I. PHOTOCHEMICAL REACTIONS OF PHENYLCYCLOBUTADIENOQUINONE

II. THERMAL REACTIONS OF PHENYLCYCLOBUTADIENOQUINONE IN METHANOL

III. THE PHOTOCHEMICAL SYNTHESIS OF PHENANTHRENES

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The author is especially grateful to Dr. Dorothy A. Semenow for help with the preparation of this thesis.

ABSTRACT

PART I

PHOTOCHEMICAL REACTIONS OF PHENYLCYCLOBUTADIENOQUINONE

The photolysis of phenylcyclobutadienoquinone in methanol gave dimethyl phenylsuccinate and a compound, $C_{21}H_{16}O_5$, of unknown structure.

PART II

THERMAL REACTIONS OF PHENYLCYCLOBUTADIENOQUINONE IN METHANOL

The thermal reaction of phenylcyclobutadienoquinone with methanol in a stainless steel bomb gave 2,4-dimethoxy-3-phenylcyclobutenone, 3-phenyl-4-hydroxy-4-methoxy-2-butenoic acid lactone and dimethyl phenylsuccinate.

PART III

THE PHOTOCHEMICAL SYNTHESIS OF PHENANTHRENES

The photochemical reactions of tetraphenylethylene and _trans_-stilbene with dissolved oxygen in cyclohexane solutions gave 9,10-diphenylphenanthrene and phenanthrene, respectively.

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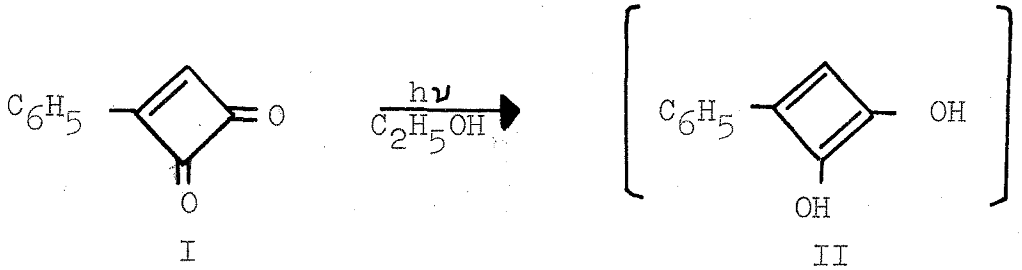
PART I

PHOTOCHEMICAL REACTIONS OF PHENYLCYCLOBUTADIENOQUINONE

INTRODUCTION

The photochemical reaction of phenylcyclobutadienoquinone (I) (1) in ethanol was carried out by Smutny (2) in an attempt to obtain evidence for the formation of the corresponding hydroquinone (II); such reduction products are typically formed by quinones under these conditions.

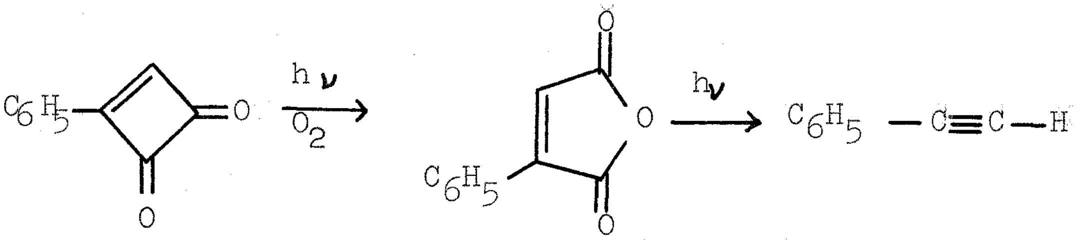


It was shown (2) that the quinone I underwent photolysis, but the products were not completely characterized.

The present work is a further study of the photolysis of the quinone I under various conditions.

RESULTS AND DISCUSSION

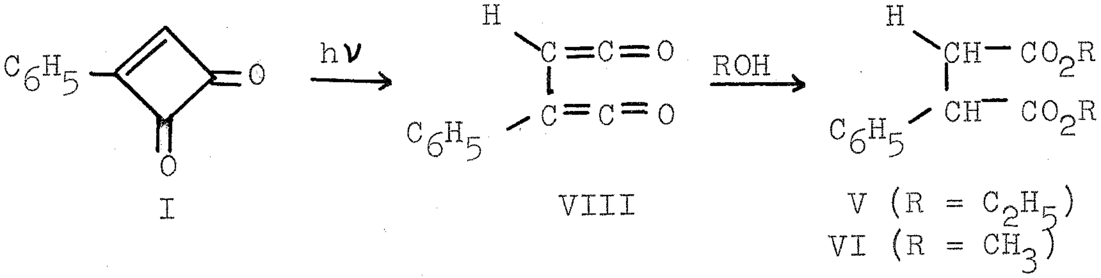
The photolysis of an extremely dilute (*ca.* 10^{-4} *M*) cyclohexane solution of phenylcyclobutadienoquinone (I) with a jacketless A-H4 mercury arc led to the formation of phenylacetylene (III) *via* phenylmaleic anhydride (IV). The presence of IV as an intermediate was indicated by ultraviolet spectra measured at intervals during the photolysis. This photochemical oxidation of I to phenylmaleic anhydride (IV) apparently involved dissolved atmospheric oxygen.



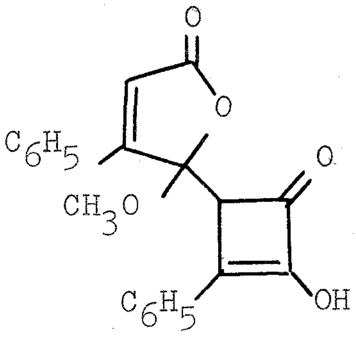
I IV III

The photolyses of alcoholic solutions of the quinone I were carried out at reflux to avoid reactions with dissolved oxygen and at higher concentrations (*ca.* 10^{-1} *M*) to allow isolation of the reaction products. The resinous product from the photolysis of I in ethanol was shown by its infrared spectrum to contain diethyl phenylsuccinate (V). The photolysis of I in methanol was investigated in greater detail; in addition to dimethyl phenylsuccinate (VI), which amounted to 15-25% of the product, there was obtained a white solid (VII), which analyzed for $C_{21}H_{16}O_5$ and amounted to 10-30% of the product. The remainder of the product consisted of dark-colored non-distillable material.

The formation of the diesters V and VI may have arisen from attack by the alcoholic solvent on an intermediate diketene (VIII) formed photochemically from the quinone I.

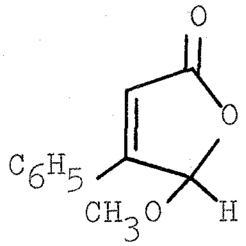


A structural representation of the photolysis product VII which is completely in accord with the experimental data has not yet been achieved. However, the best postulated structure, 3-phenyl-4-(2-phenyl-3-hydroxy-4-ketocyclobut-2-enyl)-4-hydroxy-4-methoxy-2-butenoic acid lactone (VII) is discussed to illustrate the type of problems involved. This structure is in agreement with the experi-

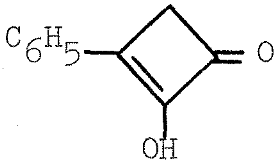


VII (?)

mentally determined molecular formula $C_{21}H_{16}O_5$ and the presence of one methoxyl group as indicated by a Zeisel determination. The observed ultraviolet spectrum with a broad absorption band in the region of 270-330 mμ (λ_{max} = 308.5 mμ, ϵ = 30,500) is, as expected for the structure VII, a composite of the spectra of 3-phenyl-4-hydroxy-4-methoxy-2-butenoic acid lactone (IX) (3) (λ_{max} = 276.5 mμ, ϵ = 20,000) and 2-hydroxy-3-phenylcyclobut-2-enone (X) (4) (λ_{max} = 308.5 mμ, ϵ = 20,000) (5). The infrared spectrum of the photolysis product VII showed peaks at 3140 cm.$^{-1}$ (OH stretch), 1742 cm.$^{-1}$ (carbonyl stretch), 1647 cm.$^{-1}$ (double bond stretch) and 1393 cm.$^{-1}$ (OH deformation) in agreement with the peaks observed (4) at 3200, 1745, 1653 and 1385 cm.$^{-1}$ for the hydroxyketone X. However, the validity of this comparison is limited since it was not possible to obtain the spectra in the same medium; the spectrum of VII was measured in a potassium bromide disc and that of X in chloroform solution. The spectrum of VII measured in a potassium bromide disc actually showed two peaks in the carbonyl region at 1769 and 1742 cm.$^{-1}$; however, in acetonitrile solution, the spectrum of VII



IX

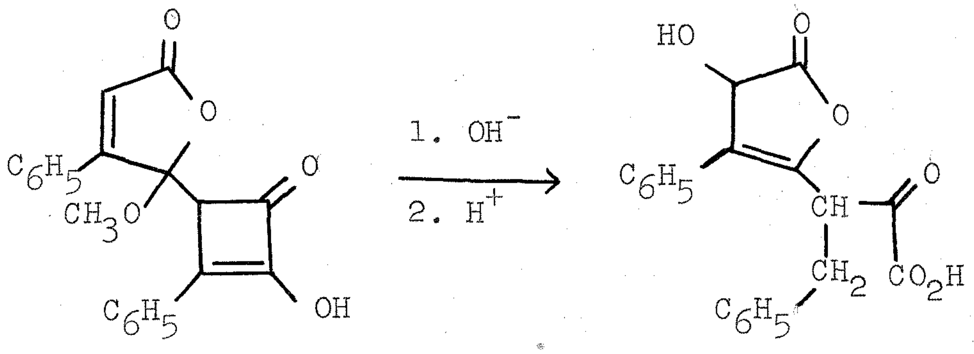


X

showed a single peak at 1769 cm.$^{-1}$ Hydrogen-bonding of some of the carbonyl groups in the crystal may account for the 1742 cm.$^{-1}$ frequency. The results obtained from qualitative tests on VII with potassium permanganate, bromine in carbon tetrachloride, ferric chloride and 2,4-dinitrophenylhydrazine are all consistent with the structure VII. The observed reaction with Tollens' reagent is expected for an α-hydroxyketone such as VII. The photolysis product was soluble in 5% aqueous sodium bicarbonate as expected for structure VII by analogy to the bicarbonate solubility of the hydroxyketone X.

