red color on heating; after 2 hr of heating, the mixture was cooled and benzene was added. No residue of the expected sodium chloride was observed. The solution was washed with water and the washings were collected and combined. Titration of the washings with standard silver nitrate solution showed the presence of 3.5 equiv of chloride ion (based on 4 equiv of nonaromatic-bound chlorine in VI). An infrared spectrum on the dried benzene solution showed broad bands indicating a mixture of products; this spectrum differed from the previous ones. No pure compounds could be isolated from the mixture. Attempted chromatography on alumina and silica gel columns was unsuccessful.

Reaction of Compound Xa with Phenol.—The diphenoxy-substituted product (Xa) (0.1700 g, 0.003300 mole) was mixed with sodium phenoxide (0.0714 g, 0.00670 mole) and heated by means of an oil bath at 135–140° for 7 hr. The mixture gradually became dark red. After cooling, 10 ml of carbon tetrachloride was added and the mixture was filtered; the filtrate was washed with three portions of water and dried with sodium sulfate. An orange-red oil which remained on removal of the solvent *in vacuo* did not crystallize on cooling or standing. An infrared spectrum of the oil in carbon tetrachloride showed the presence of a carbonyl stretching band at 6.1 μ and a broad hydroxyl stretching band at 2.9 μ and other generally broad bands indicating a mixture.

Attempted Partial Hydrolysis of VI.—The 5-chloro-2-hydroxybenzophenone–phosphorus pentachloride product (VI) (4.211 g, 0.1050 mole) was dissolved in 20 ml of dry 1,4-dioxane and the solution added to a solution of *ca.* 1 equiv of water (0.1890 g, 0.1030 mole) in 20 ml of 1,4-dioxane. The solution was stirred for 2 days and the solvent removed *in vacuo*. An infrared spectrum on a sample of the residue dissolved in benzene showed broad bands in the hydroxyl and carbonyl stretching regions as well as in the remainder of the spectrum indicating a complex mixture of products.

A complete hydrolysis was carried out by using approximately the same amounts of solvent and compound as above with an excess (40 ml) of water. After stirring for 12 hr, the solvent was partially removed *in vacuo* and the residue was extracted with benzene and dried with anhydrous sodium sulfate. An infrared spectrum on the benzene solution showed the presence of nearly pure 5-chloro-2-hydroxybenzophenone. On removal of solvent *in vacuo*, the residue melted at 89–90°. On recrystallization from methanol, the compound had the mp 94–95°[21]; mixture melting point with 5-chloro-2-hydroxybenzophenone, 93.5–95.0°.

Titrimetric Hydrolytic Studies on the 5-Chloro-2-hydroxybenzophenone–Phosphorus Pentachloride Product (VI).—A summary of the results of two typical experiments is given. (1) Potentiometric titration of a solution of VI in aqueous dioxane (*ca.* 85% water) with standard silver nitrate showed 4.1 equiv of chloride (4.0 theoretical). (2) VI was dissolved in aqueous dioxane (*ca.* 75% water) and the solution divided into 10 equal parts each of which was extracted with benzene after standing for a certain period of time. The benzene solvent would be expected to extract any unhydrolyzed VI or other benzene-soluble organic products. The aqueous portion was then titrated with standard silver nitrate. The results showed that *ca.* 4 equiv of chloride ion were present in each sample even from the shortest time of hydrolysis of *ca.* 7 min. This experiment demonstrates a fairly rapid complete hydrolysis under these conditions.

Attempted Reaction of VI and Sulfur Dioxide.—Sulfur dioxide was bubbled slowly through a solution of VI (1.325 g, 0.003300 mole) in 20 ml of benzene at room temperature for 16–18 hr. An infrared spectrum of the solution showed that no reaction had taken place.

A sample of VI (5.00 g, 0.0124 mole) was fused by being heated to 110–120° and sulfur dioxide was slowly bubbled through for 12 hr. After cooling, an infrared spectrum on a benzene solution showed that no reaction had occurred.

