15})(CT) + k_{12}(CC) - (k_9 + k_{10} + k_{16})(TT) + k_{20}}{k_{17} + k_{18} + k_{19} + k_{20}}$$

$$\phi_{TT \to CT} = \frac{(k_{10} + k_{16})(TT) + k_{11}(CC) - (k_{14} + k_{15})(CT) + k_{18} + k_{19}}{k_{17} + k_{18} + k_{19} + k_{20}}$$

$$\phi_{TT \to CT \to CC} = \frac{k_9(TT) - (k_{11} + k_{12})(CC) + k_{17}}{k_{17} + k_{18} + k_{19} + k_{20}}$$

Figure 16. Quantum yields derived from a mechanism assuming different [case (b)] triplets.

Several features of these expressions should be mentioned, discussing only the case of $\phi_{CC \to CT}$. Analogous comments may be made concerning the others. It can be seen that the quantum yield is a positive linear function of [CC], as expected. Also, it is a function of [TT], although this will not be very important because of the relatively low concentration of that isomer. More importantly, the quantum yield is a negative linear function of [CT]. This, of course, predicts a down-turn in the plot of $\phi_{CC\rightarrow CT}$ against [CC] as the concentration of the cis, trans isomer increases. This factor may not be relatively important in this case, yet such behavior is very obvious (see Figures 6 and 7) in the cases of $\phi_{CT\rightarrow TT}$ and $\phi_{CT\rightarrow CC}$ where this factor may be rationalized to be more important.

Indeed, this expression indicates that the quantum yield is dependent on time, since the concentration of the cis, trans isomer is linearly dependent on the irradiation time. An experiment was carried out in which $\phi_{CC\rightarrow CT}$ was measured as a function of time, keeping the percent conversion low enough so that the classical "back reaction" as studied by Lamola (21) should not yet be very important. The data are presented in Table X and shown in Figure 17. Thus it can be seen that this implicit prediction of the quantum yield expression is verified. It should be emphasized that it is apparently this sort of behavior which accounts for the relatively poor reproducibility of the quantum yields, since no special effort was made to give all samples equal irradiation times (or, more particularly, equal amounts of irradiation).

One problem which was very bothersome for a time was that of the photostationary states. During the earlier phases of the work, it was felt that since the mechanistic role assigned to the diene triplet was essentially that of a catalyst, the photostationary state should

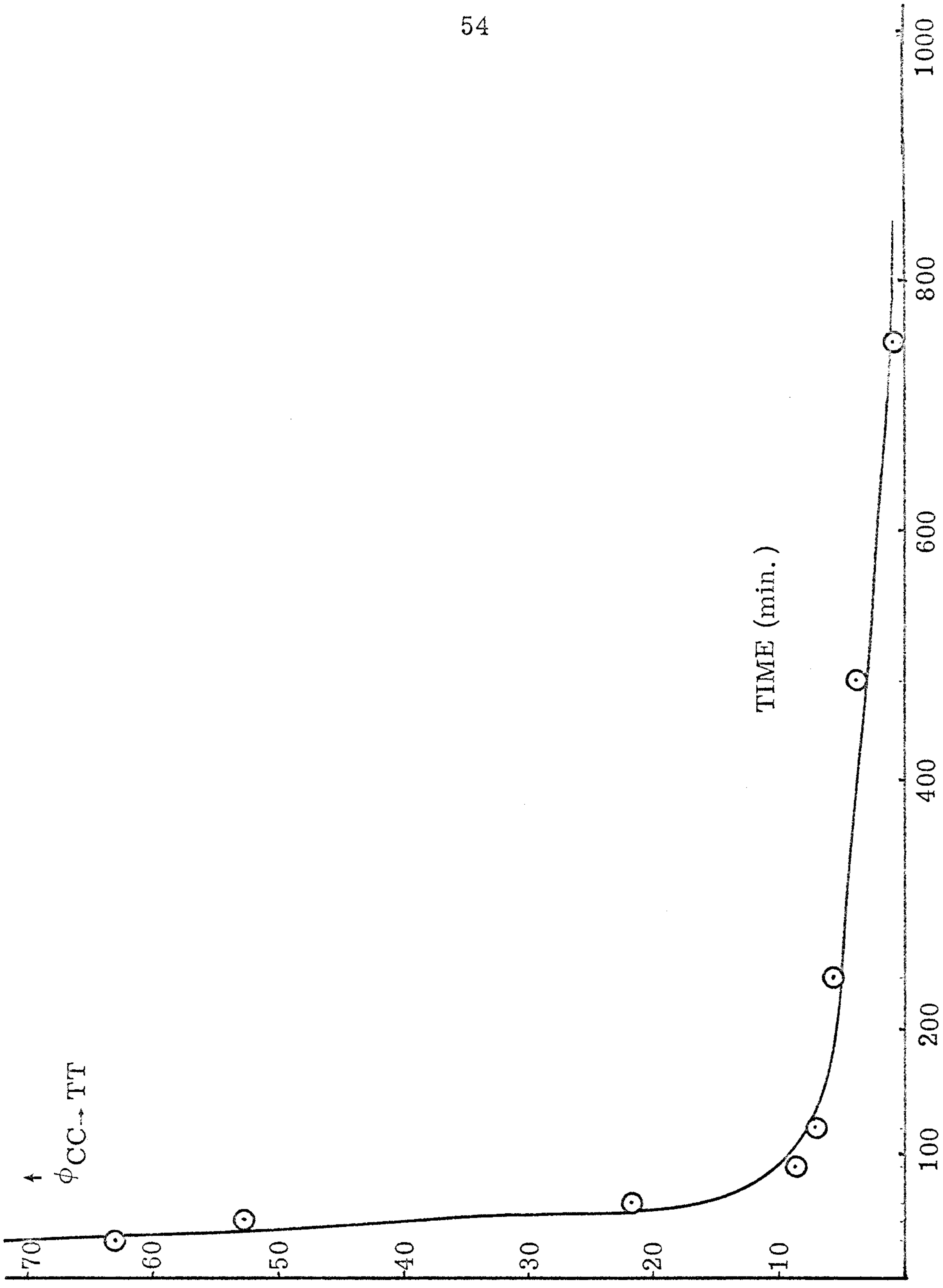

Figure 17. Quantum yield as a function of irradiation time.

Table X. Quantum Yield as a Function of Time[a]

Irradiation time (minutes)	$\phi_{CC \rightarrow CT}$[b]
15	164.3 ± 0.0
30	61.78 ± 0.70
45	53.34 ± 2.34
60	21.65 ± 0.47
90	8.16 ± 0.71
120	7.17 ± 0.54
240	5.60 ± 0.00
480	3.84 ± 0.00
720	0.93 ± 0.00
1440	0.62 ± 0.00

[a] $[CC]_0 = 1.00$ M.

[b] Maximum percent conversion was 5.8%.

represent the same equilibrium mixture as in the thermal stationary state. This was based on the elementary principle that a catalyst affects only the rate of attainment of equilibrium and not the final position of the equilibrium, so that a photocatalyst (T_1 or T_2) should give the same equilibrium mixture as a thermal catalyst (iodine, for example). However, this problem was fairly easily solved when the quantum yield expressions in Figure 16 and the data in Table X were available, since they show that the catalytic effect, in essence, disappears as the product of the isomerization appears. This indicates that, long before the solutions have reached a photostationary state, the catalytic effect has disappeared and the quantum yields have become conventional ones (that is to say, less than unity).

In fact, the photostationary state can be calculated by the method used by Hammond _et_ _al._ (5) for the piperylene case if the lines in Figures 5-8 are carefully extrapolated to zero diene concentration. This intercept represents the point where the chain process is no longer possible and where a conventional mechanism must apply, thereby allowing calculation of the photostationary state. These extrapolations are shown in Figures 18-21, which are simply enlargements of the region around the origin in the corresponding Figures 5-8. It should be noted, first, that the points shown in the following figures are taken from the corresponding lines in the larger scale figures and are not data given in Table V; and, second, that the extrapolations are done by eye, and the inherent errors of the "eyeball" method must be considered. It is not the particular intent to emphasize how well the calculated and observed values agree, although they do agree rather well, but what is intended is to show that it is quite clear that the thermal and photostationary states need not agree, and that the photostationary state obtained is a very normal one. The various quantum yields at zero diene concentration are summarized in Table XI.

Figure 18. Extrapolation of $\phi_{TT\rightarrow CT}$ to zero diene concentration.

