

under oxygen at 60° for 16 hr. The visible absorption spectra revealed that less than 0.03×10^{-3} mmole of stilbenequinone was present in the sample. On evaporation to dryness at room temperature an orange solid was obtained. This solid on dissolution in chlorobenzene yielded an absorption spectra which corresponded to the presence of 4.54×10^{-3} mmole of the stilbenequinone present in the original sample. A spot identical with that obtained from a pure sample of the stilbenequinone was also observed on a tlc plate.

Reaction of Ia with a 2,6-Di-*t*-butyl-4-Methylphenol. A mixture of 102.6 mg (0.27 mmole) of 4-(4-methoxyphenoxy)-2,4,6-tri-*t*-

butyl-2,5-cyclohexadien-1-one and 80.8 mg (0.38 mmole) of 2,6-di-*t*-butyl-4-methylphenol in 50 cc of benzene was refluxed 6 hr. The solvent was removed under reduced pressure and the residue taken up in an appropriate volume of chloroform and analyzed by infrared utilizing the absorbance at 6.26μ . Analysis shows 36.4 mg (0.084 mmole) of quinone. A spot identical with that obtained from a pure sample of stilbenequinone was observed on a tlc plate.

Acknowledgment. The authors acknowledge the expert technical assistance rendered by Mrs. L. Skewes, Miss I. Golebiewska, and Mr. F. Ferris.

Photochemical Transformations of an *o*-Vinylbenzophenone

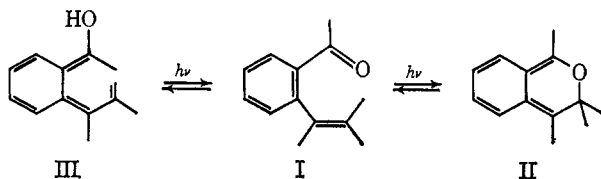
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Abstract: 2-(2-Methyl-1-phenylpropenyl)benzophenone (V) has been found to be photochromic at low temperatures. The colored species, which appears to be the valence tautomer VI, could be trapped as a Diels-Alder adduct with tetracyanoethylene. Prolonged ultraviolet irradiation of V in benzene afforded 1,1-dimethyl-2,3-diphenyl-2,3-epoxyindan (VIII), while in methanol 4,4-dimethyl-1,3-diphenyl-1-methoxyisochroman (X) was formed. The nature of the possible intermediates involved in the formation of VIII and X is discussed.

While the photolyses of a number of γ,δ -unsaturated ketones have been shown to give bicyclic oxetanes,^{1,2} the photochemistry of simple aliphatic $\alpha,\beta,\gamma,\delta$ -unsaturated ketones is complicated by light-induced polymerization.³ However, on incorporation of the γ,δ double bond into a ring such as in β -ionone,^{3,4} a photochemical ring-chain tautomerization can be established between the *cis*-dienone and a 2H-pyran.⁵ As part of a study of photochromism, an investigation of a related system containing an *o*-vinylphenone moiety (I) seemed of interest. A transformation of this compound analogous to the dienone-pyran interconversion could be envisioned in which irradiation of I might generate the colored quinonoidal structure (II), which might then undergo thermal reconversion to I in the dark.⁶ Alternatively, if I contained suitably situated alkyl groups, a reversible photoenolization ($I \rightleftharpoons III$) might take place in analogy to the photochemical reactions of *o*-alkylbenzophenones.⁷



(1) R. Srinivasan, *J. Am. Chem. Soc.*, **82**, 775 (1960).

(2) N. C. Yang, M. Nussim, and D. R. Coulson, *Tetrahedron Letters*, 1525 (1965).

(3) G. Buchi and N. C. Yang, *J. Am. Chem. Soc.*, **79**, 2318 (1957).

(4) P. de Mayo, J. B. Stothers, and R. W. Yip, *Can. J. Chem.*, **39**, 2135 (1961).

(5) E. N. Marvell, G. Caple, T. A. Gosink, and G. Zimmer, *J. Am. Chem. Soc.*, **88**, 619 (1966).

(6) For a related photochromic system in which the color changes are the inverse, see R. S. Becker and J. Michl, *ibid.*, **88**, 5931 (1966).

