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Photo-induced Reactions. V.*[1] The Photochemical Reaction of a 2-Cyclohexenone, Pummerer's Ketone

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The ultraviolet irradiation of Pummerer's ketone (VIII) in methanol yielded a 1 : 1 methanol adduct IX in a good yield; this is a new type of product in the photochemical reaction of a 2-cyclohexenone, *i. e.*, a photochemical Michael-type addition of an alcohol to form a 3-alkoxy-cyclohexanone. The irradiation of VIII in isopropyl alcohol yielded an adduct, XI, analogous to IX and a photoketone, XIII, isomeric to VIII. The photoketone was also obtained by the irradiation of VIII in *t*-butyl alcohol, dioxane, or benzene. The mechanisms of these reactions are discussed.

The photochemical reaction of 2-cyclohexenones in various organic solvents has been investigated by many workers and shown to result in the formation of several types of products.[1-5] Among these reactions, the photochemical rearrangement of 2-cyclohexenones to bicyclo[3. 1. 0.]hexan-2-ones has been widely studied. Chapman *et al.*,[2a] found the rearrangement of 4, 4-dimethyl-2-cyclohexenone (I) to afford (*inter alia*) 6, 6-dimethylbicyclo[3. 1. 0.]hexan-2-one (II); Gardner *et al.*,[1c] had earlier shown cholest-4-en-3-one to undergo the same rearrangement. Furthermore Zimmerman *et al.*, found that the irradiation of 4, 4-diphenyl-2-cyclohexenone gave the stereoisomeric 5, 6-diphenylbicyclo[3. 1. 0.]hexan-2-ones, IV and V, as major products.[4a]

From the results mentioned above, it can be shown that the rearrangements of 2-cyclohexenones to bicyclo[3. 1. 0.]hexan-2-ones involves, at least formally, a switching of bonds *a* and *b via* path A or a switching of bonds *a* and *c via* path B, as is shown in Scheme 1. In the earlier stage of our investigation, it appeared that a 4, 4-diaryl-substituted 2-cyclohexenone rearranges to the product *via*

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*[1] Part V: T. Matsuura and K. Ogura, *J. Am. Chem. Soc.*, **88**, 2602 (1966). This work was preliminary reported in *J. Am. Chem. Soc.*, **88**, 2602 (1966) and was presented at the 19th Annual Meeting of the Chemical Society of Japan, March, 1966.

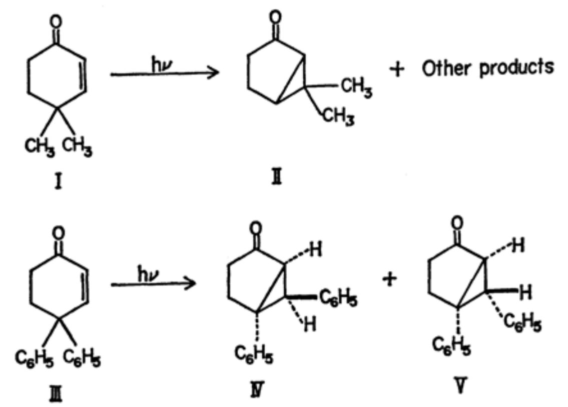
1) a) A. Butenandt, L. Poschmann, G. Failer, U. Schiedt and E. Bieckert, *Ann.*, **575**, 123 (1951); b) P. D. Gardner and H. F. Hamil, *J. Am. Chem. Soc.*, **83**, 3531 (1961); c) W. W. Kwie, B. A. Shoulder and P. G. Gardner, *ibid.*, **84**, 2268 (1962).

2) a) O. L. Chapman, T. A. Rettig, A. A. Griswold, A. I. Dutton and P. Fitton, *Tetrahedron Letters*, **1963**, 2049; b) O. L. Chapman, J. B. Sieja and W. J. Welstead, Jr., *J. Am. Chem. Soc.*, **88**, 161 (1966).

3) a) H. Wehrli, R. Wagner, K. Schaffner and O. Jeger, *Helv. Chim. Acta*, **46**, 678 (1963); b) B. Nann, D. Gravel, R. Schorta, H. Wehrli, K. Schaffner and O. Jeger, *ibid.*, **46**, 2473 (1963).