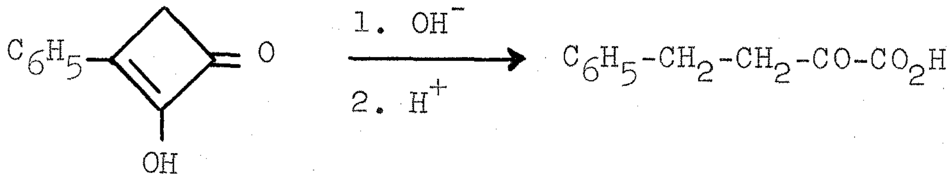
Hydrolysis of the photolysis product VII with aqueous 10% sodium hydroxide followed by acidification gave a crystalline solid (XI) which was shown by microanalysis and a Rast molecular weight determination to have the formula $C_{20}H_{16}O_6$. A Zeisel determination showed the molecule contained no methoxyl group.

No structure completely in accord with all the experimental evidence was realized; the least objectionable structure for XI is shown below.



VII (?) XI (?)

The opening of the four-membered ring in the structure VII to give a ketoacid as in XI is analogous to the formation of benzylpyruvic acid (XII) from the basic hydrolysis of the hydroxyketone X (5). The allylic rearrangement accompanying the hydrolysis of the methoxyl group in the structure VII is required to give a structure for XI which is not in serious disagreement with the observed spectral data. The ultraviolet spectrum of the hydrolysis product XI showed λ_{max} = 266 mμ , ϵ = 13,000, as expected for the structure XI by analogy to the spectrum (6) of propenylbenzene (XIII), λ_{max} = 245 mμ , ϵ = 12,600, with a shift of 21 mμ toward the visible as a result of the oxygen atom attached to the double bond. Such a shift is observed in the spectrum of the hydroxyketone X (λ_{max} = 308.5 mμ) compared to that of 3-phenylcyclobutenone (XIV) (λ_{max} = 286 mμ) (7). The highest-frequency carbonyl

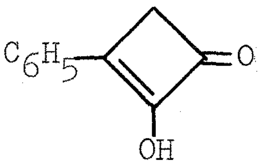


X

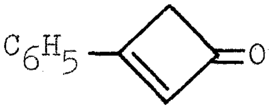
XII

C_6H_5-CH=CH-CH$_3$

XIII



X



XIV

peak at 1774 cm.$^{-1}$ observed in the infrared spectrum of the hydrolysis product XI both in a potassium bromide disc and in acetonitrile solution is attributed to the lactone carbonyl group in the structure XI. The potassium bromide disc spectrum showed a sharp hydroxyl peak at 3430 cm.$^{-1}$ and a broad hydroxyl peak at 3080 cm.$^{-1}$ attributable to the alcohol and carboxylic acid hydroxyl groups respectively, of the structure XI. The observed positive tests for unsaturation with potassium permanganate and with bromine in carbon tetrachloride, the formation of a precipitate with 2,4-dinitrophenylhydrazine, the solubility of XI in aqueous sodium bicarbonate and the reaction of XI with Tollens' reagent (characteristic of α-ketoacids) are all in accord with the structure XI. Titration of XI required two equivalents of base as would be expected for the structure XI; one equivalent would neutralize the carboxyl proton and the second would open the lactone ring.

A serious defect of the structure XI is that the ketone would be expected to enolize by analogy to phenylpyruvic acid (XV), which gives a strong green color with ferric chloride solution and shows a sharp hydroxyl peak at 3450 cm.$^{-1}$ in the infrared (5). The hydrolysis product XI gave no color with ferric chloride solution, and showed no ultraviolet absorption maximum above 300 mμ that would be expected for the conjugated system which would result from enolization.

$$C_6H_5\text{-}CH_2\text{-}CO\text{-}CO_2H \rightleftharpoons C_6H_5\text{-}CH{=}C(OH)\text{-}CO_2H$$

XV XV

Thus the proposed structure XI is probably incorrect, and the proposed structure VII for the photolysis product is not convincingly in accord with all of the experimental observations.

EXPERIMENTAL

All melting points and boiling points are not corrected. Analyses are by Dr. A. Elek, Los Angeles, California.

1,1,2-Trifluoro-2-chloro-3-phenylcyclobutene (XVI).--Trifluorochloroethylene (40 ml., *ca.* 0.5 mole) was condensed in each of twenty Pyrex combustion tubes cooled to -80° which contained 30 g. (0.294 mole) of phenylacetylene (III) and 0.1 g. of hydroquinone. The tubes were sealed and heated at 120° for 24 hours in an electric furnace. Three of the tubes exploded; apparently in some cases a side reaction which was accompanied by charring and hydrogen fluoride evolution occurred and frequently resulted in explosions. The material from the remaining tubes was distilled at reduced pressure through a 30-cm. Vigreux column. Based on the seventeen tubes that survived, the yield of XVI was 955 g. (86%); b.p. 47-52° (0.5 mm.).

Phenylcyclobutadienoquinone (I).--In a typical preparation, 100 g. (0.458 mole) of XVI was poured rapidly into a well-stirred solution of 90% sulfuric acid maintained at 90° on a steam bath. The mixture was stirred for an additional 24 minutes at 90°, and then poured onto 1 kg. of crushed ice. The crude solid was removed by suction filtration and extracted with hexane in a Soxhlet apparatus for two days. The yield of crude I from the extract was 55 g. (76%). The material was purified by recrystallization from acetone and identified by its infrared spectrum.

Photolysis of Phenylcyclobutadienoquinone (I) in Cyclohexane.--A solution of I (*ca.* 10^{-4} *M*) in cyclohexane contained in a 1-cm. quartz cell was irradiated through a Pyrex filter with a jacketless A-H4 mercury arc, and the photolysis followed by measurement of ultraviolet spectra at intervals of 30-60 seconds of irradiation. The 282 mμ peak of I decreased in intensity and new peaks appeared at 241 and 316 mμ. These latter peaks disappeared after further irradiation, and were replaced by peaks at 235, 240, 246, 262, and 271 mμ. In a similar experiment, phenylmaleic anhydride (IV) was photolyzed; the original peaks at 241 and 316 mμ disappeared and were replaced by the final set of five peaks observed in the photolysis starting from I. The first three peaks in this set are characteristic of phenylacetylene (III); the source of the last two peaks is not known.

Diethyl Phenylsuccinate (V).--The method was essentially as previously described (8), except that sulfuric acid was used in place of hydrochloric acid as a catalyst. From 3.0 g. (0.015 mole) of phenylsuccinic acid (XVII) (9) was obtained 2.0 g. (53%) of diethyl phenylsuccinate (V), b.p. 139-141° (3 mm.); lit. b.p. 160° (10 mm.) (8).

Dimethyl Phenylsuccinate (VI).--The method was essentially as previously described (8). From 1.1 g. (0.0057 mole) of phenylsuccinic acid (XVII) (9) was obtained 0.3 g. (24%) of dimethyl phenylsuccinate (VI), m.p. 58.5-59.5°; lit. m.p. 57.5-58.5° (8).

Photolysis of Phenylcyclobutadienoquinone (I) in Ethanol.--A magnetically stirred solution of 1.07 g. (0.0068 mole) of I in 100 ml. of absolute ethanol in a 100-ml. round-bottomed flask fitted with a reflux condenser was maintained at reflux and irradiated for one hour with an A-H6 mercury arc. The presence of diethyl phenylsuccinate (V) was indicated by the infrared spectrum of the yellow resinous material that remained after the solvent was removed. A bright red color developed upon the addition of a 10% solution of sodium hydroxide to the residue, and only resinous material was obtained by saponification.

Photolysis of Phenylcyclobutadienoquinone (I) in Methanol.--In a typical experiment a magnetically stirred solution of 7.3 g. (0.046 mole) of I in 800 ml. of absolute methanol contained in a 1-l. round-bottomed flask fitted with a reflux condenser was maintained at reflux and irradiated for 15 minutes with an A-H6 mercury arc. The solvent was removed at reduced pressure, and the yellow resinous residue treated with 10 ml. of chloroform. The resulting 1.8 g. (13% based on recovered I) of white solid (VII) was collected by suction filtration and washed with 40 ml. of carbon tetrachloride. Concentration of the filtrate gave 1.0 g. of the quinone I, which was removed by suction filtration and identified by its ultraviolet spectrum. The remainder of the solvent was removed from the filtrate, and the residue distilled to give 1.3 g. (15% based on recovered I) of dimethyl phenylsuccinate (VI), b.p. 121-125° (1.5 mm.), and 3.3 g. of a black tarry residue. The identity of a sample of the dimethyl phenylsuccinate (VI) which had been recrystallized from hexane, m.p. 57.9-58.5°, was established by its failure to depress the melting point of an authentic sample.

Properties of the Photolysis Product (VII).--The photolysis product (VII) was recrystallized from chloroform to give long fluffy white needles, m.p. 219° (d). A Rast molecular weight determination gave 371 (calculated 348).

Anal. Calcd. for $C_{21}H_{16}O_5$: C, 72.40; H, 4.63; CH_3O, 8.91. Found: C, 72.50; H, 4.73; CH_3O, 8.60.

The ultraviolet absorption spectrum of VII in ethanol had $\lambda_{max} = 308.5\ m\mu$, $\epsilon = 30,500$. The infrared absorption spectrum in a potassium bromide disc showed hydroxyl bands at 3430 and 3140 cm.$^{-1}$, carbonyl bands at 1769 and 1742 cm.$^{-1}$, and a double bond band at 1647 cm.$^{-1}$ A single carbonyl band was observed in acetonitrile solution at 1769 cm.$^{-1}$ and in methanol solution at 1765 cm.$^{-1}$ VII gave a precipitate with 2,4-dinitrophenylhydrazine, but it was not possible to purify the derivative. VII also gave positive tests for unsaturation with potassium permanganate and with bromine in carbon tetrachloride, gave a green color with ferric chloride and a black precipitate with Tollens' reagent. Although a 5% sodium bicarbonate solution did not dissolve solid VII at a reasonable rate, it quickly extracted VII from a benzene solution. Benzoic acid was obtained by oxidation of VII with basic sodium permanganate and identified by its failure to depress the melting point of an authentic sample. VII could not be reduced with hydrogen at atmospheric pressure and room temperature with a platinum catalyst.