(7) (a) N. C. Yang and C. Rivas, *ibid.*, **83**, 2213 (1961); (b) A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2051 (1963); (c) E. F. Ullman

Results

The compound chosen for study was the known 2-(2-methyl-1-phenylpropenyl)benzophenone (V),⁸ prepared by acid-catalyzed ring opening of 1,3-dihydroxy-2,2-dimethyl-1,3-diphenylindan (IV). While exposure of colorless solutions of V to high intensity ultraviolet light affected no visible changes at room temperature, at -78° in ethyl acetate, acetone, methylene chloride, or isopropyl alcohol a moderately intense orange color developed. The color faded slowly in the dark at -78° (~ 30 min) but the rate increased greatly at higher temperatures, and the color completely faded upon allowing the solution to warm to approximately -40° . A more intense coloration was obtained by irradiation of an ethanol-ether glass containing V at -196° . Rapid photobleaching occurred upon exposure of the colored solutions or glass to strong visible light.

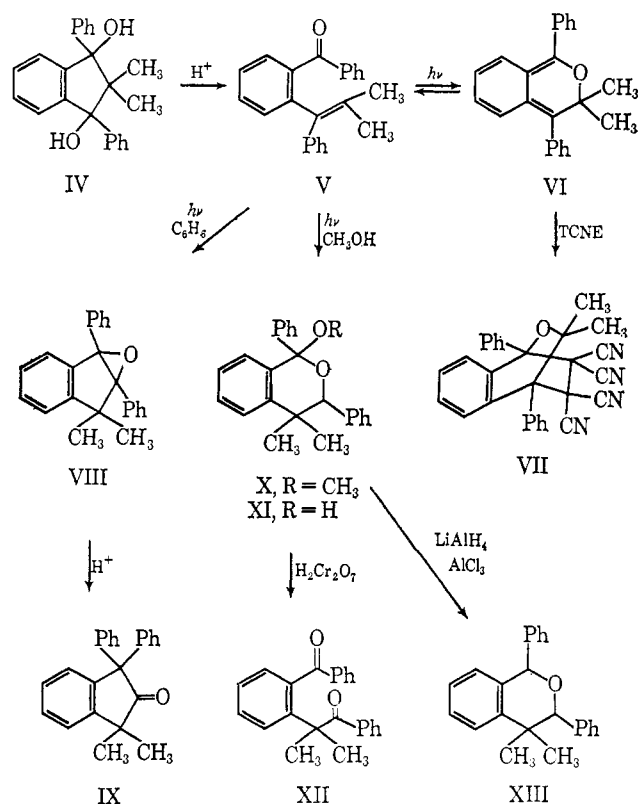
Qualitative observations on the effect of certain additives on the colored species provided no support for a photoenol structure such as III but were consistent with the assignment of the 2H-pyran structure VI to the colored species. Thus, no noticeable change in the intensity, color, or fading rate was observed when V was irradiated at -78° in the presence of small amounts of trifluoroacetic acid, triethylamine, or dilute aqueous sodium hydroxide. Since these reagents would all be expected to affect the stability or color of a photoenol, this structure can be safely eliminated. On the other hand, color formation was completely suppressed in the presence of tetracyanoethylene (TCNE), and addition of this reagent to a preformed orange solution resulted in the immediate discharge of the color. This behavior was consistent with the

and K. R. Huffman, *Tetrahedron Letters*, 1863 (1965); (d) K. R. Huffman, M. Loy, and E. F. Ullman, *J. Am. Chem. Soc.*, **87**, 5417 (1965).

(8) F. V. Brutcher and H. J. Cenci, *J. Org. Chem.*, **21**, 1543 (1956).

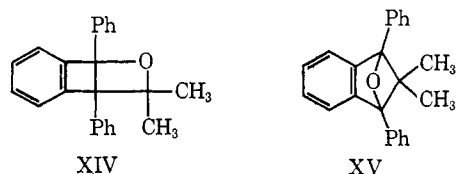
expected tendency of VI to undergo a rapid Diels-Alder reaction with tetracyanoethylene, a process which was confirmed by a preparative scale photolysis of V in the presence of 1 equiv of TCNE at room temperature. In this way an 80% yield of an adduct VII was formed which showed only benzenoid absorption in the ultraviolet, and showed in the infrared only very weak nitrile and no carbonyl or hydroxyl absorption (Chart I). The nmr spectrum was also consistent with the assigned structure and showed singlets corresponding to nonequivalent methyl groups at τ 8.43 and 8.87.