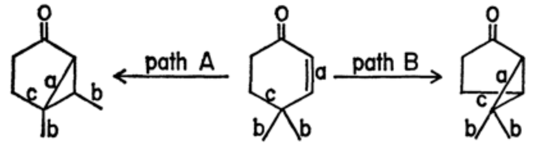
4) a) H. E. Zimmerman and J. W. Wilsom, *J. Am. Chem. Soc.*, **86**, 4036 (1964); b) H. E. Zimmerman, R. C. Hahn, H. Morrison and M. C. Wani, *ibid.*, **87**, 1138 (1965); c) H. E. Zimmerman, R. C. Lewis, J. J. McCullogh, A. Padwa, S. Stanley and M. Semmelhack, *ibid.*, **88**, 159 (1966) and references cited therein.

5) a) M. Pfau, R. Dulou and M. Vilkas, *Compt. rend.*, **254**, 1817 (1962); b) I. A. Williams and P. Blandon, *Tetrahedron Letters*, **1964**, 257.

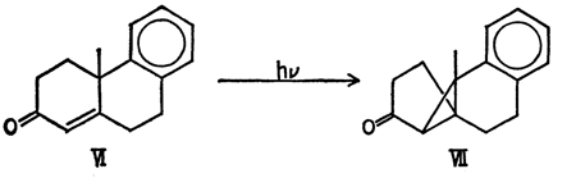


I II III IV V

path A, while a 4, 4-dialkyl-substituted 2-cyclohexenone does so *via* path B. In order to see whether a product in the rearrangement of 4-alkyl-4-aryl-substituted 2-cyclohexenones is formed *via* path A or path B, we initiated the photochemical reaction of Pummerer's ketone. While, during the course of our investigation, the rearrangement of a 4-alkyl-4-aryl-substituted 2-cyclohexenone, VI, to VII *via* path B has been reported,[2b,4c] we wish to report an additional example of a rearrangement *via* path A and a new type of photochemical reaction of 2-cyclohexenones, *i. e.*, a photochemical Michael-type addition of alcohol to form a 3-alkoxycyclohexanone.



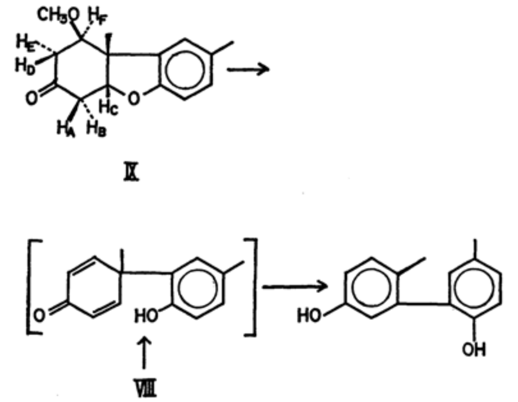
Scheme 1



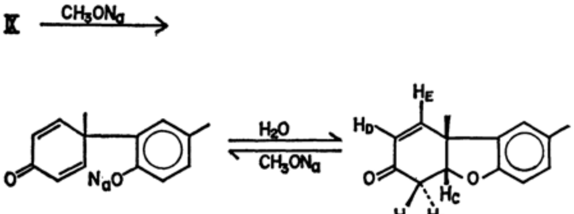
VI VII

Results and Discussion

The irradiation of a 1% solution of Pummerer's ketone VIII[6,7),*2] in methanol with a high-pressure mercury lamp (Pyrex filter) yielded 79%[*3] of a 1 : 1 methanol adduct, $C_{15}H_{18}O_3$, as a crystalline product. The infrared band at 1716 cm^{-1} (KBr) and the ultraviolet maximum at 229 mμ (log ε 4.17) of its semicarbazone indicate that the adduct is a saturated ketone. The structure IX for the adduct was suggested by the NMR spectrum (Table 1), which showed a singlet (τ 6.63) of a methoxyl group and two ABX patterns ($H_AH_BH_C$ and $H_DH_EH_F$). Structure IX was supported by the fact that both VIII and IX were converted to 2, 5'-dimethyl-2', 5-dihydroxybiphenyl with hydrobromic acid and acetic acid (1 : 1). These reaction can be interpreted as in Scheme 2.[6,7)] The structure assigned was further confirmed by the derivation of VIII from IX when the latter was treated sodium methoxide, followed by hydrolysis. Since it is known that the same treatment of VIII gives the sodium salt X which then reverts to VIII upon hydrolysis,[8)] the regeneration of VIII from IX is considered to proceed *via* X.