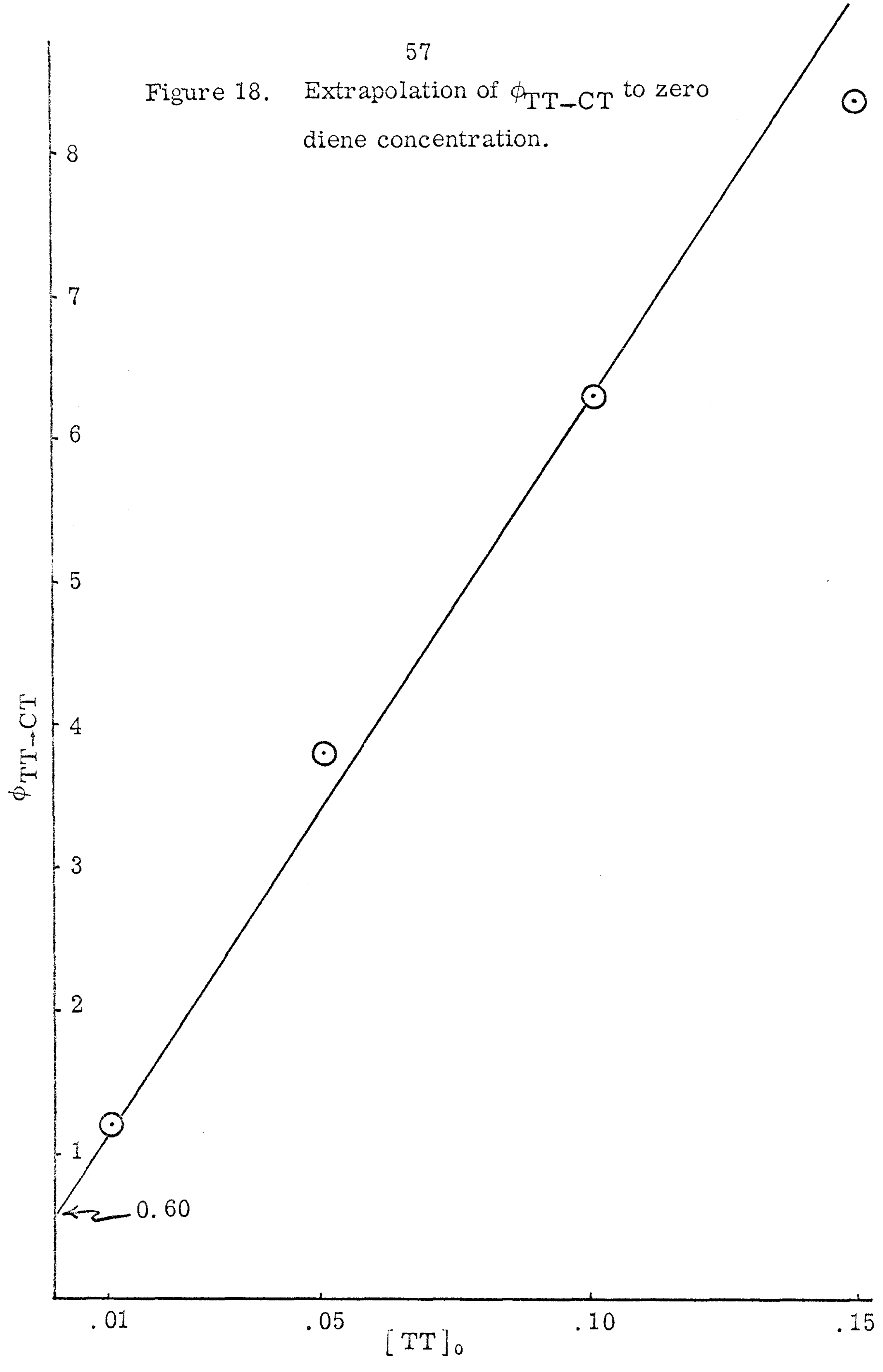

Figure 19. Extrapolation of $\phi_{CT\rightarrow TT}$ to zero diene concentration.

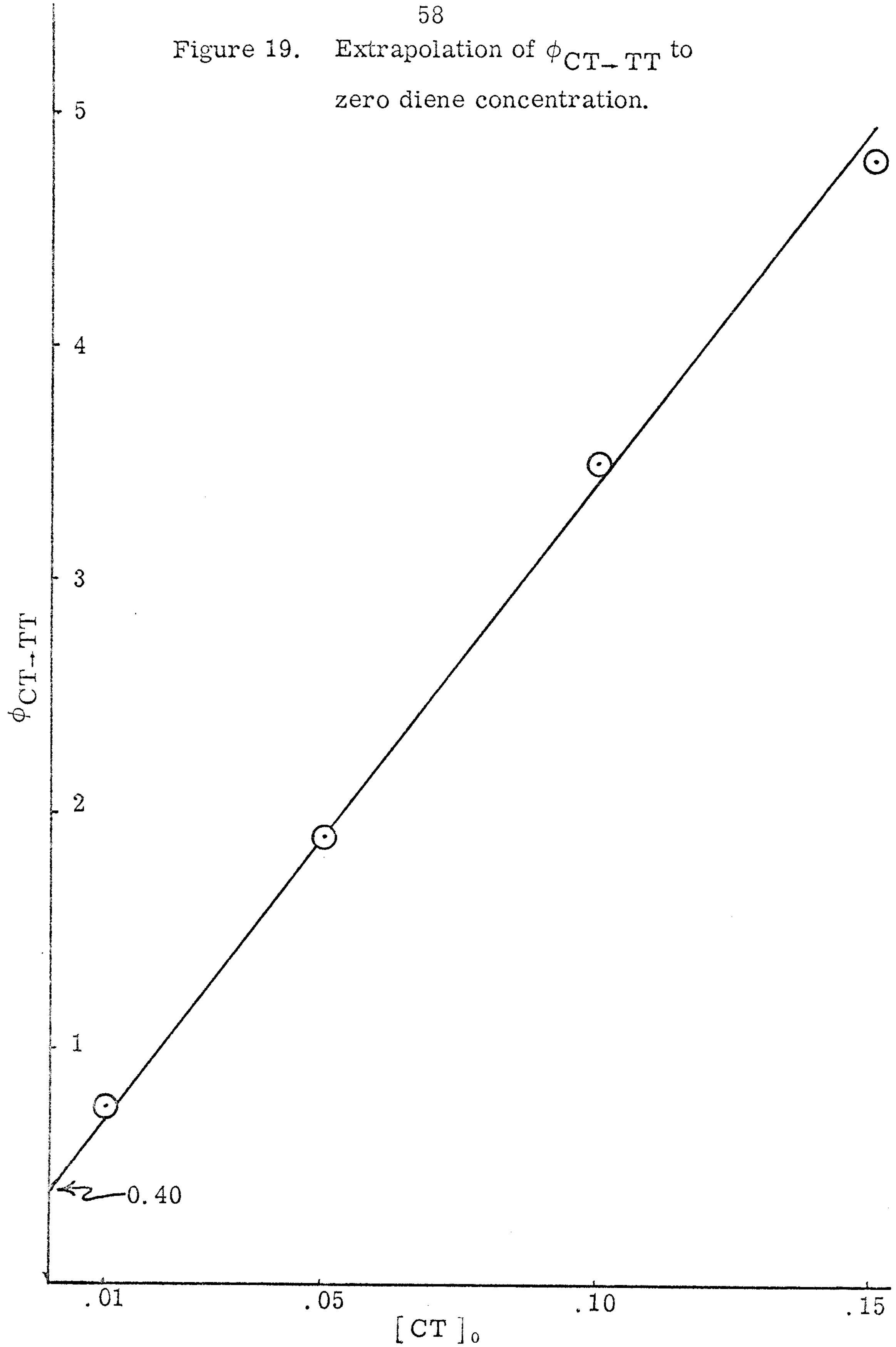

Figure 20. Extrapolation of $\phi_{CT\rightarrow CC}$ to zero diene concentration.