Hydrolysis of the Photolysis Product (VII).--Treatment of 106 mg. (0.0003 mole) of VII with 20 ml. of a 10% sodium hydroxide solution at room temperature for about ten minutes gave a deep red solution. Acidification with 7 ml. of concentrated hydrochloric acid gave 94 mg. (88%) of a slightly yellow solid (XI). After some eighteen recrystallizations from ethanol-water, XI was obtained as a white solid, m.p. 192.5-192.8° (d). A Rast determination gave a molecular weight of 288 (calculated 352).

Anal. Calcd. for $C_{20}H_{16}O_6$: C, 68.18; H, 4.58. Found: C, 67.88; H, 4.74.

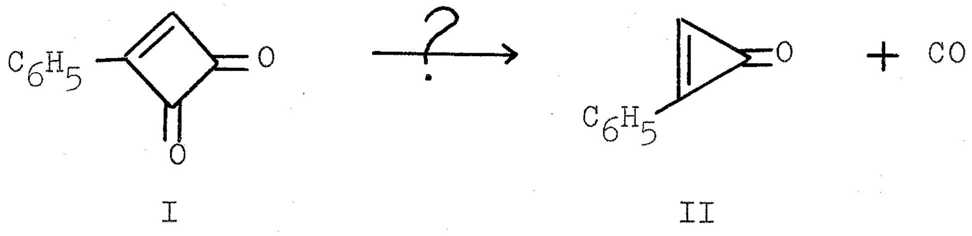
The ultraviolet absorption spectrum of XI had λ_{max} = 266 mμ, ϵ = 13,100. The infrared spectrum in a potassium bromide disc showed hydroxyl bands at 3430 and 3080 cm.$^{-1}$, carbonyl bands at 1774, 1742 and 1727 cm.$^{-1}$, and a double bond band at 1645 cm.$^{-1}$ In acetonitrile solution, XI had a carbonyl peak at 1774 cm.$^{-1}$ with a shoulder at 1750 cm.$^{-1}$ XI reacted with neutral potassium permanganate solution and Tollens' reagent, and gave a precipitate with 2,4-dinitrophenylhydrazine upon standing overnight. Although XI itself did not react with bromine in carbon tetrachloride solution, a solution of XI in aqueous sodium bicarbonate did give a positive test for unsaturation. XI gave no color with ferric chloride solution. XI was soluble in aqueous 5% sodium bicarbonate to give a yellow solution, and soluble in aqueous 10% sodium hydroxide to give a red solution. The titration curve of XI in 40% ethanol-water, followed with a pH meter, showed two inflection points at pH 5.2 and 9.0 which indicated two acidic hydrogens; the apparent pK_a values, estimated by the pH at half-neutralization, were 3.8 and 6.4, although these values are of limited significance due to the mixed-solvent medium in which the pH was measured.

PART II

THERMAL REACTIONS OF PHENYLCYCLOBUTADIENOQUINONE IN METHANOL

INTRODUCTION

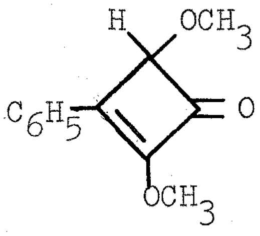
Phenylcyclobutadienoquinone (I) was decomposed thermally in an attempt to obtain phenylcyclopropenone (II) which is predicted by molecular orbital theory to have a large delocalization energy. Smutny (2) found only diethyl phenylsuccinate (III) from the thermal decomposition which occurred when a solution of the quinone I in ethanol was heated in a sealed tube at 100° for one week, although carbon monoxide was evolved upon pyrolysis of pure I. The present work deals with the characterization of the three products obtained from the thermal reactions of the quinone I with methanol in a stainless steel bomb.



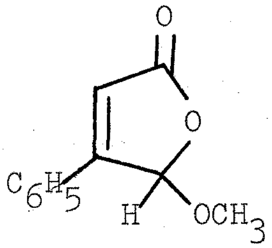
RESULTS AND DISCUSSION

Products from the Methanolysis of Phenylcyclobutadienoquinone (I)

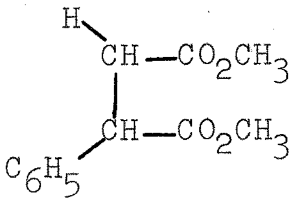
The thermal reaction of phenylcyclobutadienoquinone (I) with methanol gave three products which were assigned the structures 2,4-dimethoxy-3-phenylcyclobutenone (IV), 3-phenyl-4-hydroxy-4-methoxy-2-butenoic acid lactone (V), and dimethyl phenylsuccinate (VI). The relative yields of the three products were found to depend upon the reaction conditions.



IV



V



VI

A solution of the quinone I in methanol was maintained at reflux for twelve days to give the dimethoxyketone IV slightly contaminated with the diester VI. The same result was obtained when the reaction was carried out in a stainless steel bomb in an oil bath at 90-135°* for five to twelve hours with or without acid catalyst; the best yield (49%) of the dimethoxyketone IV was obtained from the acid-catalyzed reaction.

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[*] The oil bath temperatures are specified; since only the lower quarter of the bomb was immersed in the oil, the effective reaction temperatures were lower.

A series of bomb reactions in an oil bath at 150° * for one to two days gave equimolar mixtures of the methoxylactone V (ca. 40% yield) and the diester VI (ca. 40% yield); no dimethoxyketone IV was detected.

A bomb reaction in an electric furnace at 150° ** gave predominantly the diester VI (64% yield) and a small amount of the methoxylactone V (8% yield). It was shown that the diester VI was not formed from the methoxylactone V when V was heated with methanol in a sealed tube at 145-170°.

There was no indication that phenylcyclopropenone (II) was a product or an intermediate in any of the bomb reactions.

Mechanism of the Methanolysis of Phenylcyclobutadienoquinone (I)

Although a mechanistic study was not undertaken, it is possible to make some reasonable speculations concerning the reaction paths.

All three reaction products could be formed via a common intermediate, the hemiketal, 2-hydroxy-2-methoxy-3-phenylcyclobutenone (VII). The dimethoxyketone IV could arise from protonation followed by attack of methanol

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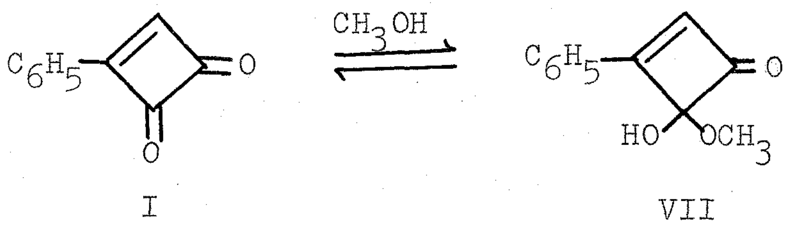
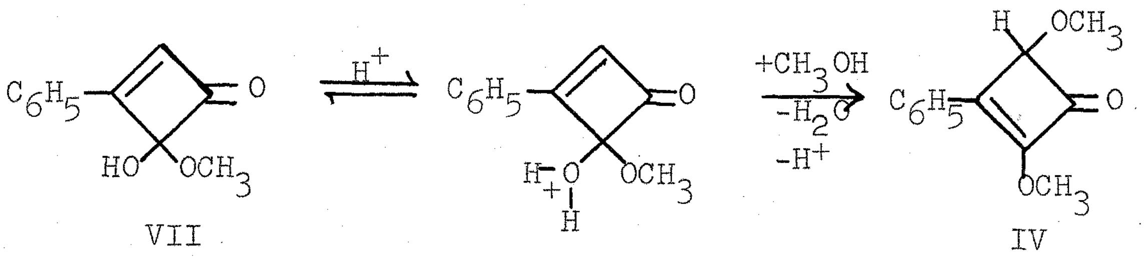
[*] See footnote, page 18.

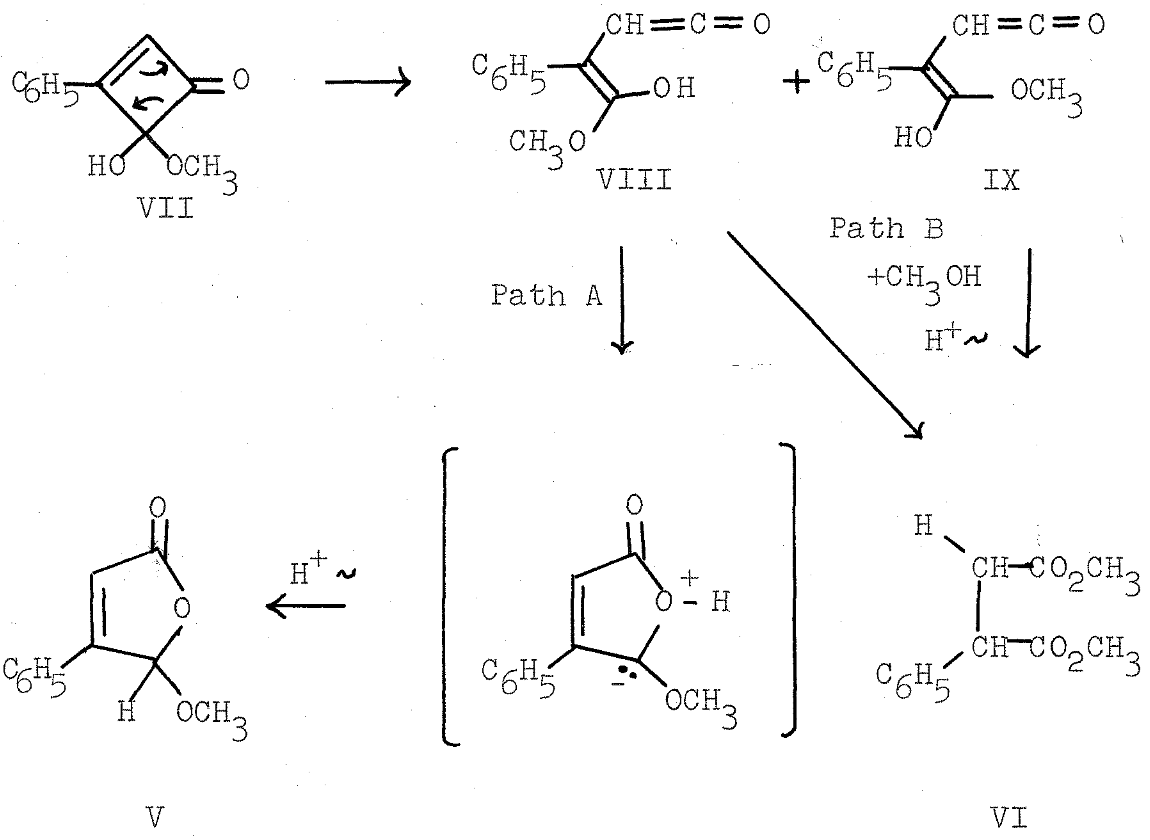
[**] In this case the effective reaction temperature was the same as the furnace temperature.