Scheme 2



X VIII

There are two possible stereochemical structures for X; their partial projection formulas are shown as i (as IX) and ii (as epimeric to IX). A comparison of the coupling constants, J_{DF} (12.0 cps) and J_{EF} (3.5 cps), indicates that the stereochemistry of the methanol adduct should be shown by formula i, but not by the formula ii, in which J_{DF} is expected to be approximately equal to J_{EF}.

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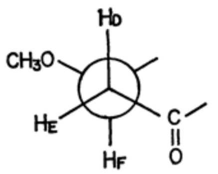
6) R. Pummerer, H. Puttfarchen and P. Schopflocher, *Ber.*, **58**, 1808 (1925).

7) D. H. R. Barton, A. M. Deflorin and O. E. Edwards, *J. Chem. Soc.*, **1956**, 530.

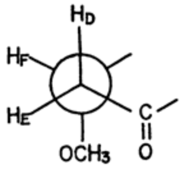
[*2] The cis ring fusion in Pummerer's ketone has been deduced by NMR spectrum in which the signal of the angular proton (H_C) appears as eight lines centered at τ 5.34 (Table 1). The same value of J_{AC} and J_{BC}, and a long-range coupling (J_{CE}=2 cps) between H_C and H_E indicate the cis fusion. Also see J. Shoji, *Chem. Pharm Bull.*, **10**, 483 (1962).

[*3] All yields were calculated on the basis of the reacted VIII.

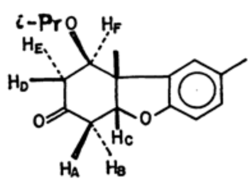
8) V. Arkley, F. M. Dean, A. Robertson and P. Sidisunthorn, *J. Chem. Soc.*, **1956**, 2322.



i



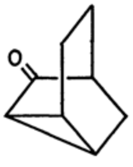
ii



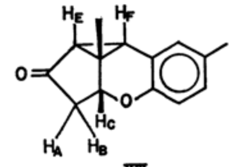
XI

The irradiation of Pummerer's ketone (VIII) in isopropyl alcohol under similar conditions yielded two crystalline products, an isopropyl alcohol adduct (37%), $C_{17}H_{22}O_3$, and a photoketone isomeric to VIII. The photoketone was also obtained by the irradiation of VIII in *t*-butyl alcohol (43%), dioxane (26%), or benzene (72%). In *t*-butyl alcohol, the adduct analogous to IX was not found in the reaction products. This is probably due to the steric hindrance of the *t*-butyl group. The spectral data of the isopropyl alcohol adduct were quite similar to those of IX (see Table 1 and Experimental Section), and structure XI was assigned.

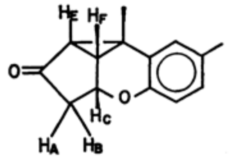
The photoketone shows an infrared band at 1734 cm^{-1}($CHCl_3$) which agrees with that of the cyclopentanone XII (1735 cm^{-1})⁹⁾ conjugated with a cyclopropane ring. The separation of the band into two bands, at 1732 and 1715 cm^{-1}, on a KBr disk measurement may be due to a Fermi-resonance coupling characteristic of cyclopentanones.¹⁰⁾ Furthermore, the photoketone shows a maximum at 240 mμ (log ε 4.14) in the differential curve between the ultraviolet spectrum of its semicarbazone and that of the photoketone or of IX. The maximum agrees with that of a semicarbazone conjugated with a cyclopropane ring.¹¹⁾ These data suggest that the photoketone possesses a bicyclo[3. 1. 0.]hexan-2-one system. Considering the paths A and B in Scheme 1, the structure of the photoketone can be represented by one of the formulas, XIII, XIV, or XV. Structure XV may be eliminated in view of the fact that the NMR signal of the aliphatic methyl group is not split. The small values of the coupling constants, J_{CE} and J_{CF}, cannot account for structure XIV in which the dihedral angle of H_C–C–C–H_F is estimated from its scale model to approximate 0°.¹²⁾ Thus it follows that structure XIII may be assigned to the photoketone; this is supported by the following reactions:



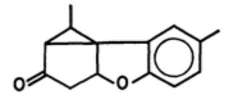
XII



XIII

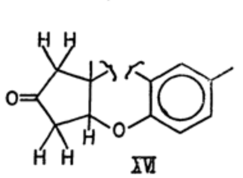


XIV

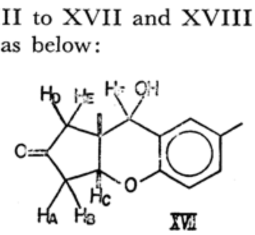


XV

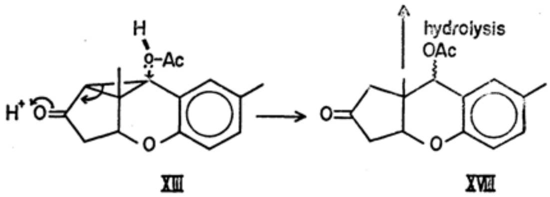
The treatment of the photoketone with 3% hydrobromic acid in acetic acid at room temperature gave 42% of a hydroxy ketone, $C_{14}H_{16}O_3$, and 34% of an acetoxy ketone, $C_{16}H_{18}O_4$, which was also obtained by the acetylation of the hydroxy ketone. The hydroxy ketone was characterized as a cyclopentanone from its infrared band at 1752 cm^{-1} ($CHCl_3$). Structure XVII was derived from the NMR spectrum (Table 1), which shows an ABX pattern (H_A, H_B and H_C), a multiplet at τ 2.8—3.5 (three aromatic protons), and a singlet at τ 7.73 (aromatic methyl protons) analogous to those of IX and XI, and a singlet at τ 8.03 (two magnetically-equivalent α-protons of the cyclopentanone, H_D and H_E). These data suggest that the hydroxy ketone has the partial structure XVI. The presence of two singlets at τ 8.78 (aliphatic methyl protons) and at τ 5.63(–$\overset{|}{C}$H–O–) leads us to assign the hydroxy ketone to structure XVII, and, thus, the acetoxy ketone to XVIII. The transformation of the photoketone XIII to XVII and XVIII can be easily rationallized as below:



XVI



XVII



XIII XVIII

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9) H. O. House, S. G. Boots and V. K. Jones, *J. Org. Chem.*, **30**, 2519 (1965).

10) a) C. L. Angell, P. J. Krueger, R. Lauzon, L. C. Leitch and K. Noack, *Spectrochim. Acta*, **1959**, 926; b) G. Allen, P. S. Ellington and G. D. Meakins, *J. Chem. Soc.*, **1960**, 1909.

11) R. H. Bastman and S. K. Freeman, *J. Am. Chem. Soc.*, **77**, 6642 (1955).

12) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

TABLE 1. NMR DATA FOR COMPOUNDS VIII, IX, XI, XIII AND XVIII[a]

	Chemical shifts (τ)						Coupling constants (cps)							
	H_A	H_B	H_C	H_D	H_E	H_F	J_{AB}	J_{AC}	J_{BC}	J_{DE}	J_{DF}	J_{EF}	J_{CE}	J_{CF}
VIII	7.03 q	2.21 q	5.34[b]	4.23 d	3.59[b]	—	17.5	3.0	3.8	10.0	—	—	—	—
IX[c]	7.17 q	7.41 q	5.53 t	7.40 q	8.04 q	6.49 q	17.0	3.5	3.5	17.5	12.0	3.5	—	—
XI[d]	7.15 q	7.41 q	5.30 t	7.51 q	7.95 q	6.32 q	17.0	3.5	3.5	17.5	12.0	3.5	—	—
XIII	7.35 q	8.11 q	4.96[e]	—	7.90[f]	7.60[f]	20.0	9.0	3.0	—	—	11.0	1	1
XVIII	7.37 q	7·85 q	5.39 t	8.03 s		5.63 s	19.5	3.5	3.5	—	—	—	—	—

a) Peak multiplicities are represented by s (singlet), d (doublet), t (triplet), and q (quartet). All four compounds show a multiplet at τ 2.8—3.5 (three aromatic proton), a singlet at τ 7.71—7.73 (aromatic methyl protons), and a singlet at τ 8.40—8.78 (angular methyl protons).

b) See footnote*2.