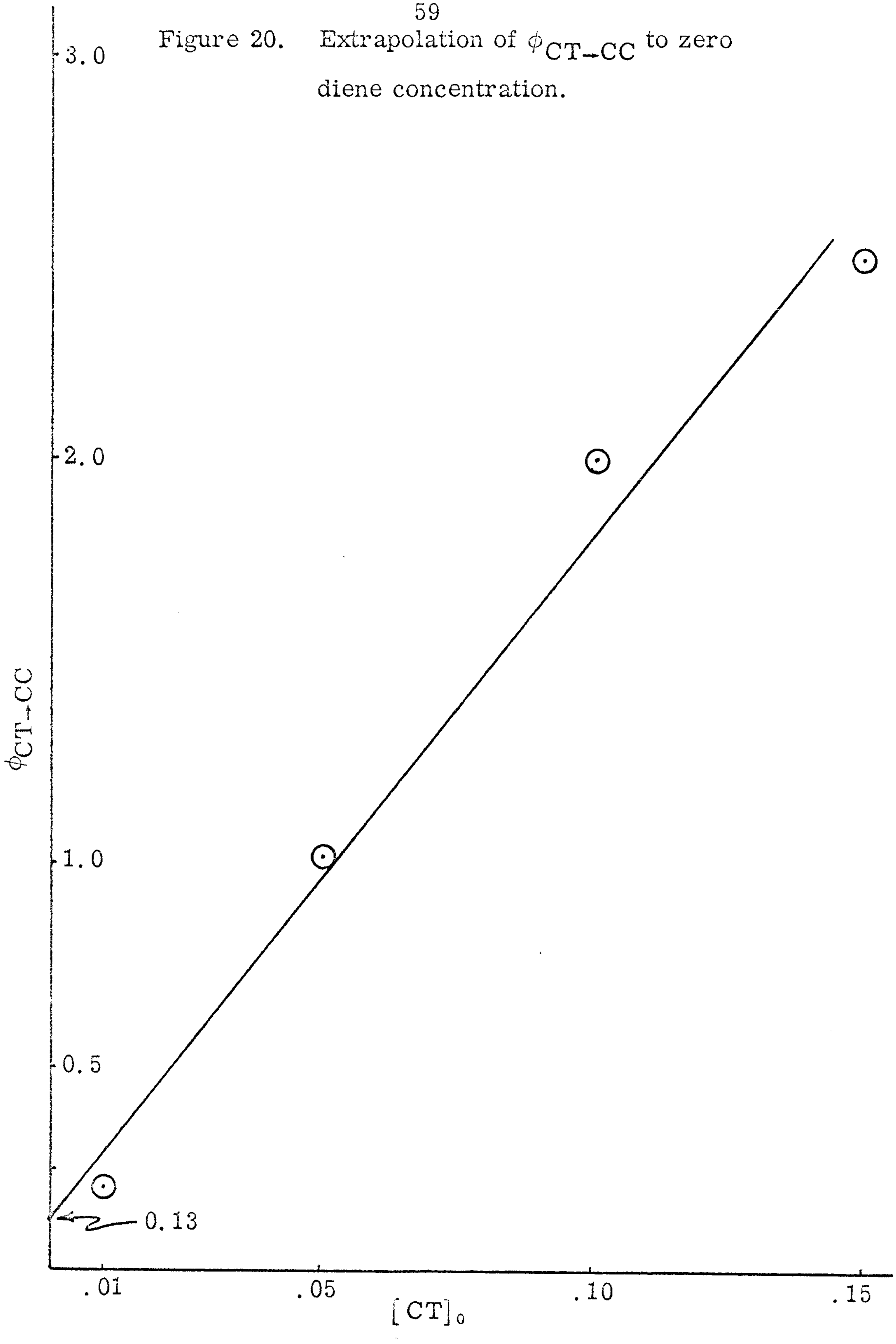

Figure 21. Extrapolation of $\phi_{CC \to CT}$ to zero diene concentration

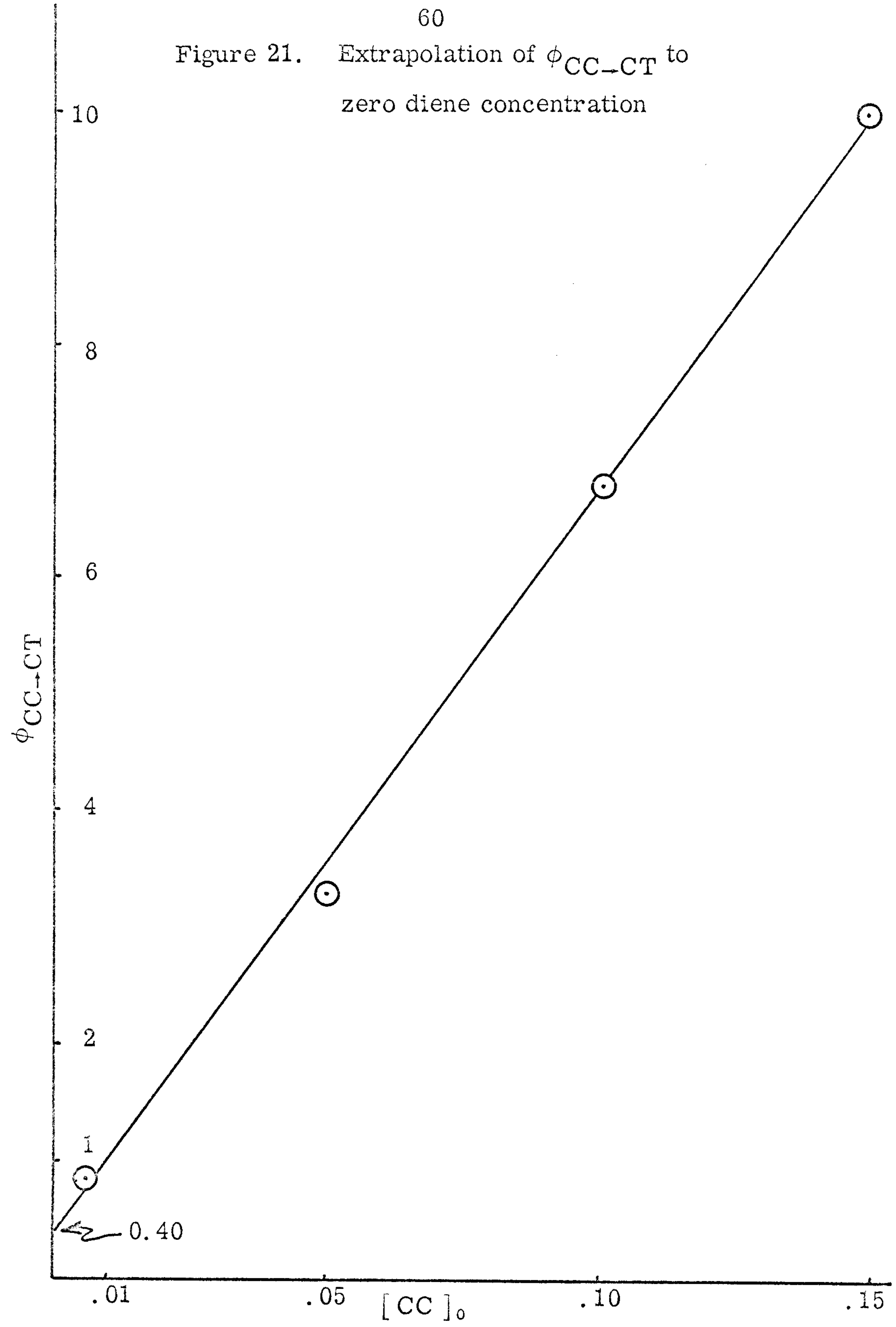

Table XI. Summary of Quantum Yields at Zero Diene Concentration

$$\phi_{TT \rightarrow CT} = 0.60$$

$$\phi_{CT \rightarrow TT} = 0.40$$

$$\phi_{CT \rightarrow CC} = 0.13$$

$$\phi_{CC \rightarrow CT} = 0.40$$

The photostationary state may be calculated by considering the equilibrium as follows:

$$\mathrm{TT} \underset{k_y}{\overset{k_x}{\rightleftharpoons}} \mathrm{CT} \underset{k_w}{\overset{k_z}{\rightleftharpoons}} \mathrm{CC}$$

where $k_x = \phi_{TT \rightarrow CT} = 0.60$

$k_y = \phi_{CT \rightarrow TT} = 0.40$

$k_z = \phi_{CT \rightarrow CC} = 0.13$

$k_w = \phi_{CC \rightarrow CT} = 0.40$

At equilibrium

$$k_x[TT] = k_y[CT]$$

$$k_z[CT] = k_w[CC]$$

$$[TT] + [CT] + [CC] = 1$$

Substituting the now known values of k_x, k_y, k_z, and k_w into the three equations and solving for the equilibrium concentration of diene isomers, the following values are obtained:

	Calculated	Observed
[CT]	0.50	0.503
[TT]	0.33	0.335
[CC]	0.17	0.162

Furthermore, one particular point is of great interest. Referring to Table XI, it can be seen the $\Sigma_\phi = 1.53$ which correlates well with the prediction, based on the idealized discussion, that for two different triplets the Σ_ϕ should equal 1^+ and fall presumably in the range of 1.2 to 1.5.

SUMMARY

Two possibilities for the geometrical configuration of the lowest excited triplet state of conjugated dienes have been suggested; and an empirical method for distinguishing between these two possibilities has been developed, based on the fact that the sums of the various quantum yields of the *cis*-*trans* photoisomerization processes should be different. However, when the quantum yields were measured, it was found that they were very high and did not fit either of the empirical explanations.

Evidence is presented which eliminates such factors as stray light, isomeric impurities, thermal catalysts, dimerization, and polymerization as causes of these high quantum yields, and which indicates that a quantum chain transfer process is the responsible factor. Concentration studies and quenching effects of piperylene and azulene seem to confirm this conclusion. Further evidence is presented which characterizes the nature of the chain propagating species as the diene triplet, and eliminates such possibilities as free radicals and surface catalytic effects.

Two mechanisms, one based on one geometrical configuration and one on the other, are discussed. Several experiments were conducted to provide evidence in support of a mechanism based on two different triplets. Quantum yield studies at low diene concentration carried to low conversion show that the processes *trans*, *trans*→*cis*, *cis* and *cis*, *cis*→*trans*, *trans* do not occur, thereby implying that a mechanism based on a single common triplet is not correct.