P^{31} Nmr and Infrared Spectra.—The P^{31} spectra were determined on the solutions sealed in glass tubes. Referencing was by means of a duplicate sealed tube containing a small sealed capillary of 85% aqueous phosphoric acid as an external standard. The solvents used for VI and Xa were benzene and carbon tetrachloride, respectively.

The infrared spectra were obtained on a KM-1 Baird-Atomic instrument. Matched 0.1-mm sodium chloride cells were used for solution spectra with concentrations in the range 3–5% (w/v). Carbon tetrachloride was the solvent for all infrared spectra except those for which another solvent is specifically mentioned. The preparation of the solutions and filling of the cells and nmr tubes for moisture-sensitive compounds were done in a drybox. The infrared spectra were calibrated against the nearest polystyrene bands which were run on the same chart as the sample.

Acknowledgment.—The authors express appreciation to the Public Health Service, National Institutes of Health, for support of this work under Research Grant No. CY-3753, and to Dr. J. R. Van Wazer and Dr. Victor Mark, Monsanto Chemical Co., for the P^{31} nmr spectra.

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[21] G. Wittig [*Ann.*, **446**, 198 (1926)] and D. Chakravasti and C. B. Bera [*J. Indian Chem. Soc.*, **21**, 109 (1944)] report 93–94 and 96–97°, respectively.

A Synthetic Entry to the Hydroazulenes. 4,5-Trimethylenetropone

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The synthesis and structure proof of 4,5-trimethylenetropone are discussed. A Robinson–Schöpf condensation of cyclopentane-1,2-dicarboxaldehyde with acetonedicarboxylic acid and methylamine yields 11-methyl-11-azatricyclo[5.3.1.0^{2,6}]undecan-9-one. Quaternization followed by Hofmann degradation yields three isomers of 6-oxohexahydroazulene. Catalytic dehydrogenation gives 4,5-trimethylenetropone. The 4,5-trimethylenetropone thus obtained differs from the material previously assigned this structure by Watanabe.

In the course of our study of troponoid compounds we have developed a potentially general synthesis of hydroazulene derivatives which is illustrated by the synthesis of 4,5-trimethylenetropone. This synthesis, which is unequivocal, takes on added interest since the properties previously ascribed to 4,5-trimethylenetropone[2] are grossly at variance with the properties of our product.

The synthetic approach was suggested by the conversion of tropinone to tropone by Meinwald, Emerman, Yang, and Büchi.[3] Bicyclo[3.2.0]hept-6-ene (I), readily accessible by photoisomerization of 1,3-cycloheptadiene,[4,5] provides a convenient source of *cis*-cyclopentane-1,2-dicarboxaldehyde (II). A Robinson–

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[1] National Science Foundation Cooperative Fellow, 1964–1966.

[2] H. Watanabe, *Pharm. Bull.* (Tokyo), **5**, 426 (1957).

[3] J. Meinwald, S. L. Emerman, N. C. Yang, and G. Büchi, *J. Am. Chem. Soc.*, **77**, 4401 (1955).

[4] W. G. Dauben and R. Cargill, *Tetrahedron*, **12**, 186 (1961).

[5] O. L. Chapman and D. J. Pasto, *Chem. Ind.* (London), 53 (1961); O. L. Chapman, D. J. Pasto, G. W. Borden, and A. A. Griswold, *J. Am. Chem. Soc.*, **84**, 1220 (1962).