accompanied by allylic rearrangement. Ring-opening of VII might occur at higher temperatures to give the vinylketene intermediates VIII and IX from which the methoxylactone V and the diester VI could be formed as shown schematically below. Ring-openings of cyclobutenones to give vinylketene intermediates have been demonstrated in other cases (10).

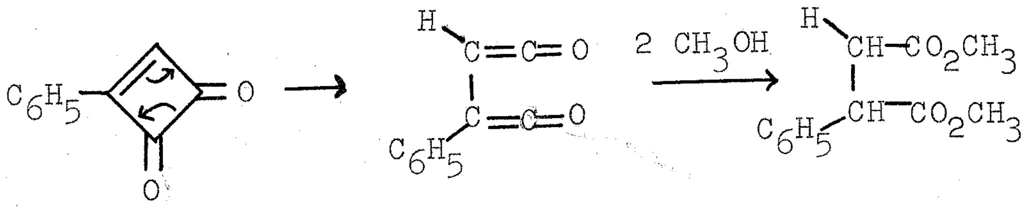


Two possible explanations may be advanced for the formation of equimolar quantities of the methoxylactone V and the diester VI from the intermediate temperature methanolyses. A 1:1 mixture of the vinylketene intermediates VIII and IX might be formed, followed by reaction of VIII exclusively by Path A and IX by Path B.



Alternatively, formation of excess VIII which reacts by both Path A and Path B in such a way as to give fortuitously an overall 1:1 mixture of the methoxylactone V and the diester VI might occur.

Several mechanistic interpretations may be invoked to explain the predominant formation of the diester VI in the methanolysis at the highest temperature. Ring-opening of the hemiketal VII could give predominantly the vinylketene IX, or it might give both VIII and IX with VIII reacting predominantly by Path B to give the diester VI. Alternatively, part or all of the diester VI could arise from the double addition of methanol to the diketene X formed directly from the ring-opening of the quinone I. It is



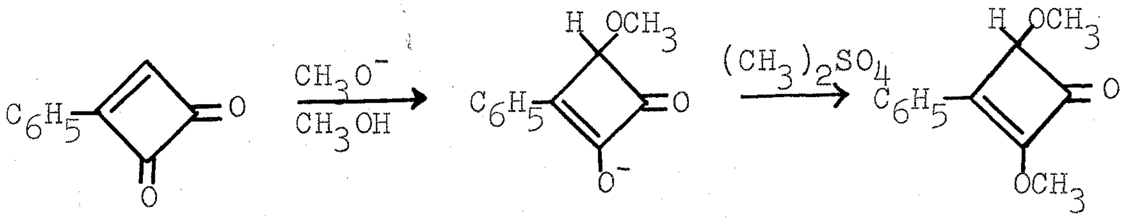
I X VI

not possible to distinguish between the various mechanisms on the basis of the available experimental evidence.

Structure Proof of 2,4-Dimethoxy-3-phenylcyclobutenone (IV)

Regeneration of the quinone I in good yield from the hydrolysis of the dimethoxyketone IV in refluxing dilute hydrochloric acid indicated that no skeletal change had occurred in the formation of the dimethoxyketone IV from the quinone I. The n-m-r spectrum of a pure melted sample of the dimethoxyketone IV showed four peaks, with approximate relative areas of 5:1:3:3, which corresponds to five phenyl hydrogens, one tertiary hydrogen, and two non-equivalent methoxyl groups. This rules out 2,2-dimethoxy-3-phenyl-cyclobutenone as the structure of IV, since this structure has two equivalent methoxyl groups and would show only three peaks in its n-m-r spectrum of relative areas 5:1:6. The infrared absorption spectrum of IV showed strong absorption bands at 1755 and 1635 cm.$^{-1}$, characteristic of carbonyl and double bond stretching frequencies, respectively, in the 3-phenylcyclobutenone series.

The ultraviolet absorption spectrum was in accord with the assigned structure. The infrared and ultraviolet spectra were identical with the corresponding spectra of a compound synthesized by Skattebøl (5) from the quinone I by treatment with sodium methoxide followed by dimethyl sulfate. Skattebøl's sample, which was shown by a Zeisel determination to contain two methoxyl groups and by microanalysis to have the formula $C_{12}H_{12}O_3$, gave an undepressed melting point on admixture with the dimethoxyketone IV obtained in the present investigation.

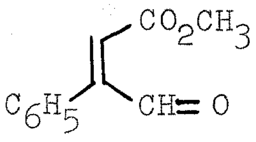


I

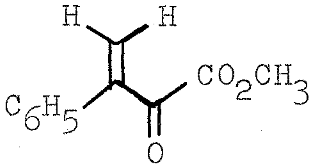
IV

Structure Proof of 3-Phenyl-4-hydroxy-4-methoxy-2-butenoic Acid Lactone (V)

The methoxylactone V, a white crystalline solid, m.p. 52.5-53.0°, was shown by microanalysis, Rast molecular weight determination and a Zeisel methoxyl determination to have the formula $C_{11}H_{10}O_3$ with one methoxyl group per molecule. The *n-m-r* spectrum of the pure melted material showed four peaks, of approximate relative areas 5:1:1:3, which corresponds to five phenyl hydrogens, one vinyl hydrogen, one tertiary hydrogen and three methoxyl hydrogens. The infrared spectrum of the methoxylactone V showed double bond absorption at 1637 cm.$^{-1}$ and a strong carbonyl absorption at 1770 cm.$^{-1}$ This carbonyl absorption supports the methoxylactone structure for V as opposed to the isomeric structures methyl β-formylcinnamate (XI) or methyl 2-keto-3-phenyl-3-butenoate (XII) by analogy

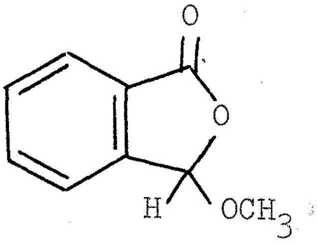


XI

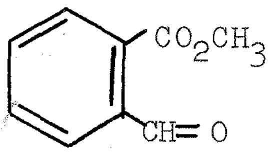


XII

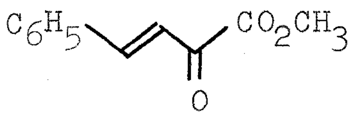
with similar molecules. Infrared carbonyl absorptions are reported (11) at 1768 cm.$^{-1}$ for 2,3-benz-4-hydroxy-4-methoxy-2-butenoic acid lactone (XIII), in good agreement with that observed for the methoxylactone V, but reported (11) at 1725 cm.$^{-1}$ and 1708 cm.$^{-1}$ for a compound analogous to XI, methyl o-formylbenzoate (XIV). A compound analogous to XII, methyl 2-keto-4-phenyl-3-butenoate (XV), shows (5) no carbonyl absorption frequency above 1740 cm.$^{-1}$ The



XIII

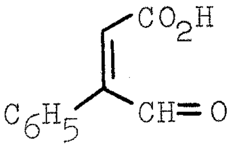


XIV



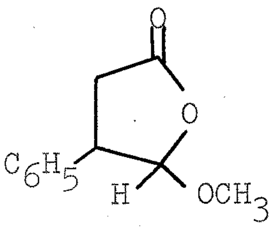
XV

aldehyde structure XI was further eliminated by the absence of a characteristic aldehyde hydrogen peak in the n-m-r spectrum of V and the failure of the methoxylactone V to form a dimedone derivative in water-ethanol during two days at room temperature. However, under the alkaline conditions used in a Tollens' test, hydrolysis of V to the open-chain aldehyde β-formylcinnamic acid (XVI) apparently occurred, since a silver mirror was obtained.



XVI

Hydrogenation of the methoxylactone V over palladium on carbon gave a white crystalline solid (XVII), m.p. 84.0-84.5°, shown by microanalysis to have the formula $C_{11}H_{12}O_3$. This solid is assigned the structure 3-phenyl-4-hydroxy-4-methoxybutanoic acid lactone (XVII). The

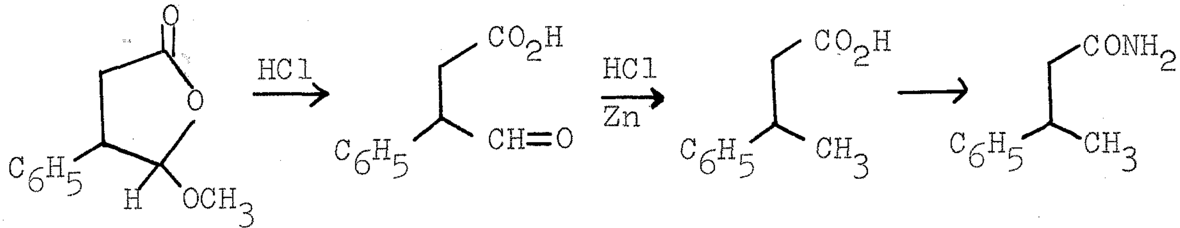


XVII

infrared absorption spectrum of the dihydromethoxylactone XVII showed no double bond absorption but a strong carbonyl absorption at 1795 cm.$^{-1}$ Such high frequency carbonyl absorption is characteristic of lactones, and the shift of 25 cm.$^{-1}$ to higher frequencies compared with the carbonyl peak of the methoxylactone V is the expected consequence of the destruction of the conjugation of the carbonyl group.