CONCLUSION

In conclusion, from the experimental results and discussion presented herein, it seems safe to state that the triplet state of the conjugated dienes is of the allyl-methylene type as pictured in Figure 1b. Apparently, the retention of the allyl resonance energy is a more significant factor than the increased electronic repulsion in this configuration. Furthermore, it is concluded that the very high initial quantum yields of isomerization encountered in this work are the result of a novel quantum chain-transfer mechanism in which the triplet state of the diene acts as the chain-propagating species, causing the photoisomerization of the diene without destruction of the triplet.

It is interesting to note, on this latter point, that Crandall and Mayer (22) in their recent work in the non-conjugated 1, 5, 9-cyclodecatriene system have speculated that "energy transfer from a relaxed triplet to generate the spectroscopic triplet of a second double bond is expected to be appreciably endothermic (~ 20 kcal/mole)... Consequently, such a transformation is not likely. However, a non-vertical transfer of triplet energy would be approximately isoenergetic and the intramolecular nature of the transfer could result in an enhanced probability over that of the inefficient intermolecular counterpart. Such an energy migration would have the interesting result of causing olefin isomerization without triplet destruction." Although their system is somewhat different (being cyclic and nonconjugated) and they reject this explanation as not being applicable, the mere fact that they have indulged in speculation along these lines is interesting and somewhat gratifying.

Of course, several questions remain as yet unanswered. For example, what other effects might one expect to see as a result of this quantum chain-transfer mechanism? Indeed, exactly what property of the 2, 4-hexadiene molecule is it that allows, or causes, this type of process and which the piperylene and stilbene molecules apparently do not have? What other systems might one expect to show this same type of behavior? Any of these might be considered the basis for future work.

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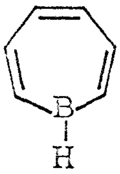
PROPOSITIONS

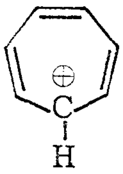
PROPOSITION I

It is proposed that product and mechanistic studies be conducted on the photolysis of B-phenyl-3-benzoborepin to determine whether it behaves similarly to an aromatic hydrocarbon or undergoes photolytic decomposition as do other triarylborons.

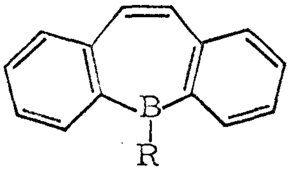
Hückel's (4n + 2)π-electron rule predicts that borepin (I), which is isoelectronic with the tropylium ion (II), will be aromatic. However, all attempts to prepare borepin have reportedly failed (1). The dibenzo derivative (III) was synthesized by van Tamelen et al. (2), and recently the synthesis of B-phenyl-3-benzoborepin (IV) was reported (1). It would be interesting to see if these compounds display photochemical behavior similar to that of aromatic hydrocarbons or whether they behave more like the triarylboron analogs such as triphenylboron. It is proposed that product and mechanistic studies be conducted on the photolysis of these unique aromatic compounds.



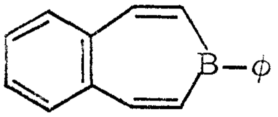
I



II



III



IV

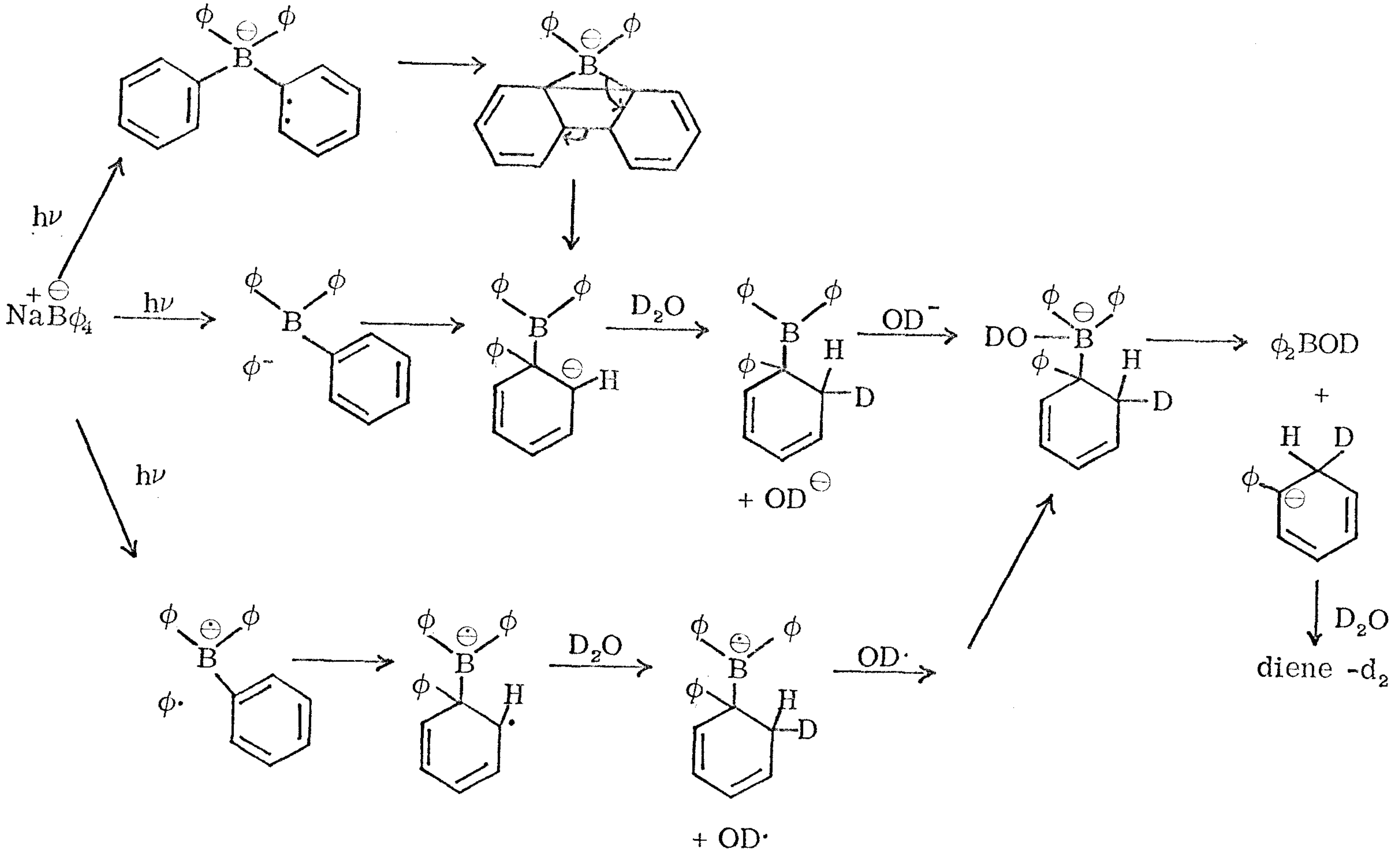
The photochemistry of aromatic hydrocarbon in solutions has been extensively studied and explained in terms of fluorescence, dimerization, photo-oxidation processes, etc. (3). In solution at low concentration, high fluorescence yields are common. In higher concentration ranges, dimerization may occur. Photodecomposition modes of the aromatic molecules occur only with low quantum efficiencies, $\phi = 0.01\text{-}0.0001$ or less.

The type of behavior that might be expected of the borepin (IV), if it exhibits behavior similar to other triarylborons, is that of a relatively efficient photodecomposition process as compared to no photodecomposition of the aromatic hydrocarbon analogs. The photodecomposition of triphenylboron and its complexes with irradiation of 2537 Å wavelength has been reported by Williams et al. (4, 5).

They observe that the quantum yield of decomposition of sodium tetraphenylborate in water is 0.22 to 0.26 at 2537 Å. The products which result in excess of 0.5% are biphenyl, 1-phenyl-1,4-cyclohexadiene, 3-phenyl-1,4-cyclohexadiene, and 1-phenyl-1,3-cyclohexadiene. In the presence of oxygen, biphenyl is the principal product, whereas, in its absence, 1-phenyl-1,4-cyclohexadiene predominates. They also report that the photochemical reaction leading to these products was found to be intramolecular by use of substituents and deuterium tagging.

Except for the determination of the intramolecular nature of the process, no work has been reported on the investigation of the mechanism of this photodecomposition although the mechanism on the following page has been suggested (5). As a further part of this work, the following experiment could provide some insight as to the nature of the mechanism.

If the photolysis were carried out in CH_3OD, the borepin (IV) should yield dihydronaphthalene-d_1 if a radical anion mechanism of the type suggested by Williams pertains. In addition, the boron-containing product in this case would be hydroxymethyl-diphenylboron which is likely to be rapidly oxidized by air. On the other hand, if the suggested anionic mechanism is operating, the diene product should be


NaBφ4
hν
hν
hν
φ⁻
φ·
D2O
D2O
+ OD⊖
+ OD·
OD⁻
OD·
DO
φ2BOD
+
D2O
diene -d2

dihydronaphthalene-d_2 and the relatively stable methyl ester of diphenylborinic acid. Mass spectral analysis should distinguish to two dienes and the methyl diphenylborinate could probably be isolated if it is produced.