Table I

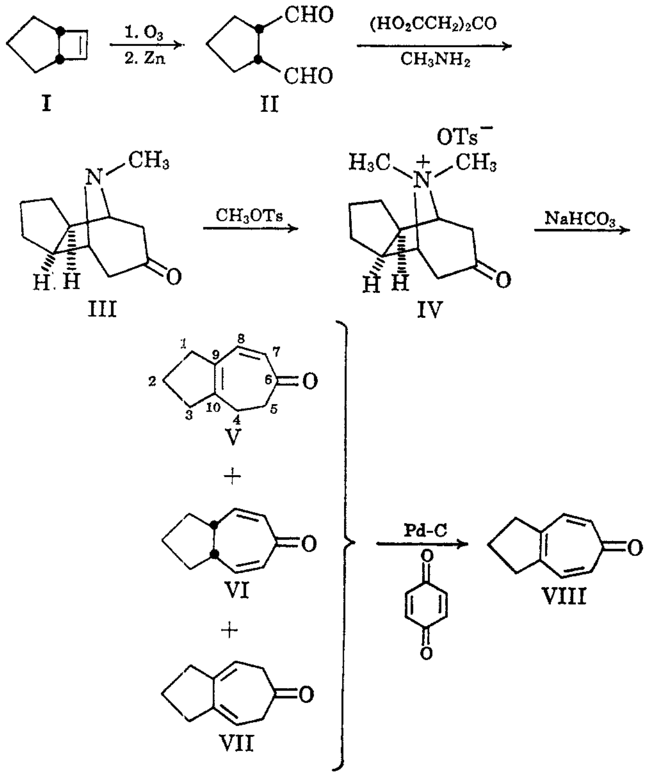
Nmr Spectra[a]

Compd	Position 1	2	3	4	5	7	8	9	10
V	2.4 (m)	1.8 (m)	2.4 (m)	2.4 (m)	2.4 (m)	5.85 (d)	6.48 (d)	...	...
						$J_{7,8} = 13.0$	$J_{8,7} = 13.0$		
VI	1.8 (m)	1.8 (m)	1.8 (m)	6.21 (c)[b]	5.87 (c)[b]	5.87 (c)[b]	6.21 (c)[b]	2.88 (m)	2.88 (m)
VII	2.5 (m)	1.7 (m)	2.5 (m)	5.46 (m)	3.0 (m)	3.0 (m)	5.46 (m)	...	...
VIII	2.9 (t)	2.0 (m)	2.9 (t)	6.66 (d)	6.93 (d)	6.93 (d)	6.66 (d)	...	...
				$J_{4,5} = 12.0$	$J_{5,4} = 12.0$	$J_{7,8} = 12.0$	$J_{8,7} = 12.0$		

[a] All spectra were taken in carbon tetrachloride; resonance positions are given as δ values relative to internal tetramethylsilane; J values are given in cycles per second; m = multiplet, c = complex, d = doublet, and t = triplet. The A_2B_2 chemical shifts and coupling constants were verified by calculation. [b] See text.

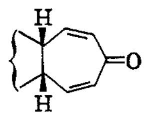
Schöpf condensation[6,7] using the dialdehyde gave a tricyclic amino ketone which is assigned structure III (Scheme I) (34% over-all yield from I). The amino ketone III shows the expected carbonyl absorption (5.86 μ) and N-methyl resonance (δ 2.57). In the ultraviolet III exhibits a charge-transfer band at 251 mμ (log ε 3.10) and no perceptible n → π* transition. When the ultraviolet spectrum of III was taken in dilute hydrochloric acid, only the normal n → π* transition at 283 mμ was observed. This behavior is characteristic of other derivatives of tropinone and in general characteristic of amino ketones in which the nonbonding electrons on nitrogen can effectively overlap with the π orbital of the carbonyl.[8,9]

Scheme I



Treatment of III with base and piperonal gives a crystalline dipiperonylidene derivative. The ring skeleton of the amino ketone is confirmed by degradative experiments described below. The stereochemistry (trimethylene bridge *cis* to nitrogen bridge) is assigned by analogy to other products derived from Robinson–Schöpf condensations. All such condensations involving *erythro*-2,3-disubstituted succindialdehydes in which the product stereochemistry has been determined give *cis-exo* products.[10]