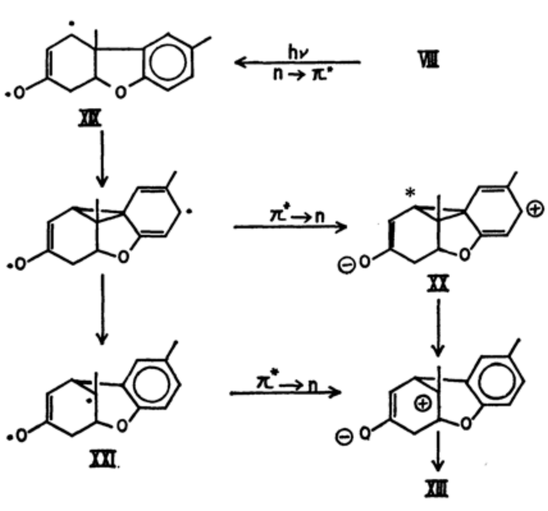
c) IX shows a singlet at τ 6.63 (methoxy protons).

d) XI shows a septet at τ 6.34 and two doublets at τ 8.80 and 8.90 with J=6 cps (isopropoxyl protons).

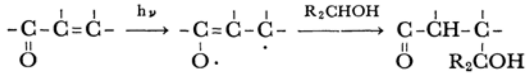
e) Doublet of diffused quartet.

f) Diffused doublet.

The rearrangement of Pummerer's ketone (VIII) to the photoketone (XIII) apparently proceeds *via* path A in Scheme 1. The yield of the photoketone in various solvents increased in the order of dioxane, *t*-butyl alcohol, and benzene. The order seems to be parallel to the ease with which a hydrogen atom of the solvents is abstracted by the triplet state of benzophenone.[13] This fact, and the fact that benzopinacol was formed by irradiation of VIII in benzene containing benzhydrol, indicate that the rearrangement of VIII to XIII may involve a radical species (*i. e.*, n-π^* or π-π^* triplet). Therefore, the photorearrangement can be rationalized by the formation of intermediates, XIX and XX or XXI, analogous to the mechanism proposed by Zimmerman *et al.*[4a] in the photorearrangement of 4, 4-diphenyl-2-cyclohexenone (III), which is the only example of a reaction *via* path A in Scheme 1.



The irradiation of some α, β-unsaturated ketones, including 2-cyclohexenone, in a primary or secondary alcohol gives adducts which are undoubtedly formed by a radical process.[5] However, the formation of the photoadducts, IX and XI, which involves an ionic process, does not appear to have any parallel in the photoreaction of α, β-unsaturated ketones in an alcoholic solvent.*4 The ionic addition reaction should not be ascribed to acidic substances which might be formed by the photochemical destruction of Pummerer's ketone (VIII). In fact, the methanol adduct (IX) was also obtained in a good yield in the presence of a sufficient amount of pyridine.



$$-\underset{\underset{\displaystyle O}{\|}}{C}-\overset{|}{C}=\overset{|}{C}- \xrightarrow{h\nu} -\underset{\underset{\displaystyle O\cdot}{|}}{C}=\overset{|}{C}-\underset{\cdot}{\overset{|}{C}}- \xrightarrow{R_2CHOH} \underset{\underset{\displaystyle O}{\|}}{C}-\overset{|}{C}H-\underset{\underset{\displaystyle R_2COH}{|}}{\overset{|}{C}}-$$

Although the nature of this addition reaction has not yet been determined, we wish to mention three possible explanations. First, the addition can simply arise from alcohol opening up the phenonium ion, XX, which is formed from the n-π^* excited state of VIII. Second, it is possible that the π-π^* excited state, which is classically pictured as ⊕C–C=C–O⊖, is involved in the reaction. Third, it is also reasonable to assume that an interaction between the π-orbitals of the benzene and enone groups of VIII leads to a polar intermediate whose β-carbon atom of the carbonyl group is electron deficient. An inspection of a scale model demonstrates that the distance (*ca.* 4 Å) between the centers of the two chromophores in VIII is close enough for them to interact with each other, as is seen in Fig. 1. Such an interaction may be

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[13] a) A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2038 (1963); b) C. Walling and M. J. Gibian, *J. Am. Chem. Soc.*, **86**, 3902 (1964); **87**, 3361 (1965).