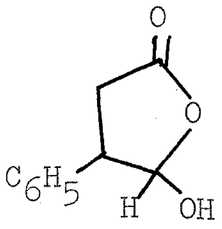
The platinum-catalyzed hydrogenation of the methoxylactone V gave a mixture of the dihydromethoxylactone XVII and another compound (XVIII) of unknown structure with a carbonyl absorption peak in the infrared at 1710 cm.$^{-1}$; this mixture (XIX) could not be separated by fractional distillation.

The mixture XIX was subjected to a Clemmensen reduction and gave some neutral product (XXI) of unknown structure but mostly β-phenylbutyric acid (XXII), identified by comparison of the amide (XXIII) with an authentic sample.

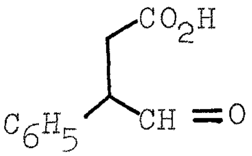


XVII XX XXII XXIII

The mixture XIX was hydrolyzed in 2 <u>N</u> hydrochloric acid to give a mixture of neutral and acidic materials. The acidic fraction was shown by its infrared spectrum to contain two compounds, a lactone (XXIV), probably 3-phenyl-4,4-dihydroxybutanoic acid lactone (XXIV), with a carbonyl stretching frequency at 1790 cm.$^{-1}$, and another compound (XXV), probably 3-phenyl-4-ketobutanoic acid (XXV), with a carbonyl stretching frequency at 1710 cm.$^{-1}$ The lactone XXIV in the acidic fraction presumably arose from lactonization of some of the aldehyde acid XXV upon treatment with hydrochloric acid in the isolation procedure. The neutral fraction was shown by its infrared spectrum to be a mixture of three unidentified compounds, XXVI, XXVII and XXVIII. XXVI was a minor constituent and had a carbonyl peak at 1755 cm.$^{-1}$ and a double bond peak at 1635 cm.$^{-1}$ in the infrared; XXVII had a carbonyl peak at 1740 cm.$^{-1}$ in the infrared; XXVIII had a characteristic lactone carbonyl peak at 1790 cm.$^{-1}$ in the infrared. This lactone XXVIII is probably identical with the lactone XXIV isolated with the acidic fraction.



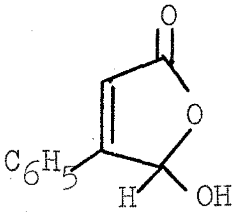
XXIV



XXV

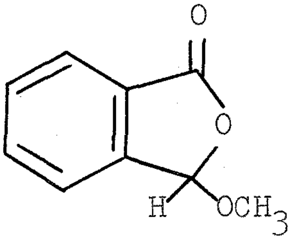
The acidic fraction from above, thought to be a mixture of the lactone XXIV and the acid XXV, was oxidized with silver oxide to give phenylsuccinic acid (XXIX), identified by comparison with an authentic sample.

Hydrolysis of the methoxylactone V with refluxing 2 N hydrochloric acid gave a white crystalline solid, m.p. 158.0-158.8°, which was assigned the structure 3-phenyl-4,4-dihydroxy-2-butenoic acid lactone (XXX). XXX was shown

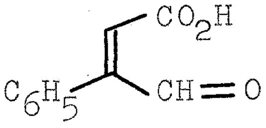


XXX

by microanalysis and a Rast molecular weight determination to have the formula $C_{10}H_8O_3$. The infrared spectrum of XXX in a potassium bromide disc showed a sharp hydroxyl absorption peak at 3240 cm.$^{-1}$, strong carbonyl absorption at 1735 cm.$^{-1}$, and double bond absorption at 1635 cm.$^{-1}$ The first two peaks agreed well with the hydroxyl peak at 3250 cm.$^{-1}$ and the carbonyl peak at 1738 cm.$^{-1}$ reported (11) for 2,3-benz-4,4-dihydroxy-2-butenoic acid lactone (XXXI),



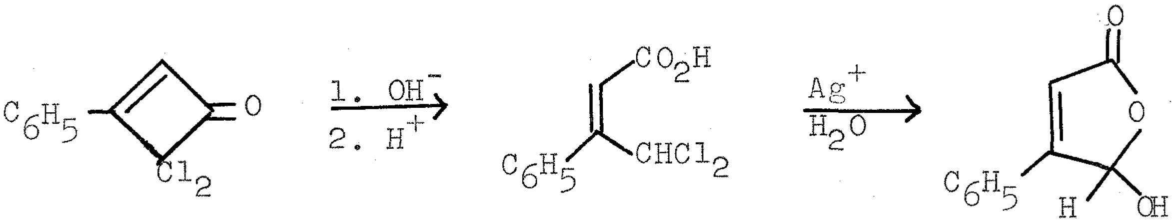
in support of the assigned lactone structure XXX. An open-chain structure such as β-formylcinnamic acid (XVI) would be expected (11) to show infrared carbonyl absorption at 1708 and 1690 cm.$^{-1}$ due to the aldehyde and acid carbonyl groups, respectively. XXX dissolved in aqueous sodium bicarbonate only after standing overnight, as expected for



XVI

a hydroxylactone but not for a carboxylic acid.

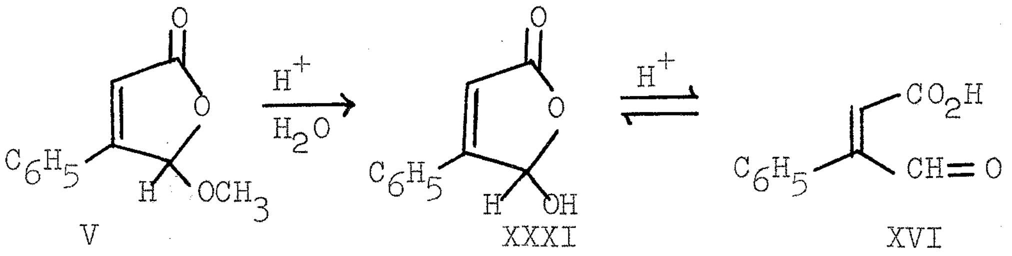
The hydroxylactone structure assigned XXX was further supported by synthesis. It has been shown previously (12) that mild basic hydrolysis of 3-phenyl-4,4-dichlorocyclobutenone (XXXII) gives 3-phenyl-4,4-dichloro-2-butenoic acid (XXXIII). In the present work, treatment of the dichloroacid XXXIII with silver nitrate in ethanol-water gave the hydroxylactone XXX.



XXXII XXXIII XXX

The hydroxylactone XXX was reconverted to the methoxylactone V by treatment with methanol in the presence of sulfuric acid catalyst.

Both the hydroxylactone XXX and the methoxylactone V were found to react slowly with 2,4-dinitrophenylhydrazine in the presence of hydrochloric acid catalyst in methanol-water solution to give identical 2,4-dinitrophenylhydrazones, presumably via hydrolysis to β-formylcinnamic acid (XVI).



Apparently the carboxyl group of XVI esterified after the formation of the derivative, since a microanalysis indicated that the derivatives were the 2,4-dinitrophenylhydrazones (XXXIV) of the corresponding methyl ester (XI) of the acid XVI. The 2,4-dinitrophenylhydrazone (XXXV) of the acid XVI itself was prepared in ethanol-water from the hydroxylactone XXX by a modification of the above procedure in which the concentrations of acid catalyst and water were increased.

Basic hydrolysis of either the methoxylactone V or the hydroxylactone XXX gave a white crystalline solid $C_{18}H_{16}O_4$ (XXXVI), m.p. 199-200°, the structure of which was not determined. This material was probably identical with that previously obtained by Simmons (13) from the basic hydrolysis of the dichloroacid XXXIII, as indicated by comparison of melting points, microanalyses, molecular weights (Rast), neutralization equivalents and ultraviolet spectra of the two compounds. It is likely that the dichloroacid XXXIII first hydrolyzed to give the aldehyde acid XVI (or the hydroxylactone XXXI), which then reacted further to give the unknown compound XXXVI.

EXPERIMENTAL

All melting points and boiling points are not corrected. Analyses are by Dr. A. Elek, Los Angeles, California.

Phenylcyclobutadienoquinone (I) with Refluxing Methanol. Run 1.--A solution of 6.0 g. (0.038 mole) of phenylcyclobutadienoquinone (I) in 300 ml. of absolute methanol was placed in a 500-ml. round-bottomed flask fitted with a reflux condenser and maintained at reflux in the dark for 279 hours. The methanol was removed and the residue treated with carbon tetrachloride to give 1.9 g. of insoluble yellow material identified as the quinone I by its infrared spectrum. The solvent was removed from the filtrate and the residue distilled to give a yellowish liquid, b.p. ca. 95° (0.5 mm.), which was shown by its infrared spectrum to be 2,4-dimethoxy-3-phenylcyclobutenone (IV) slightly contaminated by dimethyl phenylsuccinate (VI). No yield of IV is reported due to mechanical loss of some of this material. The purification and structure proof of IV are included in Run 2.

Bomb Reaction of Phenylcyclobutadienoquinone (I) with Methanol at 90-135°. Run 2.--A 1-liter stainless steel bomb containing a solution of 9.0 g. (0.057 mole) of the quinone I in 600 ml. of absolute methanol was placed in an oil bath at 90°;* the bath temperature was increased

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*In all cases the bath temperatures are reported; the effective reaction temperature was lower since only the bottom quarter of the bomb was immersed in the oil bath.

to 135° over the course of one and one-half hours, and maintained at this temperature for an additional four hours. The lack of gas pressure when the bomb was cooled and opened indicated that carbon monoxide was not formed in the reaction. The isolation procedure was as in Run 1 and there was obtained 2.2 g. of the quinone I, 2.2 g. (25% yield based on recovered I) of crude dimethoxyketone IV, 1.0 g. of unidentified red material, b.p. $>$ 150° (2 mm.) and 1.8 g. of black tarry residue.