Quaternization of III proved moderately difficult as might be expected on the basis of the assigned stereochemistry. Treatment of III with methyl iodide gave principally the hydriodide of III. Quaternization of the nitrogen was achieved, however, by heating III at 60° in neat methyl tosylate (85% yield). Steam distillation of the quaternary tosylate IV from aqueous sodium bicarbonate gave a mixture of bicyclic dienones (70% yield) which gave an acceptable element analysis. A rough nmr analysis indicated 30% V, 60% VI, and 10% VII. Chromatography on silica gel gave fractions which were sufficiently pure samples of VI and VII to permit tentative structural assignments on the basis of spectroscopic properties. Isomerization of the mixture with 5% hydrochloric acid gave a mixture which contained 85% V and 15% VII. The fully conjugated dienone V shows carbonyl absorption at 6.04 μ and double bond absorptions at 6.12 and 6.30 μ and an ultraviolet maximum (π → π*) at 323 mμ. The nmr spectrum of V (Table I) showed the expected AB pattern (δ 5.85 and 6.48, J_{AB} = 13.0 cps) for the protons on the double bond and two complex bands centered at δ 2.4 and 1.8. The AB coupling constant (13.0 cps) is normal for a double bond in a seven-membered ring.[11,12] The cross-conjugated dienone VI shows the expected infrared (C=O, 6.06 μ; C=C, 6.22 μ) and ultraviolet (238 mμ) absorption. In the nmr spectrum of VI, the protons on the double bonds give rise to a complex pattern (A_2B_2 portion of an $A_2B_2X_2$ system) which cannot be analyzed by first-order methods. Computer calculation of the system (neglecting the methylene protons), using sensible values for all expected coupling constants and chemical shifts ($J_{4,5}$, $J_{7,8}$ = 12.5 cps; $J_{5,7}$, $J_{7,9}$, $J_{5,10}$ = 1.0 cps; $J_{8,9}$, $J_{4,10}$ = 4.5 cps; $J_{9,10}$ = 3.0 cps; ν_5, ν_7 = 352.2 cps; ν_4, ν_8 = 372.6 cps), gives a pattern which is quite consistent with the observed pattern.



The remaining isomer (VII) shows infrared absorption (5.86 μ) characteristic of a nonconjugated carbonyl

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(6) R. Robinson, *J. Chem. Soc.*, **111**, 762 (1917).

(7) C. Schöpf and G. Lehmann, *Ann.*, **518**, 1 (1935).

(8) N. J. Leonard and Ō. Michinori, *J. Am. Chem. Soc.*, **77**, 6239 (1955).

(9) H. H. Jaffé and M. Orchin, "Theory and Application of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p 437.

(10) P. Karrer and J. Kebrle, *Helv. Chim. Acta*, **37**, 484 (1954).

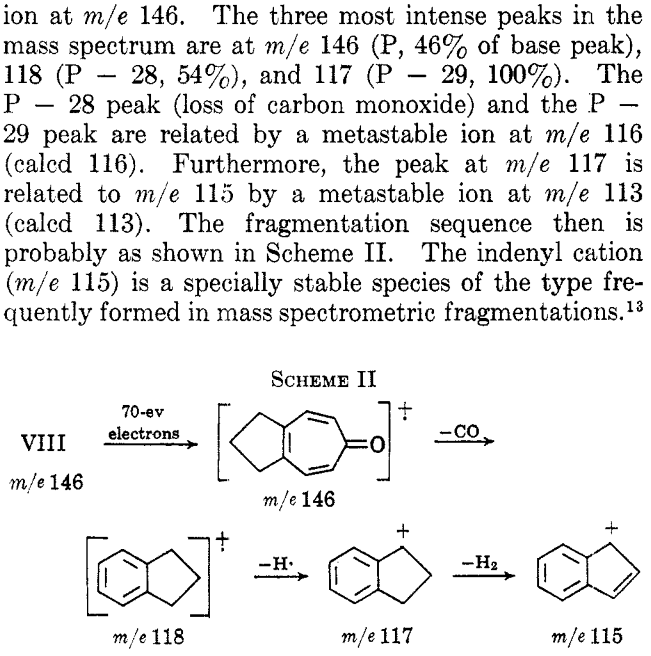
(11) O. L. Chapman, *J. Am. Chem. Soc.*, **85**, 2014 (1963).