Chart I



Prolonged ultraviolet irradiation of V in benzene or ethyl acetate solution in the absence of TCNE afforded a crystalline isomer VIII with conversions up to 56%. The absence of carbonyl or hydroxyl bands in the infrared and the presence of only benzenoid absorption in the ultraviolet suggested that this product was a cyclic ether. In the nmr spectrum a single aliphatic singlet at τ 8.68 allowed that the methyl groups might be identically situated, but of course did not eliminate the possibility of an accidental coincidence of signals from differently oriented methyls.

Since these data, together with the aforementioned photochemical conversion of γ,δ -unsaturated ketones to bicyclic oxetanes,² suggested that the photoisomer



might have structure XIV or XV,⁹ an attempt was made

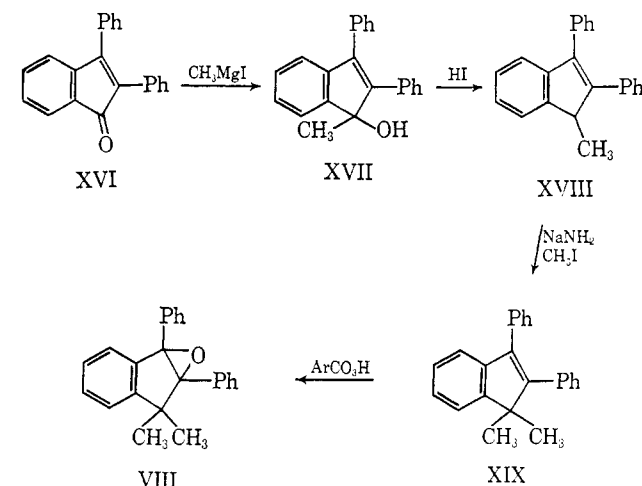
(9) Although a compound believed to be XV has been reportedly obtained from reactions of IV,¹⁰ this structural assignment has recently been questioned.¹¹

to cleave the oxetane ring with hydrochloric acid. The resulting hydrolysis product was an isomeric ketone, isolated in 94% yield, which had infrared and ultraviolet spectra [$\lambda_{\text{max}}^{\text{mull}}$ 5.72 μ ; $\lambda_{\text{max}}^{\text{C}_6\text{H}_{12}}$ 262 m μ (ϵ 1200), 268 (1550), 275 (1550), and \sim 315 (390)] that were very similar to those reported for 1,1-diphenyl-2-indanone.¹² The most plausible structure, therefore, appeared to be 1,1-dimethyl-3,3-diphenyl-2-indanone (IX), a previously reported compound¹³ of a similar melting point.

As formation of IX could not be reconciled with either of the oxetane structures XIV or XV for the photoisomer, it was necessary to consider other cyclic ethers which might be logical precursors to IX. The reported formation of IX *via* a pinacol rearrangement of 2,3-dihydroxy-1,1-dimethyl-2,3-diphenylindan¹³ suggested the possibility that the photoisomer might be 1,1-dimethyl-2,3-diphenyl-2,3-epoxyindan (VIII). An acid-catalyzed opening of the epoxide ring in VIII should lead to the same carbonium ion as in the pinacol rearrangement with the resultant formation of the indanone IX.

In order to confirm structure VIII for the photoisomer, an independent synthesis was carried out (Chart II) starting from 2,3-diphenylindenone (XVI). Treat-

Chart II



ment of XVI with methylmagnesium iodide followed by hydriodic acid led to the indene XVIII which had previously been synthesized by another route.¹⁴ Alkylation of XVIII appeared to give XIX rather than 1,3-dimethyl-1,2-diphenylindene since only a single methyl signal in the nmr was observable. The product obtained upon *m*-chloroperbenzoic acid oxidation of XIX proved to be identical with the epoxide VIII obtained by photolysis of V.

Photolysis of the ketone V in methanol solution resulted in formation of a 72% yield of a crystalline 1:1 adduct with methanol. The benzenoid ultraviolet absorption and the absence of carbonyl or hydroxyl bands in the infrared spectrum of this adduct again suggested a cyclic ether structure. The nmr spectrum

(10) T. A. Geissman and V. Tulagin, *J. Am. Chem. Soc.*, **63**, 3352 (1941).

(11) S. Searles, Jr., in "Heterocyclic Compounds with Three- and Four-Membered Rings," Part 2, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 1035.

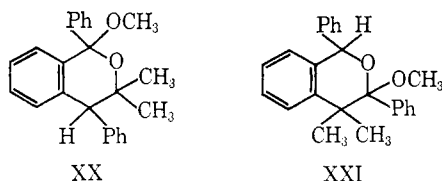
(12) A. L. Wilds, *et al.*, *J. Am. Chem. Soc.*, **84**, 1503 (1962).