The third mechanism suggested by Williams involves cycloaddition of the excited singlet of the tetraarylboron followed by electron migration. This mechanism, however, could still not be differentiated by studying the photolysis in CH_3OD.

Another factor which might be investigated in this system is sensitization of either type of photochemical behavior, although it might prove difficult to find a suitable sensitizer. Another feature which could be studied is the possible dependence on solvent of the type of photochemical behavior, which has an analogy in the triphenylboron case.

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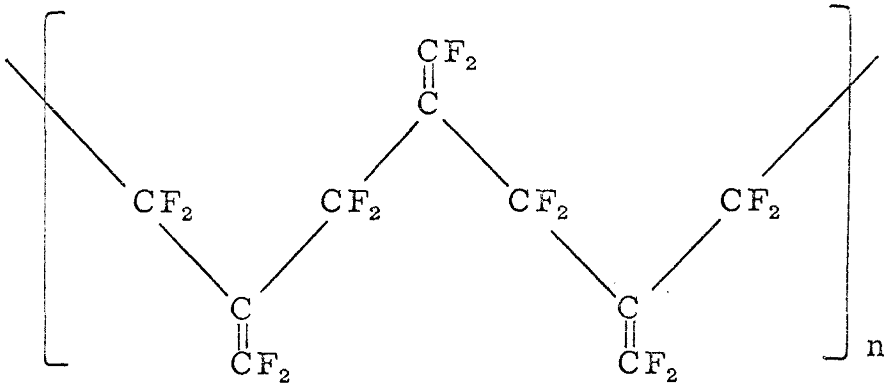
PROPOSITION II

It is proposed that tetrafluoroallene could be polymerized to provide a fluorocarbon polymer with properties similar to those of polytetrafluoroethylene and, in addition, have the potential of being very highly cross-linked without loss of its fluorocarbon properties.

Tetrafluoroallene has been synthesized and polymerized by Jacobs and Bauer (1). The structure of the polymer has been shown (2) by X-ray methods to be the following:



Of course, polytetrafluoroethylene, Teflon (or Fluon), and its many applications are well-known. These fluorocarbon polymers are not attacked by any known organic solvents or plasticizers even at high temperatures. Only molten alkali metals affect them, apparently forming carbon and alkali fluoride. Halogens are absorbed to some extent, and at high pressures polytetrafluoroethylene is attacked by fluorine. It is non-flammable and practically unaffected by water. It is incompatible with not only plasticizers and other high polymers but even with some low polymeric tetrafluoroethylene waxes and liquids. Polytetrafluoroethylene is very stable to heat. Chain cracking is important only over 400° C. Even at -100° C the polymer fibers remain flexible. The table (4) lists some of the most important properties of tetrafluoroethylene polymers. In their electrical properties, these polymers excel those of most other organic insulation products. Their quenched films are transparent to ultraviolet light in

TABLE

Specific gravity	2.2-2.3
Refractive index	1.37-1.38
Shore hardness (D)	55-65
Tensile strength, psi	3,500-4,500
Flexural strength, psi	2,000

Heat distortion (A.S.T.M. D6486-44T), °C	130
Specific heat, cal/g/°C	0.25
Coefficient of expansion per °C	1.0×10^{-4}
Brittle point	Below -80°C
Water absorption, %	0.0

Thermal conductivity (0.46 cm), cal/cm^2/hr/°C/cm	2.1
Impact strength (Izod), ft-lb/in. of notch	
at -57°C	2.0
at 25°C	4.0
at 77°C	6.0
Dielectric constant (60 to 3×10^9 cycles)	2.0-2.05
Power factor (60 to 3×10^9 cycles)	Below 0.0002
Dielectric strength (short time, 0.005 in.), volts/mil	1,500*
Arc resistance (A.S.T.M. D495-42), sec	More than 700
Volume resistivity, ohm-cm	$>10^{14}$
Surface resistivity (50% relative humidity), ohms	3.5×10^{13}

*Polytetrafluoroethylene shows lower values of dielectric strength in longer tests or after aging in service. The electric loss factor is one of the lowest known for solids.

the 2000-4000 Å region.

One disadvantage which these polymers have is that they themselves cannot be cross-linked, probably because of the strength of the C—F bond which has been estimated at 120 kcal/mole. Of course, they can be cross-linked by copolymerization with other vinyl-type monomers which are capable of cross-linking. However, the addition of these cross-linking monomers gives more casting defects such as bubbles and sheets of poorer impact strength (3). Also, of course, an obvious disadvantage of cross-linking polytetrafluoroethylene by copolymerization with other monomers is that, in most cases, the more highly cross-linked the product is, the more co-monomer must be present, and the less fluorocarbon-like is the final product.

It is suggested that polytetrafluoroallene could be produced commercially, by methods similar to those for the polytetrafluoroethylene polymers, as a useful polymer which should have many, if not all, of the properties of Teflon. In addition, it has the potential of being extremely highly cross-linked without loss of its fluorocarbon properties and of being tougher and more heat stable. It might be mentioned that the polymer prepared by thermal polymerization (with no cross-linking) was stable to 700° C without significant production of monomer. It is also perhaps possible that the remaining points of unsaturation could be used in dyeing the product.

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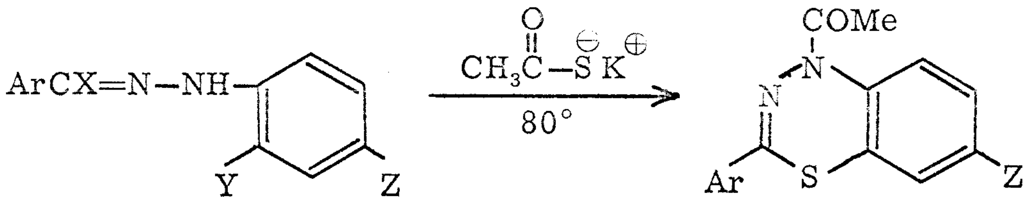
PROPOSITION III

It is proposed that a mechanistic study be conducted on the reaction for the formation of 1, 3, 4-benzothiadiazine derivatives from cyclization of the corresponding hydrazidic halides with thioacetate.

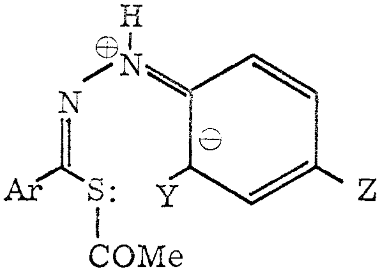
Recently Barnish and Gibson, in a very brief communication (1), reported the rather novel synthesis of a 1, 3, 4-benzothiadiazine derivative via the following reaction:



where X = Cl, Br
Y = F, Br
Z = F, Cl, Br

It is proposed that the mechanism of this reaction be more fully investigated.

One possible mechanism is that shown in Figure 1. It would seem reasonable to expect that the attack (step 3) of the nucleophile on the unactivated ring position at Y to be the slowest, and therefore rate-determining, step. If the following resonance structure is to be considered important,