The purification of IV was effected by three additional distillations through a semimicro column (14) to give a slightly yellow liquid, b.p. 105° (0.5 mm.), $\underline{n}^{23.5}$D = 1.5910. Subsequent crystallization from hexane gave nearly-white crystals, m.p. 34-37°. The ultraviolet absorption spectrum of IV in cyclohexane solution showed λ_{max} = 302 mμ with a shoulder at 314 mμ. The infrared and ultraviolet spectra of this material were identical to spectra of a compound synthesized by Skattebøl (5) which had $\underline{n}^{23.5}$D = 1.5922, m.p. 38-39°. The melting point of IV was not depressed on admixture with Skattebøl's sample, which gave the following microanalysis.

Anal. Calcd. for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92; CH_3O, 30.39. Found: C, 70.78; H, 6.10; CH_3O, 30.24.

Reconversion of 2,4-Dimethoxy-3-phenylcyclobutenone (IV) to Phenylcyclobutadienoquinone (I).--A mixture of 0.85 g. (0.0042 mole) of the dimethoxyketone IV and 10 ml.

of 1 N hydrochloric acid was heated under reflux for 15 minutes, then 1 ml. of concentrated hydrochloric acid was added and the mixture maintained at reflux for an additional eight minutes. The quinone I (0.5 g., 75%) was obtained by crystallization from the cooled reaction mixture and identified by its infrared spectrum.

Acid-Catalyzed Bomb Reaction of Phenylcyclobutadienoquinone (I) with Methanol at 112-115°. Run 3.--A 1-liter stainless steel bomb containing a mixture of 15 g. (0.095 mole) of the quinone I, five drops of concentrated sulfuric acid, and 700 ml. of absolute methanol, was heated in an oil bath at 112-115° for 12 hours. The reaction mixture was cooled to 0°, shaken with anhydrous sodium carbonate, and filtered. No solid quinone I was obtained by concentration of the filtrate. The residue was flash-distilled to give 10.4 g. of distillate and 5.9 g. of black tar. The distillate was re-distilled through a semimicro column (14) to give 9.5 g. (49%) of the dimethoxyketone IV, b.p. 115° (1 mm.), contaminated with the quinone I and possibly with dimethyl phenylsuccinate (VI).

Bomb Reaction of Phenylcyclobutadienoquinone (I) with Methanol at 150°. Run 4.--In a typical reaction, a 1-liter stainless steel bomb which contained a mixture of 20 g. (0.127 mole) of the quinone I and 500 ml. of absolute methanol was heated in an oil bath at about 150° for 40 hours. The bomb was allowed to cool, and the solvent removed. The residue was distilled through a semimicro column (14).

Fraction	Dist. Temp., °C	Press., mm.	Wt., g.
1	114-120	1.1	10.0
2	120-132	1.1	2.0
3	132-135	1.1	8.1
Residue (black tar)			5.5

It was shown by means of infrared spectra that Fraction 1 was dimethyl phenylsuccinate (VI), Fraction 3 was 3-phenyl-4-hydroxy-4-methoxy-2-butenoic acid lactone (V), and Fraction 2 was a mixture (approximately 1:1) of V and VI. Thus the total yields were 11.0 g. (39%) of the diester VI and 9.1 g. (38%) of the methoxylactone V.

The methoxylactone V was purified by re-distillation through a semimicro column (14) to give a nearly-colorless liquid, b.p. 124° (0.5 mm.), which solidified on standing; three recrystallizations from hexane gave a white solid, m.p. 52.5-53.0°. A Rast molecular weight determination gave 186 (calculated 190).

Anal. Calcd. for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30; CH_3O, 16.32. Found: C, 69.59; H, 5.38; CH_3O, 16.22.

The ultraviolet absorption spectrum in ethanol solution showed $\lambda_{max} = 276.5\ m\mu$, $\epsilon = 20{,}000$.

Hydrogenation of 3-Phenyl-4-hydroxy-4-methoxy-2-butenoic Acid Lactone (V).--The tetrahydrofuran used as a hydrogenation solvent was heated under reflux for three hours with solid potassium hydroxide, distilled from sodium and stored over sodium wire. The methoxylactone V (2.0 g., 0.01 mole) in 10 ml. of tetrahydrofuran was shaken with 50 mg. of 10% palladium on carbon (15) at a hydrogen pressure of 50 lbs./in.^{2} for 49 hours. The catalyst was removed by filtration and the solvent evaporated at reduced pressure. The residue was distilled through a semimicro column (14) to give 1.8 g. (89%) of 3-phenyl-4-hydroxy-4-methoxybutanoic acid lactone (XVII), b.p. 117-120° (1.5 mm.), which solidified on standing. After seven recrystallizations from hexane and one sublimation this material had m.p. 84.0-84.5°.

Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29. Found: C, 68.77; H, 6.19.

Hydrogenation of the methoxylactone V over a platinum catalyst gave a liquid mixture (XIX) shown by its infrared spectrum to contain the dihydromethoxylactone XVII highly contaminated with an unidentified material (XVIII).

Clemmensen Reduction of 3-Phenyl-4-hydroxy-4-methoxybutanoic Acid Lactone (XIX).--The method was as previously described (16). From 4.0 g. of crude dihydromethoxylactone XIX (obtained by catalytic hydrogenation over platinum), 5.0 g. of amalgamated zinc, 12.5 ml. of 27% hydrochloric acid and 5 ml. of toluene was obtained 1.6 g. of product, b.p. 76-133° (1 mm.). This material was dissolved in ether and the acidic portion extracted with 5% aqueous sodium bicarbonate. The neutral fraction (XXI), 0.5 g., was not characterized. Acidification of the bicarbonate extract with concentrated hydrochloric acid gave 1.0 g. of a semi-solid material (XXII). The infrared spectrum of XXII in carbon tetrachloride solution showed a broad band at about 2900 cm.$^{-1}$ characteristic of carboxylic acids. XXII was shown to be β-phenylbutyric acid by preparation (17) of its amide derivative (XXIII). After recrystallization three times from benzene-hexane and once from ethanol-water, the amide XXIII had m.p. 104.5-106°. The melting point was not depressed on admixture with authentic β-phenylbutyramide.

Hydrolysis of Crude 3-Phenyl-4-hydroxy-4-methoxybutanoic Acid Lactone (XIX).--A mixture of 3.8 g. of the crude dihydromethoxylactone XIX (obtained by catalytic hydrogenation over platinum) and 35 ml. of 2 N hydrochloric acid contained in a 50-ml. flask fitted with a reflux condenser and magnetic stirrer was stirred and maintained at reflux for 12 hours. The reaction mixture was extracted with ether and the ethereal solution separated into acid and neutral fractions by treatment with 5% aqueous sodium bicarbonate. The acid fraction (XXIV and XXV), 2.2 g., gave a precipitate with 2,4-dinitrophenylhydrazine, and showed infrared absorption in the carbonyl region at 1790 and 1715 cm.$^{-1}$ The acid fraction was oxidized by treatment with silver oxide as described below. The neutral fraction which amounted to

1.1 g. after evaporation of the ether, was shown to be a mixture of three compounds (XXVI, XXVII and XXVIII) by its infrared spectrum, and gave a precipitate rapidly with 2,4-dinitrophenylhydrazine. This mixture was not investigated further.

Silver Oxide Oxidation of a Mixture of 3-Phenyl-4,4-dihydroxybutanoic Acid Lactone (XXIV) and 3-Phenyl-4-ketobutanoic Acid (XXV).--A portion of the mixture of XXIV and XXV, 1.9 g., was dissolved in 10 ml. of ethanol and a small amount of insoluble material removed by filtration. A solution of 3.0 g. of silver nitrate in 40 ml. of water was added, and the resulting solution cooled to 0°. A solution of 2.0 g. of potassium hydroxide in 10 ml. of water was added dropwise with swirling. The flask was stoppered, wrapped in a wet towel, and shaken mechanically for four hours. The solid was removed by filtration, the filtrate acidified with concentrated hydrochloric acid and extracted with ether. The ether was removed from the extract and the residue treated with carbon tetrachloride to give 0.7 g. of insoluble material, m.p. $151\text{-}158^{\circ}$, identified as phenylsuccinic acid (XXIX) by its infrared spectrum in a potassium bromide disc. XXIX was recrystallized six times from water to give a sample, m.p. $160\text{-}162.5^{\circ}$; the melting point of this sample was not depressed on admixture with authentic phenylsuccinic acid.

3-Phenyl-4,4-dihydroxy-2-butenoic Acid Lactone (XXX) from 3-Phenyl-4-hydroxy-4-methoxy-2-butenoic acid Lactone (V).--In a typical hydrolysis, a mixture of 1.0 g. (0.0053 mole) of the methoxylactone V and 54 ml. of 2 N hydrochloric acid was heated under reflux for 1.7 hours until no insoluble oil remained. The hydroxylactone XXX crystallized from the solution cooled to 0°; the melting point was 157-160°. Purification of XXX by five recrystallizations from benzene gave a white crystalline solid, m.p. 158.0-158.8°; this material did not depress the melting point on admixture with material synthesized by another route as described below. A Rast determination gave a molecular weight of 205 (calculated 176).

Anal. Calcd. for $C_{10}H_8O_3$: C, 68.18; H, 4.58. Found: C, 68.09; H, 4.52.

An ultraviolet absorption spectrum of the hydroxylactone XXX measured in ethanol solution showed λ_{max} = 275.5 mμ, ϵ = 19,200.