*4 Chapman, *et al.* found that irradiation of VI in aqueous acetic acid gave water adducts analogous to IX as minor products.[2b]

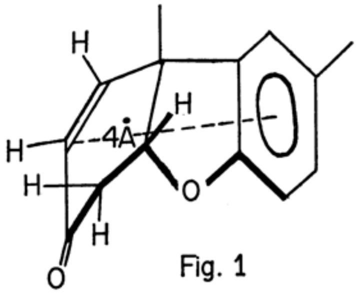

Fig. 1

suggested by the unusual bathochromic shift of the ultraviolet maximum (302 mμ, log ε 3.39) of VIII compared to those of IX (284 mμ, log ε 3.58) and of the dihydro-derivative of VIII (286 mμ, log ε 3.58). This has an analogy in the spectrum of flavothebaone.[14)] It should be noted that only the normal benzenoid band and the usual unsaturated ketone band with a typical *n*-π* band have been observed in the ultraviolet spectrum of VI, which, on irradiation in methanol, gives exclusively a photoisomer (VII) *via* path B in Scheme 1.[4c),*5]

The first possibility seems to lack an explanation of the driving force appropriate to the attack of an alcohol on the marked carbon atom (*) in the intermediate (XX). The second explanation, which involves the π-π* excitation, also seems less probable, because the light (<280 mμ) in the π-π* region of VIII can be neglected in the irradiation conditions. Recently Helgeson and Cram have found that the irradiation of [2.2]paracyclophane in an alcoholic solvent gives solvolytic products; they have suggested a polar character due to the interaction between the π-orbitals of two benzene rings for the excited state of [2.2]paracyclophane.[15)] This is similar to our third explanation.

Experimental[*6]

The photolysis of Pummerer's Ketone (VIII) in Methanol. A solution of 4.13 g of VIII in 430 m*l* of methanol was irradiated for 54 hr with a 450-W high-pressure mercury vapor lamp (Ushio UM 450) surrounded by a Pyrex cooling jacket under bubbling nitrogen. The progress of the reaction was followed by the decrease in the intensity of the infrared band at 1680 cm^{-1} and by the appearance of a new band at about 1720 cm^{-1}. After the solvent had been removed under reduced pressure, the residue was crystallized from methanol to give 3.14 g (66.3%) of the methanol adduct IX. Recrystallization from methanol gave colorless needles, mp 106—107°C. ν_{max}^{KBr} 1716, 1219, 1102 and 1010 cm^{-1}.

Found: C, 72.91; H, 7.36%. Calcd for $C_{15}H_{18}O_3$: C, 73.14; H, 7.37%.

The mother liquor was evaporated, and the residue was chromatographed on 15 g of silica gel. Elution with 100 m*l* of chloroform yielded 0.61 g of an oil which was shown by infrared spectroscopic analysis to consist of a mixture of 0.24 g of VIII and 0.37 g of IX and which was shown by thin-layer chromatography to be contaminated with a trace of XIII. The total yield of IX was calculated as 79% on the basis of the reacted VIII.

The semicarbazone of IX was prepared as usual. Recrystallization from acetone gave needles, mp 206—207°C. λ_{max}^{EtOH} 229 mμ (log ε 4.19).

Found: C, 62.80; H, 7.15; N, 14.08%. Calcd for $C_{16}H_{21}O_3N_3$: C, 63.35; H, 6.98; N, 13.85%.

The Reaction of the Methanol Adduct (IX) with Sodium Methoxide. A solution of 160 mg of IX in 30 m*l* of dry ether was stirred with 380 mg (large excess) of sodium methoxide in an atomosphere of nitrogen at room temperature for 30 min. The insoluble solid, which consisted of a mixture of sodium methoxide and the sodium salt X, was then collected by filtration, dissolved in 40 m*l* of water, and acidified with 2 N hydrochloric acid. The semicrystalline solid (79 mg, 57%) which precipitated was identified as Pummerer's ketone (VIII) by a comparison of its infrared spectrum with that of an authentic sample.