(13) C. F. Koelsch and C. D. LeClaire, *J. Org. Chem.*, **6**, 516 (1941).

(14) C. F. Koelsch and P. R. Johnson, *J. Am. Chem. Soc.*, **65**, 567 (1943).

showed, in addition to the aromatic protons, singlets at τ 4.91 (one tertiary H), 6.88 (one OCH₃), 8.72 (one CH₃), and 8.77 (one CH₃). The compound was rapidly demethylated by treatment with hot dilute mineral acid, and the resulting alcohol (OCH₃ signal replaced by a single proton singlet at τ 7.25 in the nmr) could be reconverted to its precursor by recrystallization from methanol containing a trace of sulfuric acid.

These data strongly suggest that the methanol adduct is a cyclic ketal which can be reversibly hydrolyzed to a stable cyclic hemiketal. Although structure XX appears to fit all these data, and its formation can be rationalized by assuming a 1,4 addition of methanol to the proposed valence tautomer VI, the rearranged



nature of the photoproduct VIII raised the possibility that the methanol adduct might have arisen from a rearranged precursor. This suspicion was borne out by the chromic acid oxidation of the methanol photoadduct which afforded the known 2-(*o*-benzoylphenyl)-isobutyrophenone (XII)¹³ in 97% yield. This oxidation product could not have been formed from XX, but might be expected to form from either X or XXI. Of these alternatives, only structure X for the photoadduct (and thus XI for the hemiketal) appears to be consistent with the nmr and mass spectral data.

The mass spectrum of the methanol photoadduct displayed its most intense peak corresponding to the loss of benzaldehyde at m/e 238 together with a weak parent peak and a somewhat stronger peak corresponding to the loss of OCH₃. This fragmentation pattern is in far better accord with X than with XXI which might be expected to readily lose methyl benzoate rather than benzaldehyde. Further, the differences in the nmr spectra of the photoadduct and its lithium aluminum hydride-aluminum chloride reduction product, 4,4-dimethyl-1,3-diphenylisochroman (XIII), strongly favored structure X over XXI for the photoadduct. Thus, the reduction product XIII displayed a new tertiary hydrogen singlet at τ 4.06 in addition to a τ 5.23 singlet that appears to correspond to the τ 4.91 tertiary hydrogen signal of the photoadduct. The hydrogen giving the τ 4.06 signal therefore appears to have replaced the methoxy group during the reduction. Since this signal is very similar to the tertiary hydrogen signal of benzhydrol at τ 4.20,¹⁵ while the nearly unchanged signal at τ 5.23 is close to that of the 3-hydrogen in 3-phenylisochroman at τ 5.42,¹⁶ the new hydrogen appears to have been introduced into the 1 rather than the 3 position of the isochroman XIII. The methanol photoadduct must therefore be X and not XXI.

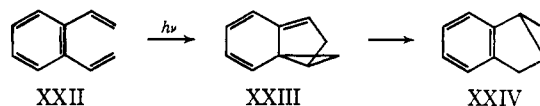
Discussion

The photochemical reactions described above are summarized in Chart I. The over-all photochemical

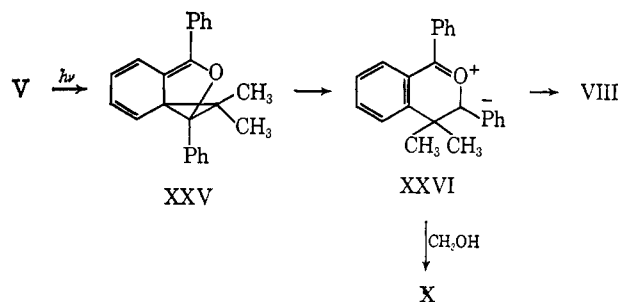
(15) Nmr Spectra Catalog, Varian Associates, Palo Alto, Calif., 1963, p 607.

(16) R. L. Vaulx, F. N. Jones, and C. R. Hauser, *J. Org. Chem.*, **29**, 1387 (1964).