Synthesis of 3-Phenyl-4,4-dihydroxy-2-butenoic Acid Lactone (XXX). 3-Phenyl-4,4-dichloro-2-butenoic Acid (XXXIII).--The method was as previously described (12). From 2.0 g. (0.0094 mole) of 3-phenyl-4,4-dichlorocyclobutenone (XXXII) (18) and 20 ml. of 10% aqueous sodium hydroxide was obtained 1.5 g. (69%) of 3-phenyl-4,4-dichloro-2-butenoic acid (XXXIII), m.p. 124-125°. Recrystallization from ethanol-water gave 1.1 g. (51%) of XXXIII, m.p. 125.0-125.3°; lit. m.p. 124.5-125° (12).

3-Phenyl-4,4-dihydroxy-2-butenoic Acid Lactone (XXX).--A solution of 438 mg. (1.9 mmol.) of the dichloroacid XXXIII and 703 mg. (4.1 mmol.) of silver nitrate in 25 ml. of ethanol and 10 ml. of water was allowed to stand at room temperature in the dark for 27 hours. Silver chloride (322 mg., 59%) was removed, an additional 0.7 g. of silver nitrate and 20 ml. of water added to the reaction mixture, and the reaction allowed to continue for five more days to give an additional 62 mg. of silver chloride, which brought the total to 384 mg. (71%). After removal of the silver chloride, the ethanol was removed under reduced pressure and the aqueous residue extracted with ether. The ether was removed and the residue treated with carbon tetrachloride to give a yellow solution and an insoluble white solid which was recrystallized three times from water to give 20 mg. (6%) of the hydroxylactone XXX, m.p. 152-158°; the melting point was not depressed on admixture with XXX obtained by the hydrolysis of the methoxylactone V. The remainder of the reaction product obtained after removal of the carbon tetrachloride was a yellow gummy solid.

Methylation of 3-Phenyl-4,4-dihydroxy-2-butenoic Acid Lactone (XXX).--A solution of 0.6 g. (0.0034 mole) of the hydroxylactone XXX and 1.5 ml. of concentrated sulfuric acid in 35 ml. of absolute methanol was allowed to stand at room temperature for 24 hours, then concentrated to 20 ml.

on a steam bath over a period of two hours. The solution was cooled to 0° and diluted with ether, then washed with water and with 5% aqueous sodium bicarbonate. The ethereal solution was dried over anhydrous magnesium sulfate, filtered, and the ether removed. The residue was distilled to give 0.4 g. (62%) of the methoxylactone V, b.p. 131° (1 mm.), identified by its infrared and n-m-r spectra.

An attempt to methylate the hydroxylactone XXX with diazomethane was unsuccessful and gave only a viscous red oil.

2,4-Dinitrophenylhydrazones from 3-Phenyl-4,4-dihydroxy-2-butenoic Acid Lactone (XXX).--The hydroxylactone XXX slowly formed a 2,4-dinitrophenylhydrazone in ethanol-water when treated with 2,4-dinitrophenylhydrazine reagent prepared by the method of Shriner, Fuson and Curtin (19). Four recrystallizations from ethanol gave the pure derivative (XXXV), m.p. 201.5° (d).

Anal. Calcd for $C_{16}H_{12}O_6N_4$: C, 53.93; H, 3.40. Found: C, 53.99; H, 3.39.

Preparation of the derivative in 93% methanol-water by the procedure of Vogel (20) (except that a small amount of water was added to cause precipitation of the derivative) was accompanied by methylation of the carboxylic acid group. After three recrystallizations from methanol, the derivative (XXXIV) had m.p. 171.6-172.2°. The melting point was not depressed on admixture with the derivative melting at 172.4-172.5° obtained from the methoxylactone V as described below.

2,4-Dinitrophenylhydrazone from 3-Phenyl-4-hydroxy-4-methoxy-2-butenoic Acid Lactone (V).--The preparation of the 2,4-dinitrophenylhydrazone from the methoxylactone V in 93% methanol-water by the procedure of Vogel (20) (except that a small amount of water was added to cause precipitation of the derivative) was also apparently accompanied by methylation of the carboxylic acid group. After three recrystallizations from methanol the derivative (XXXIV) had m.p. 172.4-172.5°.

Anal. Calcd. for $C_{17}H_{14}O_6N_4$: C, 55.13; H, 3.81; N, 15.13. Found: C, 55.30; H, 3.97; N, 15.03.

Saponification of 3-Phenyl-4,4-dihydroxy-2-butenoic Acid Lactone (XXX).--A solution of 391 mg. (2.2 mmol.) of the hydroxylactone XXX and 2.0 g. of potassium hydroxide in 50 ml. of water was maintained at reflux for two hours and then acidified with concentrated hydrochloric acid. The resulting precipitate was recrystallized from ethanol-water to give 139 mg. (43%) of a slightly yellow solid (XXXVI), m.p. 200-201°. After seven recrystallizations from ethanol, a white crystalline sample (XXXVI), m.p. 199-200°, was obtained. A Rast molecular weight determination gave 277 (calculated 296). The neutralization equivalent was found to be 341 (calculated 296 for one acidic hydrogen).

Anal. Calcd. for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44. Found: C, 72.92; H, 5.45.

The ultraviolet absorption spectrum of XXXVI measured in ethanol solution showed λ_{max} = 252, 257.5 and 263 mμ, with ϵ = 303, 379 and 316, respectively.

This material XXXVI of unknown structure was also obtained from a similar saponification of the methoxylactone V, and was probably identical with a compound obtained from the basic hydrolysis of 3-phenyl-4,4-dichloro-2-butenoic acid (XXXIII) by Simmons (13). Simmons' compound had the following properties: m.p. 197.5-199°; molecular weight 270 (Rast); neutralization equivalent 296.

Anal. Calcd. for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44. Found: C, 72.70; H, 5.36.

The ultraviolet spectrum of Simmons' material in ethanol solution showed λ_{max} = 252, 257.5 and 263.5 mμ, with ϵ = 346, 418 and 318, respectively.

Additional properties of XXXVI observed in the present work included an infrared spectrum in chloroform solution which showed a strong carbonyl absorption peak at 1738 $cm.^{-1}$, with no indication of a double bond absorption peak. XXXVI was soluble in 5% aqueous sodium bicarbonate, evolved hydrogen bromide when treated with bromine in carbon tetrachloride, showed a negative test for unsaturation with 2% aqueous potassium permanganate, gave no color change with ferric chloride solution and no precipitate with 2,4-dinitrophenylhydrazine.

Bomb Reaction of Phenylcyclobutadienoquinone (I) with Methanol in an Electric Furnace. Run 5.--A 1-liter stainless steel bomb containing a mixture of 20 g. (0.127 mole) of the quinone I and 500 ml. of absolute methanol was maintained at 150° in an electric furnace and rocked for 31 hours. The isolation procedure was as in Run 4 and there was obtained 18 g. (64%) of dimethyl phenylsuccinate (VI), 2 g., (8%) of the methoxylactone V, and 5 g. of tarry residue.

Thermal Reaction of 3-Phenyl-4-hydroxy-4-methoxy-2-butenoic Acid Lactone (V) with Methanol.--A sealed tube containing a solution of 0.6 g. (0.032 mole) of the methoxylactone V in 30 ml. of absolute methanol was heated in an oil bath at 145° for 22 hours, then at 170° for an additional two hours. The solvent was removed and the residue distilled to give 0.4 g. (67% recovery) of the methoxylactone V, b.p. 135° (1 mm.), identified by its infrared spectrum. No dimethyl phenylsuccinate (VI) was detected.

PART III

THE PHOTOCHEMICAL SYNTHESIS OF PHENANTHRENES

INTRODUCTION

In connection with other research, it was of interest to examine the photochemical behavior of tetraphenylethylene (I). It was found, unexpectedly, that I underwent a novel photochemical reaction with dissolved oxygen to give 9,10-diphenylphenanthrene (II). Subsequently, it was found that *trans*-stilbene (III) underwent a similar reaction to give phenanthrene (IV). After the present work had been undertaken, a published report appeared (21) which described the formation of phenanthrene (IV) from *cis*-stilbene (V) or *trans*-stilbene (III), although it was not realized that the reaction involved oxygen and the procedure was of little preparative value. Recently, another example of this reaction was reported (22) in which 9,10-dicyanophenanthrene (VI) was observed as a product of the photolysis of *cis*-dicyanostilbene (VII). It is probable that the side-product obtained by previous workers (23,24) in studies of the photochemical isomerizations of *cis*- and *trans*-stilbenes (V and III) was phenanthrene (IV), although it was not identified.

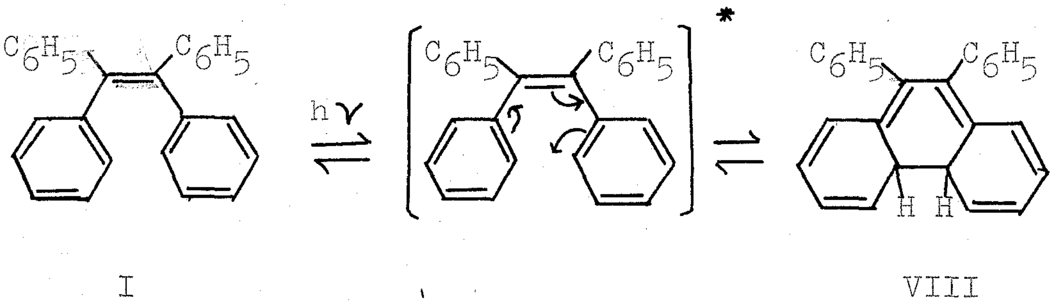
RESULTS AND DISCUSSION

The spectral changes accompanying the irradiation by a jacketless A-H4 mercury arc of extremely dilute solutions (*ca*. 5 x 10^{-5} *M*) of tetraphenylethylene (I) in cyclohexane indicated that the product was 9,10-diphenylphenanthrene (II). The identity of the product was confirmed by comparison with an authentic sample of II. No reaction occurred when more concentrated solutions (*ca* 0.1 *M*) of I were irradiated under comparable conditions. Apparently, the ratio of the concentration of oxygen (dissolved from the atmosphere) to the concentration of I was sufficiently high to cause reaction only in the very dilute solutions. However, it was possible to obtain II in 63 percent yield from the more concentrated solutions required for convenient synthetic preparations by bubbling pure oxygen through the solution during irradiation.