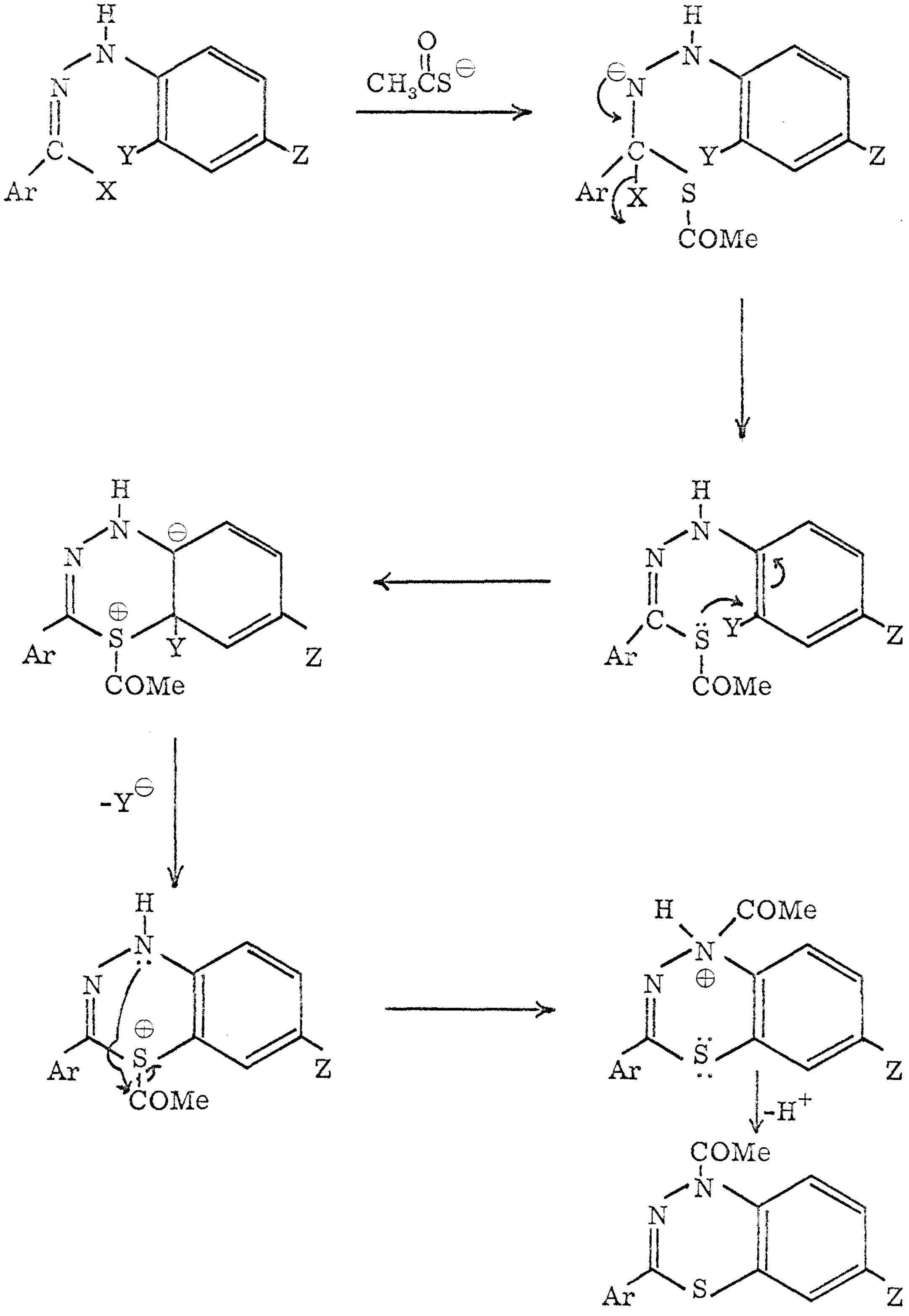


Figure 1.

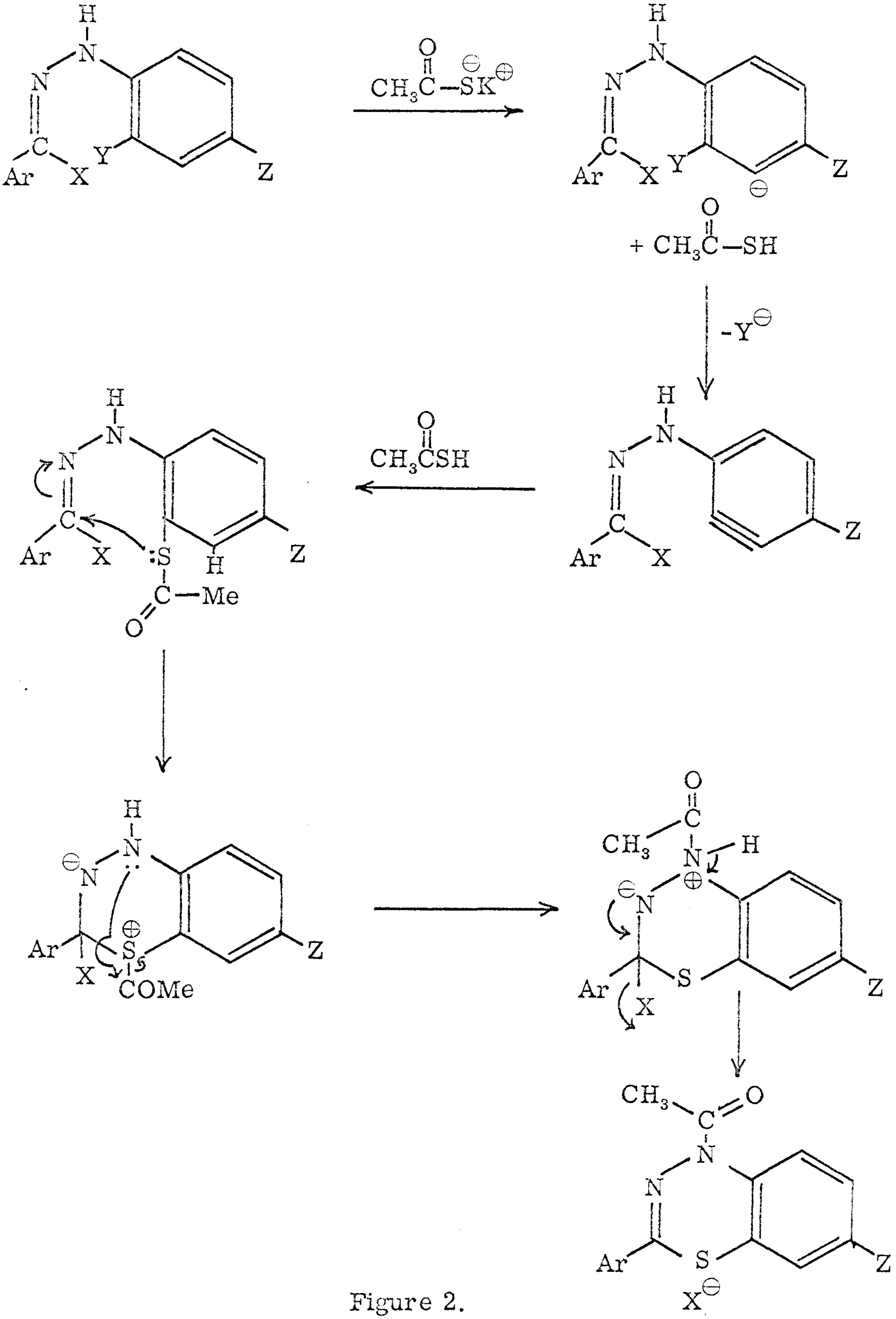
this position should be somewhat deactivated for nucleophilic attack in this manner. If step 3 is the rate-determining step, this could be determined by the fact that electron-withdrawing substituents (para to Y) should increase the rate of product formation while electron-donating substituents in that position should decrease the rate. If elimination of halide (step 4) or intramolecular acyl transfer (step 5) is rate-determining, convenient tests as in the other cases are not so readily available. Addition of excess halide could possibly yield some information if the rate were decreased. Because of the gain in aromatic resonance stabilization, elimination of Y^- is expected to be relatively fast.

One other experiment which could be done is to sterically block the acyl transfer step by substitution of a bulky group on the nitrogen alpha to the substituted phenyl ring. The sulfonium salt could possibly be isolated if the acyl transfer were not concerted with the attack by sulfur on the C—Y bond. If the acyl transfer and sulfur attack are concerted, then the reaction would most likely stop with the elimination of X^- when the transfer step is blocked by a substituent on nitrogen.

Another feature of the mechanism which should be verified is the nature of the S→N acyl transfer. In Figure 1, it is represented as an intramolecular transfer, although the acyl group could be transferred in an intermolecular solvolysis catalyzed by the basic amino group in a second molecule. If this were the case, then another appropriate amine, present as a solvent or cosolvent, should also cause the solvolysis and thus intercept the acyl group. Furthermore, if the acyl transfer were both intermolecular and rate-determining, the rate should depend on the square of the concentration of starting material.

Another factor which could be considered in deciding if step 3 is rate-determining is that a better nucleophile than bivalent sulfur should show an increased rate under the same conditions. Conversely, a weaker nucleophile should show a decreased rate. This might be accomplished by the use of acetate rather than thioacetate anion. It would seem then that acetate should cause a decreased rate because it is a weaker nucleophile than thioacetate since oxygen is less polarizable than sulfur. However, it is possible that development of a full positive charge on oxygen under these conditions might be avoided by forcing the acyl transfer to occur concertedly (and presumably intramolecularly) with the attack of the acetate oxygen on the phenyl ring.

Another conceivable, although less reasonable, mechanism of a somewhat different type is that shown in Figure 2. This mechanism involves the abstraction of the acidic (2, 3) proton located between substituents Y and Z. Clearly, to verify this mechanism it should be determined whether thioacetate anion is a strong enough base to abstract that proton. This could be accomplished by determining the rate of proton exchange in the various m-dihalobenzenes in D_2O in the presence of thioacetate. Shatenshteǐn (2) reports that the <u>ortho</u> hydrogen in fluorobenzene is about 10^6 times more easily



H
N
N
C
Ar
X
Y
Z
$CH_3C(=O)-S^{\ominus}K^{\oplus}$
+ $CH_3C(=O)-SH$
$-Y^{\ominus}$
$CH_3C(=O)SH$
S
C
Me
O
H
COMe
CH_3
X$^{\ominus}$

Figure 2.

abstracted by KNH_2 in NH_3 than is the hydrogen in benzene. The *ortho* proton in *meta*-difluorobenzene should be an estimated 10^{10}-10^{11} times more easily abstracted. However, as the fluorine atoms are replaced by the other halogens, the acidity of this proton decreases rapidly and it is rather doubtful that thioacetate could abstract the proton when neither Y nor Z was fluorine.

Of course, the desirable thing for the anionic species, formed in the initial step, to do would be to eliminate Y^- and form the benzyne. However, that species could also eliminate Z^- and form the "wrong" benzyne species, which would not lead to the desired product. At this point, it should be mentioned that this process cannot be eliminated by the available data (1). No mass balance was made for the reaction and the reported yields of product were less than 50%. Therefore, it is possible that these products are being formed but are not isolated.