(12) G. V. Smith and H. Kriloff, *ibid.*, **85**, 2016 (1963).

group and double bond absorption at 6.03 and 6.13 μ. The nmr spectrum (Table I) shows two olefinic protons (multiplet centered at δ 5.46), four allylic protons adjacent to the carbonyl group (multiplet centered at δ 3.0), and six methylene protons (multiplets centered at δ 2.5 and 1.7).

Dehydrogenation of the dienone mixture by heating in decalin with 10% palladium on carbon and *p*-benzoquinone gave 4,5-trimethylenetropone (VIII, 17% yield) as a crystalline solid, mp 107–108°. The infrared spectrum shows bands at 6.16 and 6.40 μ. The ultraviolet absorption is typical for troponoid compounds, 231 mμ (log ε 4.29) and 325 mμ (log ε 4.12). The nmr spectrum (Table I) is in complete accord with the assigned structure. The mass spectrum of 4,5-trimethylenetropone (VIII) shows a parent ion at *m/e* 146. The three most intense peaks in the mass spectrum are at *m/e* 146 (P, 46% of base peak), 118 (P − 28, 54%), and 117 (P − 29, 100%). The P − 28 peak (loss of carbon monoxide) and the P − 29 peak are related by a metastable ion at *m/e* 116 (calcd 116). Furthermore, the peak at *m/e* 117 is related to *m/e* 115 by a metastable ion at *m/e* 113 (calcd 113). The fragmentation sequence then is probably as shown in Scheme II. The indenyl cation (*m/e* 115) is a specially stable species of the type frequently formed in mass spectrometric fragmentations.[13]

SCHEME II



The data presented above leave no reasonable doubt concerning the identity of 4,5-trimethylenetropone (VIII). The material to which this structure had previously been ascribed[2] is described as an oil (bp 95–96° at 0.4 mm) with an infrared absorption at 6.05 μ (neat) and an ultraviolet maximum at 252 mμ (EtOH, log ε 4.12). It was obtained by selenium dioxide oxidation of 1,2,3,6,7,8-hexahydroazulene and characterized by catalytic hydrogenation to a ketone which gave a semicarbazone with a melting point identical with that reported for 6-oxo-*cis*-decahydroazulene. The ultraviolet spectrum, contrary to Watanabe's statement,[2] does not resemble that of known derivatives of tropone. Tropones in general have two intense bands, one in the vicinity of 230 mμ and the other about 300 mμ.[14] Alkyl substitution has little effect on the position of the maxima.[14] The structure of Watanabe's compound cannot be assigned with certainty at the present time.

Variants of the synthesis of VIII should provide facile synthetic entries to naturally occurring hydroazulene derivatives. These possibilities are currently under investigation.

Experimental Section

11-Methyl-11-azatricyclo[5.3.1.0^{2,6}]undecan-9-one (III).—Ozone was bubbled through a solution of 17.4 g (0.185 mole) of bicyclo[3.2.0]hept-6-ene (I) in 250 ml of absolute ethanol at −78° until no more ozone was absorbed by the solution (approximately 5 hr with a Welsbach ozonolysis apparatus at 90 v). After the addition of the ozonide solution to a solution of 31 ml of glacial acetic acid in 78 ml of water, powdered zinc (18 g) was slowly added with vigorous stirring. A saturated solution of sodium carbonate was then added, and the precipitated zinc hydroxide and the excess powdered zinc were filtered off under vacuum. The filtrate was then treated a second time with saturated sodium carbonate, to ensure complete removal of zinc ions, and filtered. The resulting ethanolic solution of cyclopentane-1,2-dicarboxaldehyde was added to 54.0 g (0.37 mole) of acetonedicarboxylic acid and 18.5 g (0.28 mole) of methylamine hydrochloride. The pH was buffered with a saturated solution of sodium dihydrogen phosphate and adjusted to approximately 5.5 with a saturated solution of sodium bicarbonate. The total volume was increased to 5 l. by the addition of water, and the reaction mixture was stirred at room temperature for 44 hr. Then the solution was made basic with sodium carbonate, saturated with sodium chloride, and continuously extracted with ether for 24 hr, changing the receiving flask several times to accommodate the ethanol extracted. Upon evaporation of the ethanol and ether at reduced pressure, the resulting crude material was vacuum distilled through a short distillation column to separate III from polymeric material. Redistillation at 59–60° (0.12 mm) yielded 11.3 g of III (34%), $\lambda_{\max}^{\mathrm{EtOH}}$ 251 mμ (log ε 3.10), $\lambda_{\max}^{\mathrm{CCl_4}}$ 5.86 μ.