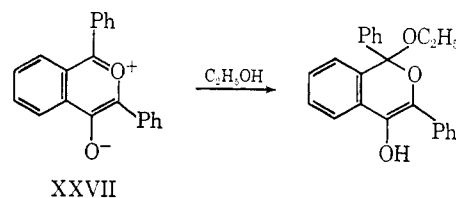
change that occurs on irradiation of V in benzene finds close analogy with the photochemical rearrangement of *o*-divinylbenzene (XXII) in which the benzobicyclo[3.1.0]hexene (XXIV) is formed.¹⁷ In both these reactions the formation of the nonaromatic intermediates



XXIII and XXV, respectively, appears required by the



structure of the products. Moreover, the existence of additional intermediates giving rise to or being derived from XXIII or XXV cannot be excluded. Indeed, the observation that the ketal X rather than the epoxide VIII is formed in methanol suggests that another intermediate may possibly be formed, since it seems unlikely that methanol would trap XXV in an uncatalyzed reaction.¹⁸ On the other hand, if XXV underwent spontaneous ring cleavage to give the zwitterion XXVI followed by collapse of XXVI to the epoxide VIII, methanol might be expected to interfere by rapid uncatalyzed addition to XXVI. The methanol addition reaction finds analogy in the uncatalyzed addition of ethanol to the zwitterionic benzopyrylium oxide XXVII,¹⁹ and would be expected to lead to the observed product X. The zwitterion XXVI, therefore, is very



probably an intermediate in the photochemical formation of the epoxide VIII, although it is problematical if there exists a related intermediate in the divinylbenzene rearrangement.

The probable intermediacy of XXVI raises a question concerning the identity of the colored species formed on irradiation of the ketone V at low temperature. Specifically, it is now necessary to consider whether this colored species may, in fact, be XXVI rather than the above suggested cyclic enol ether VI. Although this possibility appears particularly plausible since, like VI, the zwitterion XXVI would be expected to add TCNE, it could be shown to be incorrect by several lines of reasoning. First, methanol did not accelerate the rate of

(17) (a) M. Pomerantz, *J. Am. Chem. Soc.*, **89**, 694 (1967); (b) J. Meinwald and P. H. Mazzocchi, *ibid.*, **89**, 696 (1967).

(18) Although catalyzed addition of methanol to XXV by adventitious acid is possible, products other than X might result.

(19) E. F. Ullman and W. A. Henderson, Jr., *J. Am. Chem. Soc.*, **88**, 4942 (1966).

fading of the colored transient as would be required if this species had structure XXVI. Secondly, it was found that on irradiation of the ketone V in the presence of TCNE the ketone was destroyed approximately twice as rapidly as on irradiation in the absence of this reagent, even though the TCNE did not absorb the light that was used. This suggests that the TCNE must react with a transient species which reverts to the starting ketone at a rate that is competitive with possible rearrangement of the transient to the epoxide VIII. Since it would be unlikely for the zwitterion XXVI to revert spontaneously to the starting ketone, we conclude that the colored species must be the cyclic enol ether VI. Thirdly, the structures of the TCNE adducts derived from VI and XXVI would be different, and the mass spectrometry data are in better accord with the adduct VII derived from VI. Thus, while no parent peak could be observed, at low voltages (10 eV) the first principal fragment corresponded to the loss of acetone (m/e 382), and at 70 eV all the major peaks observed in the mass spectrum of the starting ketone V were found with similar relative intensities. The adduct, therefore, appears to fragment to acetone and V, which is consistent with a structure resulting from TCNE addition to VI but not to XXVI.

The identification of VI as the colored species raises an additional question concerning its possible intermediacy in the formation of the nonaromatic intermediate XXV. Although the data are not demanding on this point, it appears very probable that VI is not an intermediate but represents the product of a second primary process competitive with the formation of intermediate XXV. This tentative conclusion follows from the high rate of thermal rearrangement of VI at room temperature as demonstrated by the absence of observable color even under intense irradiation. The very low concentrations of VI that must prevail under these conditions would, therefore, militate against any photochemical reaction of this intermediate as a step in the moderately efficient formation of XXV.

Experimental Section²⁰

Photochemical Reactions. Ultraviolet irradiations were carried out using a 1000-w General Electric B-H6 high-pressure mercury arc equipped with filters transmitting 300–370-m μ light or with a Rayonet photochemical reactor equipped with 16 1.5-w tubes having a peak emission at 350 m μ . Studies using visible light that are referred to in the text were conducted using a 500-w Argus slide projector equipped with a 430-m μ cutoff filter. The reactions were carried out in Pyrex glass vessels, and the solutions were deoxygenated by bubbling with nitrogen prior to irradiation.