The Reaction of the Methanol Adduct IX with Hydrobromic Acid and Acetic Acid. A solution of 130 mg of IX in a mixture of 2 m*l* of acetic acid and 1.8 m*l* of hydrobromic acid (sp. gr. 1.48) was allowed to stand at room temperature overnight. The addition of 20 m*l* of water yielded 101 mg (78%) of pale yellow plates, mp 157—158°C (lit.[6)] mp 158°C), which were identified as 2, 5′-dihydroxy-2′, 5-dimethylbiphenyl by a mixed melting point determination and by a comparison of their infrared spectra. The authentic specimen was obtained by the same treatment of VIII.[6,7)]

Photolysis of Pummerer's Ketone (VIII) in Isopropyl Alcohol. A solution of 1.67 g of VIII in 430 m*l* of isopropyl alcohol was irradiated for 54 hr under conditions similar to those described in the photolysis in methanol. After the removal of the solvent under reduced pressure, the residue was crystallized from methanol to give 433 mg of the isopropyl alcohol adduct XI. The mother liquor was evaporated and chromatographed on 20 g of silica gel. Elution with 125 m*l* of benzene-chloroform (1 : 1) yielded 363 mg of XI. The total yield of XI amounted to 37%. Recrystallization from methanol gave colorless needles, mp 109.5—110.5°C. ν_{max}^{KBr} 1721, 1218, 1120, 1089 and 1000 cm^{-1}.

Found: C, 74.73; H, 8.22%. Calcd for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08%.

Elution of the chromatogram with 425 m*l* of chloroform yielded 375 mg (22.4%) of the photoketone XIII. Recrystallization from methanol containing a small volume of water and subsequent sublimation gave

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14) A. I. Scott, "Interpretation of the Ultraviolet Spectra of Natural Products," Pergamon Press, New York (1964), p. 347.

[*5] Also see the foot note[*4]. We are indebted to Dr. H. E. Zimmerman for his kind information of the spectra data.

15) R. C. Helgeson and D. J. Cram, *J. Am. Chem. Soc.*, **88**, 509 (1966).

[*6] Melting points were determined in capillary tubes and were uncorrected. The infrared spectra were measured with a Japan Spectroscopic Co. recording spectrophotometer, Model DS-402G. All ultraviolet spectra were measured in ethanol with a Shimazu recording spectrophotometer, Model SV-50. The NMR spectra were taken with a Varian A-60 spectrometer, by Dr. Tetsuro Shingu, Faculty of Pharmaceutical Science of this University, to whom the authors are indebted.

colorless plates, mp 86.5—87.5°C. $\nu_{max}^{CCl_4}$ 1734, 1210 and 1024 cm^{-1}.

Found: C, 78. 37; H, 6.48%. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59%.

The semicarbazone of the photoketone (XIII) was prepared as usual. Recrystallization from methanol-ethanol-water gave colorless crystals, mp 220—223°C (dec).

Found: C, 66.30; H, 6.29; N, 15.49%. Calcd for $C_{15}H_{17}O_2N_3$: C, 66.40; H, 6.32; N, 15.49%.

The Reaction of the Photoketone (XIII) with Hydrobromic Acid in Acetic Acid. A solution of 308 mg of XIII in a mixture of 0.3 m*l* of hydrobromic acid (sp. gr. 1.48) and 9.7 m*l* of acetic acid was allowed to stand at room temperature for 24 hr. The mixture was then diluted with 30 m*l* of water and extracted with ether (50 m*l*×3). The ethereal extracts washed with a saturated aqueous sodium bicarbonate solution (50 m*l*×3) and then with water (50 m*l*×4). The organic layer was dried over anhydrous sodium sulfate and evaporated to yield 313 mg of a yellow liquid, which was then chromatographed on 10 g of silica gel. Elution with 75 m*l* of chloroform yielded 134 mg (34%) of the acetoxy ketone (XVIII). Recrystallizations from methanol gave colorless crystals, mp 132—135°C. ν_{max}^{KBr} 1748 and 1735 (sh) cm^{-1}.

Further elution with 10 m*l* of chloroform yielded 80 mg of the hydroxy ketone (XVII). Two recrystallization from carbon tetrachloride gave colorless crystals, mp 101—101.5°C. $\nu_{max}^{CHCl_3}$ 3600, 3480, 1752, 1234 and 1004 cm^{-1}.

Found: C, 71.93; H, 7.05%. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94%.

Elution of the above chromatogram with 50 m*l* of chloroform yielded 79 mg of an oil which was shown, by thin-layer chromatography on silica gel, to consist of XVII, contaminated with a minor product. The chromatography of this oil yielded 61 mg of XVII. The total yield of XVII amounted to 42%.