Anal. Calcd for $C_{11}H_{17}NO$: C, 73.70; H, 9.56; N, 7.81. Found: C, 73.55; H, 9.88; N, 7.76.

Dipiperonylidene Derivative of III.—A solution of potassium hydroxide (0.30 g) in 1.0 ml of water was added to a solution of 0.11 g (0.61 mmole) of III and 0.35 g (2.3 mmole) of piperonal in 5 ml of ethanol. After stirring at room temperature for 24 hr, the resulting yellow precipitate was collected by vacuum filtration to yield 0.25 g (93%) of the dipiperonylidene derivative of III. Two recrystallizations from absolute ethanol yielded an analytical sample: mp 208–209°; $\lambda_{\max}^{\mathrm{CHCl_3}}$ 3.42 (m), 6.01 (m), 6.27 (s), 6.73 (s), and 6.93 μ (s); nmr, δ 7.79 (singlet, 2 H), 6.81 (singlet, 6 H), 6.00 (singlet, 4 H), 3.99 (singlet, 2 H), 2.6 (multiplet, 2 H), 2.88 (singlet, 3 H), and 1.8 (multiplet, 6 H).

Anal. Calcd for $C_{27}H_{25}NO_5$: C, 73.12; H, 5.68; N, 3.16. Found: C, 73.13; H, 5.74; N, 3.14.

Quaternary Tosylate IV.—A mixture of 5.30 g (0.029 mole) of III and 25 ml of methyl tosylate was heated (60 ± 5°) for 30 hr under an atmosphere of purified nitrogen. Approximately 50 ml of dry ether was added, and the quaternary tosylate IV was collected by vacuum filtration and washed with dry ether, yield 8.92 g (85%), mp 182–185°. Two recrystallizations from absolute ethanol yielded an analytical sample: mp 185.5–186.5°; $\lambda_{\max}^{\mathrm{KBr}}$ 3.38 (m), 5.78 (s), 5.84 (s), 8.30 μ (s); nmr, δ 7.36 (doublet, 2 H), 7.67 (doublet, 2 H), 4.0 (broad doublet, 2 H), 3.28 (singlet, 3 H), 2.34 (singlet, 3 H), 3.1 (multiplet), 2.7 (multiplet), and 1.8 (multiplet).

Anal. Calcd for $C_{19}H_{27}NO_4S$: C, 62.45; H, 7.45; N, 3.83. Found: C, 62.16; H, 7.45; N, 3.97.

6-Oxo-1,2,3,6,7,8-hexahydroazulene (V), 6-Oxo-1,2,3,6,9,10-hexahydroazulene (VI), and 6-Oxo-1,2,3,5,6,7-hexahydroazulene (VII).—Quaternary tosylate IV (9.75 g, mp 182–185°) and sodium bicarbonate (20 g) in water (25 ml) were steam distilled for 30 min. The steam distillate was saturated with sodium chloride and extracted four times with ether. The combined ether extracts were extracted with 50 ml of 5% hydrochloric acid, 50 ml of 5% sodium bicarbonate, and 25 ml of saturated sodium chloride solution. After drying over magnesium sulfate, the ether was evaporated at reduced pressure to yield 3.57 g (87%) of crude dienone mixture (V, VI, and VII). The crude material was then vacuum distilled with a microcolumn to yield 2.89 g (70%), bp 70–72° (0.50 mm). Analysis of the nmr spectrum showed the composition to be approximately 30% V, 60% VI, and 10% VII (vapor phase chromatographic analysis could not be trusted because of thermal isomerization).

Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 81.17; H, 8.11.

The dienone mixture (0.78 g) was chromatographed on a silica gel column (35 × 140 mm) packed in Skellysolve B. After elution with approximately 1 l. of 5% ether–Skellysolve B, VII

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[13] F. W. McLafferty, "Mass Spectrometry of Organic Ions," Academic Press Inc., New York, N. Y., 1963, p 309.

[14] P. L. Pauson, *Chem. Rev.*, **55**, 9 (1955).

(40 mg) was obtained. Further elution with 5% ether–Skellysolve B yielded VI (100 mg). Product V was not recovered. VI had λ_{max}^{neat} 3.30–3.49 (s), 6.06 (s), and 6.22 μ (s); λ_{max}^{EtOH} 238 mμ. VII had $\lambda_{max}^{CCl_4}$ 3.39–3.52 (s), 5.86 (s), 6.03 (m), and 6.13 μ (m); λ_{max}^{EtOH} 253 (sh), 314 mμ.

Heating the dienone mixture (V, VI, and VII) with 5% hydrochloric acid at 60° for 30 min gave the following approximate product composition: 85% V and 15% VII. V had λ_{max}^{neat} 3.38–3.52 (m), 6.04 (s), 6.12 (s), and 6.30 μ (s); λ_{max}^{EtOH} 323 mμ.

6-Oxo-1,2,3,6-tetrahydroazulene (VIII).—A stream of dry carbon dioxide was bubbled through a stirred reaction mixture consisting of 75 ml of decalin, 0.262 g of dienone mixture (V, VI, and VII), 0.5 g of 10% palladium on charcoal, and 0.2 g of *p*-benzoquinone at 150 ± 5° for 18 hr. After cooling to room temperature, the palladium on charcoal was filtered off under vacuum and washed with ether. The ether was evaporated at reduced pressure, and the decalin was removed by chromatography on silica gel, eluting with Skellysolve B. Elution with 10% ether-benzene gave unreacted dienone (predominantly V) and unreacted *p*-benzoquinone. Further elution with chloroform gave VIII followed by hydroquinone. Extraction of VIII with boiling hexane and evaporation of the hexane at reduced pressure gave 0.046 g (17%) of a light yellow solid, mp 97–105°. Sublimation followed by two low-temperature recrystallizations from ether gave an analytical sample: mp 107–108° (white needles); λ_{max}^{EtOH} 231 mμ (log ε 4.29), 335 (4.12), and 336 (sh) (4.00); $\lambda_{max}^{CHCl_3}$ 3.42 (m), 6.16 (s), and 6.40 μ (s).

Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.90; mol wt, 146. Found: C, 81.84; H, 6.86; mol wt, 146 (mass spectrum).

Acknowledgment.—The authors are indebted to Dr. T. H. Kinstle for assistance with the mass spectrum and to Dr. G. F. Morris for assistance with the nmr calculations.

The Effect of Solvent on the Electronic Transitions of Benzophenone and Its *o*- and *p*-Hydroxy Derivatives

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The ultraviolet absorption spectra of benzophenone, *o*- and *p*-hydroxybenzophenones, and 2,4-dihydroxybenzophenone in the 215–400-mμ range were determined in 14 solvents of varying polarity. Both the n → π* and π → π* absorption maxima of benzophenone were correlated well by Kosower's solvent polarity parameter *Z*. The π → π* absorptions of the hydroxy derivatives were separated into two groups, those in nonhydroxylic solvents and those in hydroxylic solvents, by the *Z* factor. Possible interpretations of these data are presented based on hydrogen bonding and electrostatic interactions.