One of the methods of verifying the validity of this mechanism would be to alkylate the ring at the position between the halide substituents. This should block the hydrogen abstraction step and stop the reaction if this step is an important one in the overall mechanism. Also the same arguments about the inter- or intramolecular nature of the acyl transfer apply in this case.

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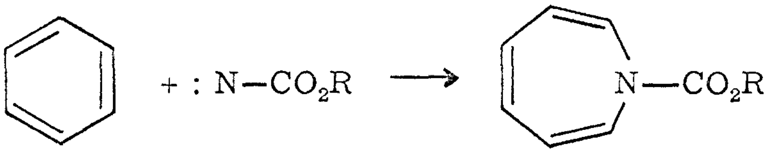
PROPOSITION IV

It is proposed that a study be made of the addition of carbethoxynitrene to thiophene.

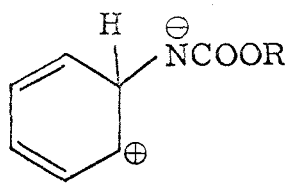
Thermal or photochemical decomposition of alkyl azidoformates causes these compounds to lose nitrogen and generate carbalkoxynitrenes, which may react with benzene nuclei to give N-carbalkoxyazepines (1-5).



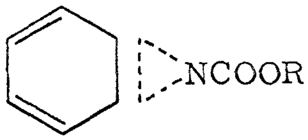
This reaction was used to synthesize the first parent azepine ring system (2).

Recently a study of this reaction was reported by Baldwin and Smith (6). In their study, they investigated the relative reactivity of carbethoxynitrene and carbethoxycarbene with mono-substituted benzenes. The relative rates of addition were found to correlate satisfactorily, using the Hammett equation and σ_p substituent constants. They report that the best linear least-squares fit of log k_{rel} with σ_p were found to be log $k_{rel} = 0.052 - 1.32\ \sigma_p$ for the carbethoxynitrene reactions and log $k_{rel} = -0.033 - 0.38\ \sigma_p$ for the carbethoxycarbene reactions.

From the observed substituent effects ($p = -0.38$ for the carbethoxycarbene and $p = -1.32$ for the carbethoxynitrene), they conclude that the intermediates are electrophilic, and that the carbethoxynitrene is by far the more discriminate in the selection of its substrates in a competitive situation. Furthermore, they conclude that the activated complex is not an ionic one such as (I) where direct substituent resonance effects could operate to stabilize the positive



(I)

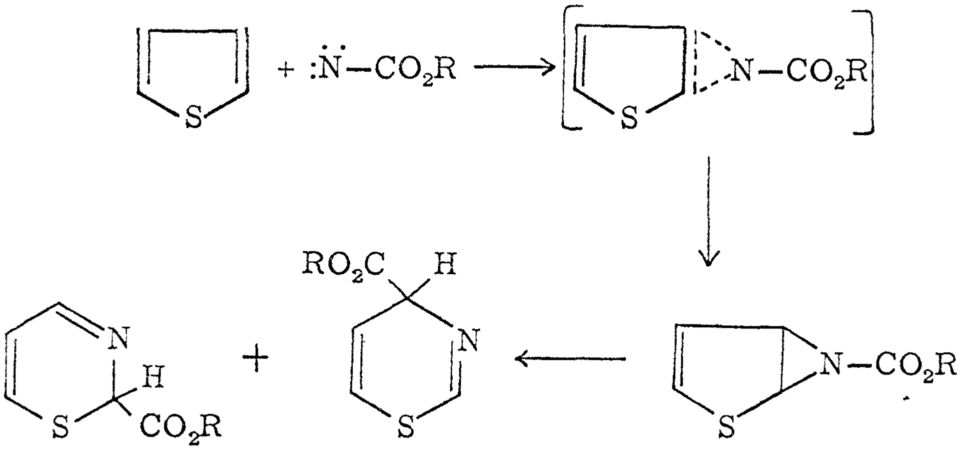


(II)

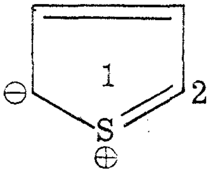
charge in the aromatic position; in a concerted process with an intermediate such as (II), substituents could not. Since the reactions are observed to be much less sensitive to substituent effects than other electrophilic aromatic substitution reactions, Baldwin and Smith suggest the intermediate (II) as representing the activated complex in a concerted cycloaddition reaction. They add that, of course, these latter conclusions are based on the assumptions that (I) or (II) is a fair model of the activated complex in these reactions and that data from aromatic substitution reactions may serve as a valid criterion of what comprises a "large" substituent effect.

With this background on the reaction of carbethoxynitrene with aromatic hydrocarbons, it is proposed that a study be made of the products of the reaction of carbethoxynitrene with the heteroatomic aromatic compound, thiophene, in order to determine what effect the introduction of a heteroatom into the aromatic ring might have on the course of the reaction. In this case, as in others (6), insertion of the nitrene into the aromatic C—H bonds is anticipated to be of negligible importance.

In the reaction of carbethoxynitrene with thiophene, several products are possible because of the positional labeling caused by the sulfur atom. These products could be formed via a cyclic intermediate in the following way:

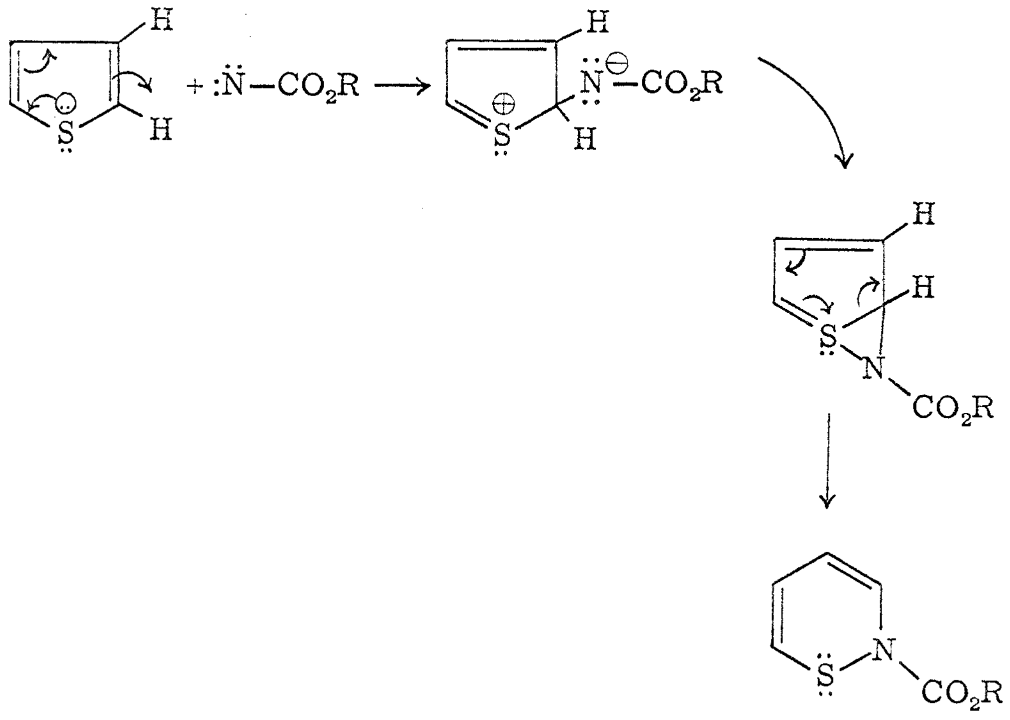


It is also possible, although not very probable, that the carbethoxynitrene could attack in a similar manner at the 1, 2 or 3, 4 bond of thiophene. However, this requires that the nitrene intercept the resonance form of thiophene shown below.



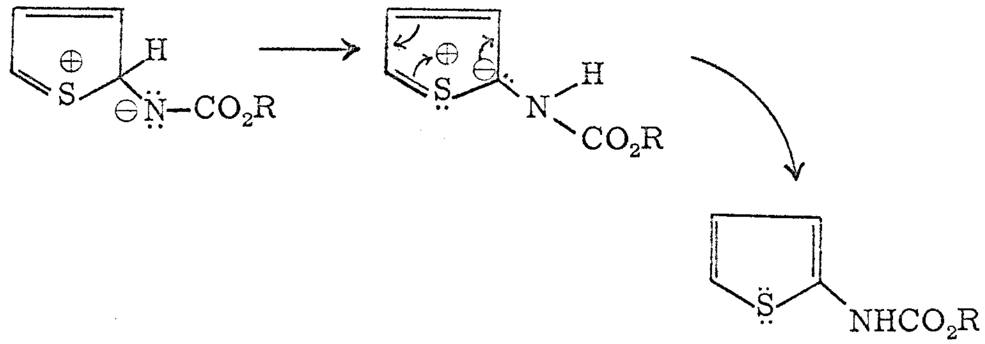
This resonance form of thiophene is not considered to be a very important one because of the charge separation, and the nitrene may well be selective enough in its attack to react only at the 2, 3-bond. Furthermore, if such a resonance form were involved, it seems much more likely that the electrophilic nitrene should attack the anionic electron density in the 5 position rather than the π-electron density of the 1,2 or 3,4 double bond.