2-(2-Methyl-1-phenylpropenyl)benzophenone (V). A. The procedure of Brucher and Cenci⁸ afforded V as a pale yellow fluorescent oil, which was purified by chromatography over neutral alumina. It showed $\lambda_{\text{max}}^{\text{soln}}$ 6.00 μ and $\lambda_{\text{max}}^{\text{CH}_2\text{OH}}$ 245 m μ (ϵ 22,700). The nmr spectrum in CDCl₃ showed a singlet methyl signal at τ 8.30, but in C₆D₆ the spectrum showed two peaks at τ 8.29 and 8.34.

Anal. Calcd for C₂₃H₂₀O: C, 88.42; H, 6.45; mol wt, 312. Found: C, 88.16; H, 6.60; m/e 312.

B. A solution of 10.0 g of 1,3-dihydroxy-1,3-diphenyl-2,2-dimethylindan (IV), prepared according to the method of Alder and Fremery,²¹ in 225 ml of methanol was treated with 50 ml of concentrated hydrochloric acid and refluxed for 3.5 hr. The cooled mixture was diluted with water and extracted twice with ether.

(20) All nmr spectra were measured in deuteriochloroform unless otherwise noted. Infrared spectra were run in mineral oil suspensions. Melting points are corrected.

(21) K. Alder and M. Fremery, *Tetrahedron*, **14**, 190 (1961).

The extracts were washed once with water and once with dilute sodium bicarbonate, then dried, and evaporated to give 9.2 g (97%) of V as a pale yellow oil. The spectra of this material were identical with those of the chromatographed product obtained by method A.

Photoaddition of Tetracyanoethylene to 2-(2-Methyl-1-phenylpropenyl)benzophenone (V). A solution of 155 mg of V and 65 mg of tetracyanoethylene in 15 ml of ethyl acetate was irradiated for 6 hr using a GE B-H6 lamp. The solution was then evaporated, and the solid residue was triturated with ether to give 175 mg (80%) of VII, as colorless crystals, mp 149–150° dec. Recrystallization from methylene chloride–petroleum ether raised the melting point to 150.5–151.5° dec.

Anal. Calcd for C₂₃H₂₀N₄O: C, 79.07; H, 4.58; N, 12.72. Found: C, 79.44; H, 4.51; N, 12.87.

Photolysis of V in Benzene. A solution of 2.50 g of 2-(2-methyl-1-phenylpropenyl)benzophenone (V) in 200 ml of benzene was irradiated under nitrogen with a Rayonet photochemical reactor. After 24-hr irradiation the solution was evaporated and the resulting oil was crystallized from ether–petroleum ether to give 1.35 g of colorless crystals of 1,1-dimethyl-2,3-diphenyl-2,3-epoxyindan (VIII), mp 151–156°. Chromatography of the mother liquor over 25 g of grade I neutral alumina gave an additional 0.05 g of VIII (total of 56%) together with 0.43 g (17%) of recovered V. Two recrystallizations of VIII from petroleum ether afforded colorless crystals, mp 155.5–157.5°.

Anal. Calcd for C₂₃H₂₀O: C, 88.42; H, 6.45; mol wt, 312. Found: C, 88.59; H, 6.56; m/e 312.

1,1-Dimethyl-3,3-diphenyl-2-indanone (IX) from Acid-Catalyzed Rearrangement of VIII. A refluxing solution of 0.31 g of 1,1-dimethyl-2,3-diphenyl-2,3-epoxyindan (VIII) in 45 ml of methanol was treated with 30 ml of concentrated hydrochloric acid and the resulting solution was refluxed for 1 hr. The cooled mixture was filtered to give 0.29 g (94%) of IX as colorless crystals, mp 120.5–122°. Recrystallization from methanol–water raised the melting point to 121–122°. Koelsch and LeClaire report mp 125–126°.¹³

Anal. Calcd for C₂₃H₂₀O: C, 88.42; H, 6.45. Found: C, 88.12; H, 6.45. The nmr spectrum showed a singlet methyl peak at τ 8.70.