Solvents often have a considerable effect on the ultraviolet absorption spectra of organic compounds.[1] These solvent effects are useful in determining the type of electronic transitions which are observed, *i.e.*, the blue shift of n → π* transitions and the red shift of π → π* transitions on changing to a more polar solvent from a less polar one.[1,2] Kosower[3] has developed a solvent polarity parameter, *Z*, which has been used successfully in correlating a number of solvent effects on n → π* and π → π* transitions.[4] In this paper are presented data on the solvent effects on the energy[5] of the n → π* and π → π* transitions of benzophenone and the various π → π* transitions of *o*- and *p*-hydroxybenzophenone and 2,4-dihydroxybenzophenone.

Experimental Section

Materials.—The compounds used in this study were recrystallized to constant melting points (benzophenone, 48–48.5°; *p*-hydroxybenzophenone, 132–132.5°; *o*-hydroxybenzophenone, 38.5–39°; 2,4-dihydroxybenzophenone, 143.5–144°) and vacuum dried. No impurities were detected in these samples by infrared and mass spectral analyses. The solvents were either spectroquality reagent grade or center-cut redistilled materials. Reliable absorption maxima in dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) could not be determined below *ca.* 270 mμ due to absorption by the solvent. All other solvents were usable down to *ca.* 215 mμ.

Spectra.—The ultraviolet spectra were obtained with Cary recording spectrophotometers, Models 11MS and 14, at 21 ± 2°. Maxima were reproducible to better than ±0.5 mμ. The true absorption maxima may be in error by as much as 5 or 10 mμ due to overlapping bands from different transitions and due to the fine structure (shoulders) of the bands themselves. These errors may account for some of the scatter observed in Figures 5–11. A twofold change in concentration or slight acidification of the alcoholic solvents with concentrated aqueous hydrochloric acid (2 drops/100 ml) failed to change the maxima. The wavelengths were calibrated with the mercury arc lines from 253.7 to 404.7 mμ.

The infrared spectra were obtained with a Beckman IR9 in 0.1-mm cells at room temperature. All $\nu_{C=O}$ are accurate to ±3 cm^{-1}.

Results and Discussion

We have applied the *Z* parameter in our correlation study, and have determined approximate *Z* values for cyclohexane and diethyl ether based on the n → π* and π → π* transitions of benzophenone which were

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[1] (a) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, pp 186, 206; (b) J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," Methuen and Co., Ltd., London, 1963, pp 163, 272; (c) A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," Edward Arnold Ltd., London, 1957, p 301.

[2] (a) N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1002, 1006 (1954); (b) M. Kasha, *Discussions Faraday Soc.*, **9**, 14 (1950); (c) K. B. Wiberg, "Physical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1964, p 187; (d) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, p 158; (e) C. Reichardt, *Angew. Chem. Intern. Ed. Engl.*, **4**, 29 (1965); (f) P. A. Leermakers and H. T. Thomas, *J. Am. Chem. Soc.*, **87**, 1620 (1965).

[3] (a) E. M. Kosower, *ibid.*, **80**, 3253 (1958); (b) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, p 309.

[4] (a) E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3261 (1958); (b) W. D. Closson and P. Haug, *ibid.*, **86**, 2384 (1964); (c) H. W. Davies and M. Schwarz, *J. Org. Chem.*, **30**, 1242 (1965); (d) ref 2e.

[5] The absorption maximum was used to calculate the energy of the excited state since the wavelength of the O—O band is unknown.[2a,6] This energy in kcal/mole was calculated from the wavelength of the absorption maximum by the usual procedure; *cf.* ref 1a, p 7.

[6] See (a) W. M. Schubert, J. Robins, and J. L. Haun, *J. Am. Chem. Soc.*, **79**, 910 (1957); (b) H. H. Jaffé and H. L. Jones, *J. Org. Chem.*, **30**, 964 (1965).