The Acetylation of the Hydroxy Ketone (XVII) to the Acetoxy Ketone (XVIII). A solution of 58 mg of XVII in 1 m*l* of acetic anhydride and 0.5 m*l* cf pyridine was allowed to stand at room temperature overnight. The mixture was then diluted with 30 m*l* of water and extracted with ether (50 m*l*×3). The ethereal extracts, after concentration to 30 m*l*, were washed successively with 60 m*l* of 2 N hydrochloric acid, 30 m*l* of water, 60 m*l* of aqueous 5% sodium bicarbonate, and 60 m*l* of water. The organic layer was dried over anhydrous sodium sulfate and evaporated to yield 60 mg of a pale yellow oil which was identified as the acetoxy ketone (XVIII) by a comparison of its infrared spectrum with that of the authentic sample obtained above. The thin-layer chromatography (alumina and silica gel) showed that the product was identical with XVIII.

The Photolysis of Pummerer's Ketone (VIII) under Various Conditions. *In Dioxane.* A solution of 1.52 g of VIII in 430 m*l* of absolute dioxane was irradiated 76 hr under conditions similar to those described in the photolysis in methanol. After the removal of the solvent, the residue was chromatographed on 60 g of silica gel. Elution with 950 m*l* of chloroform yielded 0.78 g of an oil which was then further chromatographed on 120 g of neutralized alumina (activity I). Elution with 3 *l* of petroleum ether - benzene (3 : 2) and then with 200 m*l* of ether yielded 288 mg of the photoketone (XIII), which was identified by a comparison of its infrared spectrum with that of the authentic sample obtained above. Further elution with 250 m*l* of methanol yielded 344 mg of an oil which was estimated by infrared spectroscopic analysis to consist of 221 mg of VIII and 103 mg of XIII. The total yield of XIII amounted to 26%.

In Benzene. A solution of 700 mg of VIII in 430 m*l* of benzene was irradiated for 70 hr under the conditions described above. After the removal of the solvent, the residue was chromatographed on 60 g of neutralized alumina. Elution with 1.3 *l* of petroleum ether - benzene (1 : 1) yielded 288 mg of crystals; these crystals were identified as consisting of the photoketone (XIII) by a comparison of their infrared spectrum with that of an authentic sample. Further elution with 1 *l* of ether yielded 266 mg of an oil which was estimated by NMR analysis to consist of 175 mg of VIII and 91 mg of XIII. The total yield of XIII amounted to 72%.

In the Presence of Benzhydrol in Benzene. A solution of 535 mg of VIII and 460 mg of benzhydrol in 430 m*l* of benzene was irradiated for 25 hr under the conditions described above. After the removal of the solvent, the residue was chromatographed on 40 g of silica gel. Elution with 200 m*l* of benzene yielded 80 mg of a semi-crystalline solid which, on recrystallization from benzene, gave 33 mg of plates mp 179—181°C, identified as benzopinacol (by infrared spectrum and thin-layer chromatography). Elution with an additional 100 m*l* of benzene yielded 194 mg of a yellow oil; this oil was shown by thin-layer chromatography to consist of several minor products, including benzhydrol and benzopinacol. Elution with 230 m*l* of chloroform yielded 257 mg of crystals, which were identified as benzhydrol by a comparison of their infrared spectrum with that of an authentic sample. Further elution with 25 m*l* of acetone-chloroform (1 : 19) yielded 438 mg of an oil which was then rechromatographed on 8 g of silica gel. Elution with 90 m*l* of chloroform yielded 225 mg of a yellow oil which was shown to consist of VIII and XIII (by infrared spectrum and thin-layer chromatography).

In t-Butyl Alcohol. A solution of 362 mg of VIII in 110 m*l* of *t*-butyl alcohol was irradiated for 48 hr with a 100-W high pressure mercury vapor lamp (Ushio UM 120) surrounded by a Pyrex cooling jacket under bubbling nitrogen. After the removal of the solvent under reduced pressure, the residue was chromatographed on 15 g of silica gel. Elution with 90 m*l* of benzene-chloroform (1 : 1) and then with 110 m*l* of chloroform yielded 221 mg of an oil which was then rechromatographed on 20 g of neutralized alumina (Activity I). Elution with 100 m*l* of benzene - petroleum ether (1 : 1) yielded 26 mg of the photoketone (XIII). Further elution with 400 m*l* of benzene, 200 m*l* of chloroform, and 100 m*l* of methanol successively yielded 169 mg of an oil which was estimated by infrared spectroscopic analysis to consist of 69 mg of VIII and 100 mg XIII. The total yield of XIII amounted to 43%.