1-Methyl-2,3-diphenylindene (XVIII). A solution of 3.33 g of 1-hydroxy-1-methyl-2,3-diphenylindene (XVII)²² in 55 ml of acetic acid containing 6 ml of 47% hydriodic acid was placed in an oil bath which had been preheated to 130°. After 15 min the dark solution was poured into ice water containing enough sodium bisulfite to destroy the iodine which was present. The resulting amorphous solid was filtered off while the mixture was still cold and crystallized from petroleum ether to yield 1.22 g of colorless crystals, mp 102–105°. A second crop of 0.20 g, mp 101.5–104.5°, was obtained from the filtrate giving a total yield of 45%. Two recrystallizations from ethanol afforded material of mp 104.5–106.5°. Koelsch and Johnson report mp 106.5°.¹⁴ The assigned structure XVIII was supported by the nmr spectrum which displayed a doublet (3 H) centered at τ 8.75 and a quartet (1 H) centered at τ 6.03.

1,1-Dimethyl-2,3-diphenylindene (XIX). To a 20-ml liquid ammonia solution of sodamide prepared from 0.10 g of sodium, was added dropwise with stirring a solution of 0.56 g of 1-methyl-2,3-diphenylindene in 20 ml of ether followed by 1.4 g of iodo-methane. After stirring for 3 hr, solid ammonium chloride was added and the ammonia was allowed to evaporate. An ethereal extract of the reaction mixture was filtered and evaporated. The resulting yellow oil crystallized from ethanol to give 0.12 g (20%) of XIX as colorless crystals, mp 114–115°. One recrystallization from ethanol increased the melting point to 115.5–116.5°. The nmr spectrum showed only one singlet at τ 8.53 corresponding to two methyl groups.

Anal. Calcd for C₂₃H₂₀: C, 93.20; H, 6.80. Found: C, 93.25; H, 6.78.

1,1-Dimethyl-2,3-diphenyl-2,3-epoxyindan (VIII). A solution of 13 mg of 1,1-dimethyl-2,3-diphenylindene and 10 mg of *m*-chlorobenzoic acid (1.25 equiv) in 3 ml of methylene chloride was kept at room temperature for 40 hr. The solution was diluted with more solvent and washed once with 5% sodium carbonate. The dried solution, on evaporation, gave an oil which was crystallized twice from petroleum ether to give colorless crystals of VIII, mp 153–156°. The identity of this material with the sample from photolysis of V was established by mixture melting point and comparison of infrared spectra.

(22) R. C. Fuson and F. E. Mumford, *J. Org. Chem.*, **17**, 255 (1952).

Photolysis of V in Methanol. A solution of 2.50 g of 2-(2-methyl-1-phenylpropenyl)benzophenone (V) in 200 ml of methanol was irradiated in the Rayonet reactor for 24 hr. The solution was concentrated *in vacuo* and chilled to give 2.0 g (72%) of 4,4-dimethyl-1,3-diphenyl-1-methoxyisochroman (X), mp 125–130°. After one recrystallization from methanol the melting point was 128–145°. Although a sharp melting product could not be obtained, the nmr was consistent with the presence of a single isomer with singlets at τ 4.91 (one tertiary H), 6.88 (one OCH₃), 8.72 (one CH₃), and 8.77 (one CH₃).

Anal. Calcd for C₂₄H₂₄O₂: C, 83.69; H, 7.02; mol wt, 344. Found: C, 83.62; H, 7.00; *m/e* 344.

4,4-Dimethyl-1,3-diphenyl-1-hydroxyisochroman (XI). A solution of 100 mg of X in 5 ml of acetic acid and 5 ml of 6 *N* sulfuric acid was warmed on the steam bath for 1 hr. The solution was poured into ice water to give XI as a colorless solid, mp 60–80°. Attempted recrystallization of this material was unsuccessful, presumably due to equilibration between the two possible stereoisomers.

Anal. Calcd for C₂₃H₂₂O₂: C, 83.60; H, 6.71. Found: C, 83.73; H, 6.74.

Infrared spectra of the product in a mull or solution showed no carbonyl absorption. The nmr spectrum in CCl₄ showed an aromatic multiplet centered at τ 2.73 (14 H) and singlets at τ 4.75 (one tertiary H), 7.25 (one OH, exchanged with D₂O), 8.71 (one CH₃), and 8.79 (one CH₃).

Oxidation of 4,4-Dimethyl-1,3-diphenyl-1-methoxyisochroman. A warm solution of 172 mg of X in 10 ml of acetic acid was diluted to the cloud point with 6 *N* sulfuric acid and then treated with 300 mg of solid sodium dichromate dihydrate. The resulting solution was heated on the steam bath for 2 hr, cooled, and diluted with a large volume of water. The colorless product, which crystallized on standing, was filtered off and washed with water to give 160

mg (97%) of 2-(*o*-benzoylphenyl)isobutyrophenone (XII), mp 113–114.5°. Recrystallization from ethanol–water raised the melting point to 115–116° which was identical with the melting point previously reported for this compound.¹³ The infrared spectrum displayed aryl and diaryl ketone absorption at $\lambda_{\text{max}}^{\text{mull}}$ 5.97 and 6.02 μ .