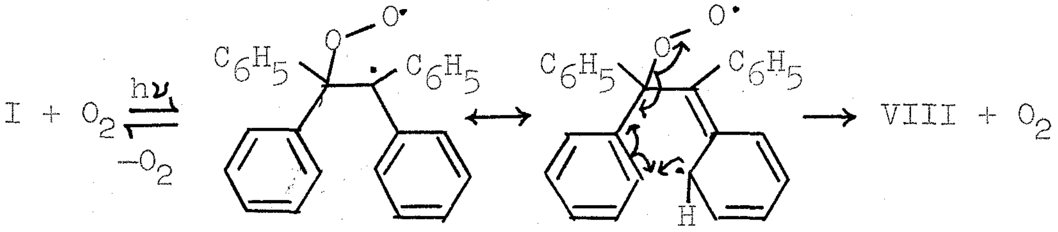
Although a mechanistic study was not made, it seems reasonable to postulate that the reaction proceeds *via* an unorthodox dihydrophenanthrene intermediate (VIII) which is subsequently oxidized by oxygen to the phenanthrene II. VIII may be formed from photochemically activated molecules of tetraphenylethylene indicated in scheme A. Alternatively, oxygen may act as a catalyst in the formation of the intermediate VIII as shown in scheme B.

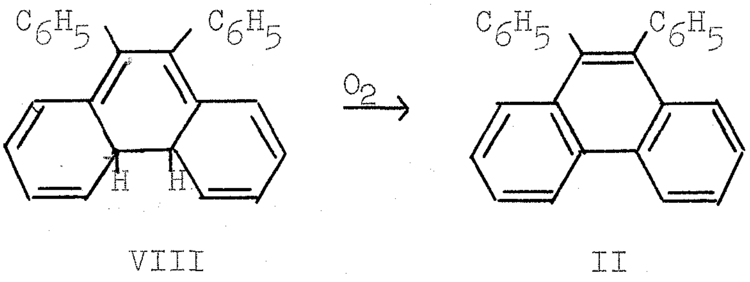
The photolysis of *trans*-stilbene (III) in a magnetically stirred cyclohexane solution under a pressure of

(A)

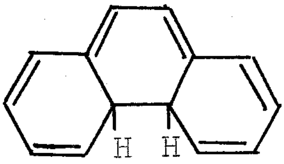


(B)





10 lbs./in.^{2} of oxygen gave phenanthrene in 46 percent yield. In this case, either light or oxygen may initiate the isomerization to the cis configuration required for ring-closure. A dihydrophenanthrene IX similar to VIII is postulated as the intermediate in this case.



IX

EXPERIMENTAL

All melting points are not corrected.

Benzopinacol.--The method was essentially as described previously (25). The reaction mixture was irradiated for 52.5 hours with an A-H4 mercury arc with Pyrex jacket removed. From 101 g. (0.555 mole) of benzophenone was obtained 70 g. (69%) of benzopinacol, m.p. 187-190°; lit. m.p. 188-190° (25).

Benzopinacolone.--The method was as described previously (26). From 70 g. (0.191 mole) of benzopinacol and 0.7 g. (0.003 mole) of iodine was obtained 58.5 g. (88%) of benzopinacolone, m.p. 182.2-182.6°; lit. m.p. 179-180° (26).

Tetraphenylethylene (I).--The method was as described previously (27). From 28 g. (0.08 mole) of benzopinacolone, 7.5 g. (0.31 mole) of powdered magnesium and 7.5 g. (0.03 mole) of iodine was obtained 16.5 g. (62%) of I, m.p. 223.6-224.6°.

9,10-Diphenylphenanthrene (II).--The method was as described previously (28), via reaction of tetraphenylethylene with chlorine to give 1,1,2,2-tetraphenyl-1,2-dichloroethane, which was treated with anhydrous stannic chloride to give II. From 1.0 g. (0.003 mole) of tetraphenylethylene (I) was obtained after several recrystallizations from ethanol-benzene 0.1 g. (10%) of II, m.p. 236-238°; lit. m.p. 235° (28).

Photolysis of Tetraphenylethylene (I).--A 500-ml. round-bottomed quartz flask fitted with a reflux condenser and containing 835 mg. (0.0025 mole) of I dissolved in 300 ml. of cyclohexane was irradiated by means of an A-H4 mercury arc with Pyrex jacket removed during 78.5 hours while oxygen gas was bubbled through the solution. Evaporation of the solvent gave a yellowish solid which after recrystallization from acetone amounted to 450 mg., m.p. 225-235°; the infrared spectrum of this material indicated that it was essentially pure II. Further concentration of the mother liquors gave an additional 90 mg. of material which was shown by its infrared spectrum to be about 80 percent pure product. The total yield of II was 63 percent. Material from another run purified by six recrystallizations from ethanol-benzene melted at 239-240°; the melting point was not depressed on admixture with authentic 9,10-diphenylphenanthrene.

A quartz flask was used because it was shown that Pyrex absorbed light of the wavelengths effective in causing the photolysis.

Photolysis of trans-Stilbene (III).--A 500-ml. round-bottomed quartz flask containing a magnetically stirred solution of 2.3 g. (0.013 mole) of trans-stilbene (III) in 125 ml. of cyclohexane under an oxygen pressure of 10 lbs./in.^{2} was cooled by a jet of air and irradiated with a jacketless A-H4 mercury arc for 70 hours. Evaporation of the solvent and recrystallization of the residual solid from ethanol gave 0.8 g. of phenanthrene (IV), m.p. 99.5-100.5°; the melting point was not depressed on admixture with authentic phenanthrene. Concentration of the mother liquors gave an additional 0.25 g. of phenanthrene, m.p. 99.0-100.5°. The total yield of phenanthrene (IV) was 46 percent.

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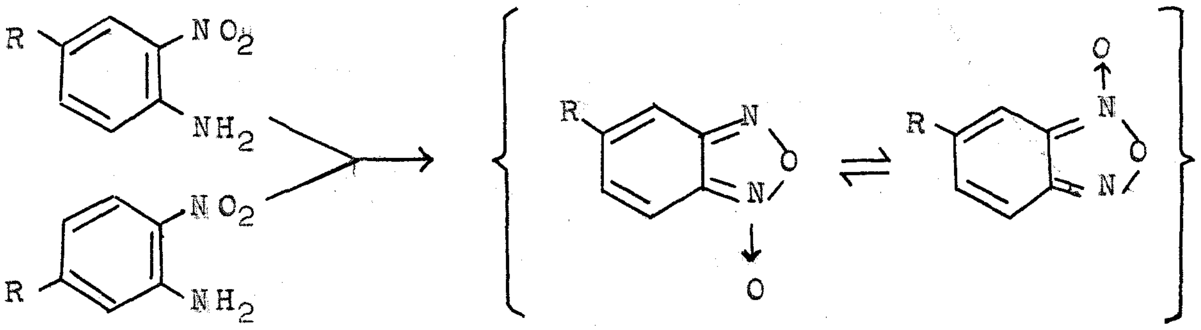
PROPOSITIONS

1. The most satisfactory explanation for the fact that a single substituted benzfurazan oxide is obtained from the oxidation of either 4- or 5-substituted o-nitroanilines involves the equilibration of the two possible benzfurazan oxide tautomers.



It is proposed that by a suitable choice of substituent and reaction conditions it should be possible to isolate the less stable tautomer and demonstrate its facile conversion to the more stable form.

2. It is proposed that a study using ^{14}C-diazomethane would serve to distinguish between the two postulated (1) mechanisms for the reaction of diazomethane with alkyl ethers.

3. It is proposed that the scope and the mechanism of the photochemical synthesis of phenanthrenes from stilbenes be studied.

4. It is proposed that an Arndt-Eistert reaction of 2-phenyl-3-butenoic acid provides a favorable case for the previously unobserved formation of an abnormal product, 5-phenyl-4-pentenoic acid.

5. It has been postulated (2) that selenium oxychloride undergoes auto-ionization.

$$2SeOCl_2 \rightleftharpoons SeOCl_2 \cdot SeOCl^+ + Cl^-$$

This hypothesis could be tested by a kinetic study of the exchange of radioactive chloride ion in solutions of KCl^{36} in selenium oxychloride.

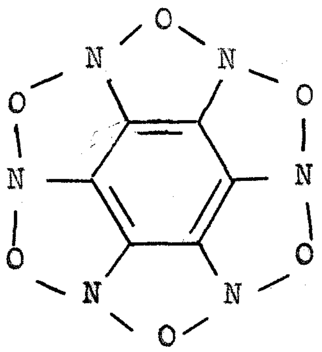
6. It is proposed that an electron diffraction study and a re-determination of the molecular weight of "phosphorous tetroxide" be carried out to elucidate its structure.

7. Although diphosphine, P_2H_4 is considered to be the phosphorous analog of hydrazine, it is possible that free-rotation occurs about the P-P bond in diphosphine whereas the rotation about the N-N bond in hydrazine is restricted (3). A structural study is proposed.

8. An attempt (4) to synthesize tetraphenylcyclobutadiene from diphenylacetylene photochemically yielded instead 1,2,3-triphenylnaphthalene. It is proposed that the photolysis be carried out with 2,6,2',6'-tetrafluorodiphenylacetylene in an effort to avoid the formation of a naphthalene derivative.

9. A synthesis of cyclopropandione is proposed. Enolization of this molecule would produce a structure predicted by molecular orbital theory to have a substantial delocalization energy.

10. The molecule shown below might have interesting chemical and physical properties as well as practical uses as an explosive, a dye or a fungicide. A synthesis for this compound is proposed.



11. The quality and style of Czechoslovakian folk-dance music played in this country is found by the majority of people of Czechoslovakian descent to be far inferior to the same music as it is played in Europe. In view of the importance of this music to these people, an effort should be made to raise the standards in this field of music in this country. Methods of achieving this goal are proposed.

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