If the nitrene does react via an ionic intermediate, it could do so either by attack on an ionic resonance form of thiophene or by the more likely route of attack on the predominant resonance form causing rearrangement of electron density during the attack (rather than before the attack as with the ionic resonance form). But this is merely a matter of timing, and the products are the same in either case.



Because of the greater stability of the sulfonium ion intermediate as compared to the analogous carbonium ion intermediate, it is expected that the ionic pathway may be more important in the reaction with thiophene than with benzene (6).

The ionic intermediate could also undergo a 1, 2 proton transfer as shown below.



However this, of course, amounts to the insertion of the nitrene into an aromatic C—H bond, which by analogy with the benzene case is not expected to be an important reaction. If it were observed, however, the above would certainly be a possible mechanism to account for the process.

It can be seen that the two different mechanisms should lead to different products. The cyclic mechanism leads to the 1, 3-thiazine series, while the ionic mechanism should give the 1, 2-thiazines. It should be mentioned that an ionic mechanism could also give 1, 3-thiazine products by interaction with a carbonium ion formed at the C_3-position, although studies of 3-substituted thiophenes reveal that they are relatively unstable toward the formation of a carbonium ion in the 3-position (7). Under the circumstances, this may cause some, but relatively little, side reaction. Furthermore, the formation of these products could provide easy access to these relatively little known compounds, which with the carbethoxy substituent could perhaps be useful synthetic intermediates.

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PROPOSITION V

It is proposed that the photochemistry of a series of five-membered heterocyclic aromatic compounds (such as thiazole, oxazole, and furan) be investigated in order to possibly provide more evidence on known photorearrangements of this type of molecule.

It is proposed that the photochemistry of a series of 5-membered heterocyclic compounds, such as thiazole, oxazole, and furan, be investigated in order to possibly provide more evidence on known rearrangements of this type of molecule and to look for possible new types of processes that these compounds might undergo as a result of the presence of a second heteroatom.

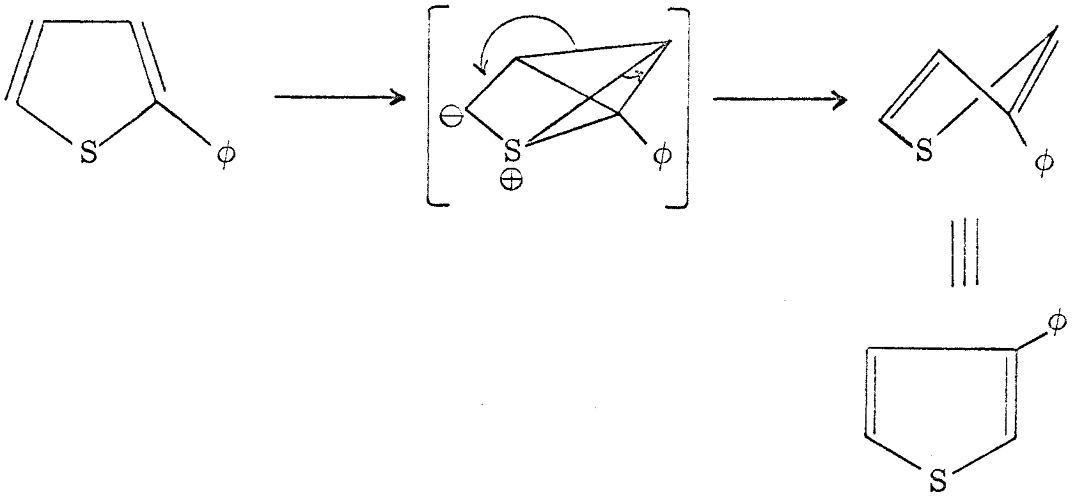
The only extensive study which has been reported in this particular area of photochemistry is a recent series of articles by Wynberg et al. (1-4) on the photochemical rearrangements of arylthiophenes. They report that, under the influence of ultraviolet light, arylthiophenes undergo rearrangements which are seemingly unprecedented in the area of thermal reactions. The conclusions that they draw from their investigation are the following:

1. Rearrangement must involve a photoreorganization of the thiophene ring with rebonding of the carbon and sulfur atoms. This was confirmed by ^{14}C labeling experiments with 2-phenylthiophene.
2. 2-Arylthiophenes rearrange irreversibly to 3-arylthiophenes and do not form any other detectable products.
3. In the phenylthiophenes, rearrangement is confined to the thiophene ring and no rearrangement occurs in the aryl substituent.

4. The major path of photorearrangement of phenyl-, deuterio-, and methyl-substituted 2-phenylthiophenes involves an interchange of the C_2—C_3 carbon atoms without concomitant inversion of the C_4-C_5 carbon atoms.
5. Phenyl-, deuterio-, and methyl-substituted 3-phenylthophenes exhibit considerable specificity or rearrangement.

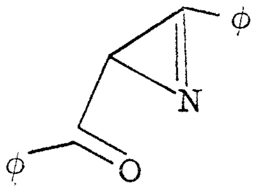
In addition to the above work, Ullman and Singh (5) have reported the rearrangement of 3, 5-diphenylisoxazole to 2, 5-diphenyloxazole. Here also the result is inversion of the 2 and 3 positions of the isoxazole ring without reversal of the 4 and 5 positions. Similar results have been reported by Tiefenthaler et al. (6) for the indazole-benzimidazole and pyrazole-imidazole systems. Eğe (10) has reported a similar rearrangement in the non-aromatic pyrazolone system. In the six-membered heterocycles Lahmani and Ivanoff (11) have recently reported the conversion of 1, 2-pyrazine to the 1, 3-pyrazine isomer via a benzvalene type of intermediate. However, no report has yet been made of studies of arylthiazole, aryloxazole, or arylfuran. It is suggested that the photochemistry of these systems be investigated.

The mechanism of the observed photorearrangement proposed by Wynberg (4) on the basis of his results is the following:



This mechanism invokes the valence shell expansion of the sulfur atom and the interaction of the sulfur 3d orbitals with the presumably more activated C_2—C_3 carbons.

In the isoxazole case, an intermediate analogous to the one in the thiophene case would be more highly energetic and less likely to occur. Ullman and Singh, in their work, isolated an aziridine molecule which they established to be the intermediate in the isoxazole-oxazole conversion.

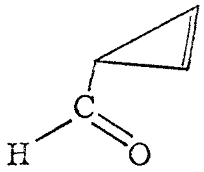


The work by Wynberg substantiates this type of intermediate if it is assumed that the relatively unstable thioaldehyde supposedly formed in that case can be stabilized by the interaction of the C_2-C_3 double bond with the d orbitals of sulfur. Of course, the oxygen aldehyde (or ketone) is more stable and the oxygen atom has no empty d orbitals so that such an interaction need not be invoked and the slightly different intermediate might well be expected .

However, one important difference can be noted. In the arylthiophenes, the isomer substituted in the 3 position is the more photolytically stable one. In the arylisoxazoles, the photolytically stable isomer is the one with the aryl substituent in the 2 position (i. e. , the oxazole derivative). It is not clear from these studies whether the factor causing this contrast is the introduction of a nitrogen atom into the ring system or the substitution of an oxygen atom for the sulfur atom.

The results of the proposed studies could provide important evidence on this matter. Comparison of the results of arylthiophene photolysis with those of arylfuran photolysis should isolate the effect of the substitution of oxygen for sulfur. Comparison of arylthiophene photolysis with that of arylthiazole should isolate the effect of the introduction of a nitrogen atom into the ring.

Difficulties might be expected in photolysis of arylfuran since photolysis of furan in the vapor phase with $Hg(^3P_1)$ sensitization is reported (7, 8) to undergo entirely different photochemistry than that reported above. Two points on this matter, however, are worthy of note. First, Srinivasan (7) presented evidence for the production of a cyclopropene intermediate



analogous to those reported by Ullman and Wynberg in their systems. Second, he (8) reports that none of the products produced in the gas phase photolysis were produced by direct irradiation of furan in solution. No mention is made of what the products of such a liquid phase photolysis were, or even whether any products were formed. It is interesting to note that no products would be expected in the furan photolysis if the energy absorbed by furan were dissipated in the type of rearrangement which thiophene appears to undergo.

Baykin and Lutz (9) have reported the formation of a cyclopropyl ketone upon direct irradiation of 2, 3, 5, 5-tetraphenyl-4, 5-dihydrofuran, although no rearranged product was reported. In this case, the double bond is no longer available for any sort of interaction in the transition state or intermediates previously suggested by Wynberg and Ullman.

If these difficulties with the furan system should become too great, the effect of substituting oxygen for sulfur in the ring system could also be seen by comparing the photolysis of 3-arylisothiazole with that already reported by Ullman for the 3-arylisoxazole.

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