Anal. Calcd for C₂₃H₂₀O₂: C, 84.12; H, 6.14. Found: C, 83.75; H, 6.18.

4,4-Dimethyl-1,3-diphenylisochroman (XIII). A cold stirred slurry of 40 mg (0.001 mole) of lithium aluminum hydride in 5 ml of ether was treated dropwise with a solution of 530 mg (0.004 mole) of anhydrous aluminum chloride in 20 ml of ether.²³ A solution of 340 mg (0.001 mole) of X in 10 ml of ether was then added, and the reaction mixture was stirred at room temperature for 2 hr and then at reflux for 0.5 hr. After cooling the mixture in an ice bath and decomposing the unreacted lithium aluminum hydride by cautious dropwise addition of water, about 10 ml of 6 *N* sulfuric acid was added, and the ether layer was separated, dried, and evaporated. The colorless solid residue was recrystallized from methanol to give 220 mg (70%) of XIII as colorless crystals, mp 117–118°. The nmr spectrum displayed singlets at τ 4.06 (one H), 5.23 (one H), and 8.70 (six H) together with a 14 H aromatic multiplet.

Anal. Calcd for C₂₃H₂₂O: C, 87.86; H, 7.05. Found: C, 88.08; H, 7.10.

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(23) Cf. procedure of E. L. Eliel, V. G. Badding, and M. N. Rerick, *J. Am. Chem. Soc.*, **84**, 2371 (1962).

The Photochemistry of 2,3-Homotropone¹

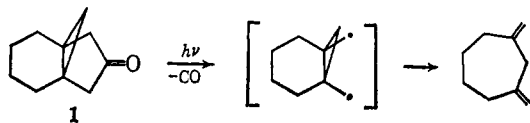
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Abstract: Irradiation of 2,3-homotropone under a variety of conditions gives rise principally to a lone tricyclic photoisomer (two are possible) and lesser quantities of tropilidene, bicyclo[4.2.0]octa-4,7-dien-2-one, and 1,3,5-cyclooctatrien-7-one. The configuration of the tricyclic ketone has been established by an unequivocal synthesis of its dihydro derivative starting with norbornene. The possible mechanistic pathways to the four photoproducts are discussed.

An organic molecule which possesses a cyclopropane ring in close proximity to a carbonyl group may be expected to be photolabile because of the unsaturated character of the three-membered ring.^{3,4}

Thus, the effect of a cyclopropyl group positioned β, γ to a ketone carbonyl function frequently is to facilitate photodecarbonylation because of the stabilization available to the resulting (di)radical.⁴ In the case of



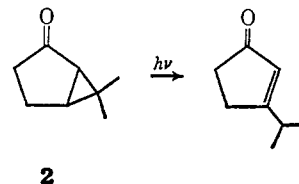
(1) Support of this research by means of a grant from The Graduate School of The Ohio State University is gratefully acknowledged.

(2) Alfred P. Sloan Foundation Research Fellow.

(3) For a recent compilation of many examples, see R. O. Kan, "Organic Photochemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1966.

(4) J. E. Starr and R. H. Eastman, *J. Org. Chem.*, **31**, 1393 (1966).

"conjugated" ketones such as 2,⁵ the primary photochemical process often involves ring opening.³



The presence of added unsaturation of the type displayed by the bicyclo[3.1.0]hexenones 3⁶ and 4⁷ may or may not foster more deep-seated rearrangements.⁸

(5) O. L. Chapman, T. A. Rettig, A. A. Griswold, A. I. Dutton, and P. Fitton, *Tetrahedron Letters*, 2049 (1963).

(6) J. W. Wheeler, Jr., and R. H. Eastman, *J. Am. Chem. Soc.*, **81**, 236 (1959).

(7) H. E. Zimmerman, R. Keese, J. Nasielski, and J. S. Swenton, *ibid.*, **88**, 4895 (1966).

(8) For additional recent examples, refer to A. M. Small, *Chem. Commun.*, 243 (1965); H. Dürr, *Tetrahedron Letters*, 5829 (1966);