Table XIV

Effect of Solvent on Chemical Shift of Ring Protons of Some Naphthoquinones

Compound	Position of H	Chemical shift, δ CDCl₃	Chemical shift, δ $(CD_3)_2$-CO	Chemical shift, δ $(CD_3)_2$-SO
2-Hydroxy-1,4-naphthoquinone	C-3	6.37	6.27	6.18
2-Methoxy-1,4-naphthoquinone	C-3	6.17	6.30	6.32
Naphthopurpurin	C-3	6.37	6.29	6.17
Methoxynaphthazarin	C-3	6.17	6.34	6.32
2,7-Dihydroxy-3-acetylnaphthazarin	C-6	6.68	6.63	6.55
2,7 Dimethoxynaphthazarin	C-3 and C-6	6.40	6.57	
2-Hydroxy-6-methoxynaphthazarin	C–3	6.42	6.41	
	C-7	6.48	6.58	
2-Hydroxy-7-methoxynaphthazarin	C-3	6.47	6.45	
	C-6	6.53	6.58	

naphthazarins. No rational explanation can be offered at this time for these shifts.

The acetyl protons of spinochrome A (2,7-dihydroxy-3-acetylnaphthazarin) resonate at δ 2.85 in deuteriochloroform. In acetone-d_6, there is observed only a minor difference in the chemical shift (δ 2.80). However, in dimethyl sulfoxide-d_6 there is a pronounced diamagnetic shift of the acetyl signal to δ 2.58, a chemical shift which is reminiscent of an acetyl group in a hindered environment. The same chemical shift is observed for the acetyl signal of spinochrome C (2,3,6-trihydroxy-7-acetylnaphthazarin) in dimethyl sulfoxide-d_6. The strong intramolecular hydrogen bond of the acetyl carbonyl and the adjacent β-hydroxyl is apparently broken. Hydrogen bonding of the hydroxyl next to the acetyl with the solvent forces the acetyl to assume a different configuration to relieve steric hindrance, thereby resulting in a diamagnetic shift of its signal.

Experimental Section

All nmr spectra were determined in deuteriochloroform solution unless designated otherwise on a Varian A-60 instrument. The chloroform peak (δ 7.27) was used as the internal standard and the chemical shifts were checked using tetramethylsilane (δ 0.00) as the reference. The acetone-d_5 (δ 2.06) and dimethyl sulfoxide-d_5 (δ 2.52) peaks were used as internal standards for acetone-d_6 and dimethyl sulfoxide-d_6, respectively. Sample concentration was 2–20 mg/0.50 ml. The chemical shifts are reproducible within ±0.01 ppm. For comparison of signals of different compounds which differed closely or within the experimental error, the spectrum of the mixture was also determined as a check. The preparation of all new compounds used in this investigation will be presented elsewhere.

Photochemical Reactions of Diketones. IV.[1,2] The Photoaddition of *o*- and *p*-Xylene to Camphorquinone

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Photoirradiation of DL-camphorquinone (CQ) in *p*-xylene solution in the absence of oxygen at wavelengths above 3000 or 4000 A led to a mixture of DL-3-*endo*-(*p*-methylbenzyl)-3-*exo*-hydroxy-2-bornanone (**6a**, 45%), DL-2-*endo*-(*p*-methylbenzyl)-2-*exo*-hydroxy-3-bornanone (**7a**, 20%), 1,2-di-(*p*-tolyl)ethane (**14a**, 4%), and 3-hydroxy-2-bornanones (**15**) plus 2-hydroxy-3-bornanones (**16**) (total yield of hydroxy bornanones 6%). The same mixture of products was obtained by addition of *p*-methylbenzylmagnesium chloride to CQ. The structures of **6a** and **7a** were established by sodium borohydride reduction of each to a separable mixture of glycols whose stereochemistry was established by infrared and nmr spectroscopy. These were cleaved with sodium periodate to keto aldehydes **12a** or **13a**. The aldehyde proton of **12a** (derived from **6a**) appeared as a sharp singlet in the nmr while that of **13a** (derived from **7a**) appeared as a doublet. Similar results were obtained with *o*-xylene. It is suggested that these reactions proceed *via* hydrogen abstraction by excited CQ leading to a pair of radicals whose principal course of reaction is radical combination in a manner similar to that observed with 9,10-phenanthrenequinone. The photoaddition reaction (quantum yield 0.07) is a less efficient process than the photochemical oxidation (quantum yield 0.16) of CQ which afforded camphoric anhydride and camphoric acid.

An investigation of solution photochemical reactions of the nonenolizable α-diketone, DL-camphorquinone (CQ), has been undertaken. The rigid skeleton and known orientation of the carbonyl groups appeared to make this readily available substance[4a] a particularly suitable choice for an investigation of diketone photochemistry.[4b] The related monoketone, camphor, has been shown to undergo two competing, solvent-dependent ring cleavages upon direct[5] photoirradiation

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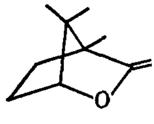
(1) (a) For the previous paper in this series, see M. B. Rubin and P. Zwitkowits, *Tetrahedron Letters*, 2453 (1965). (b) Supported in part by a grant (GP-5038) from the National Science Foundation.

(2) Presented in part at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966.

(3) Weizmann Fellow, supported by Yad Chaim Weizmann, The Weizmann Memorial Foundation, 1964–1965, on leave from Carnegie Institute of Technology.

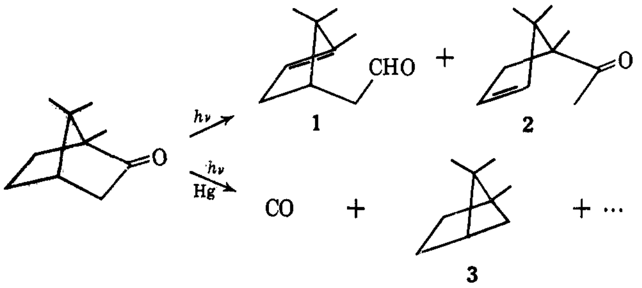
(4) (a) W. C. Evans, J. M. Ridgion and J. L. Simonsen, *J. Chem. Soc.*, 137 (1934). (b) After this manuscript was submitted for publication, J. Meinwald and H. O. Klingele [*J. Am. Chem. Soc.*, **88**, 2071 (1966)] reported an investigation of photochemical reactions of CQ. These authors reported that, in the absence of oxygen, CQ failed to react in solvents such as benzene, carbon tetrachloride, *t*-butyl alcohol, methyl alcohol, or aqueous acetone using a variety of light sources. In the presence of oxygen, a variety of products were observed, depending upon the experimental conditions. These included camphoric anhydride and products derived from it as was also observed in the present work. In benzene solution carbon dioxide was evolved and camphono lactone (i) and the isomeric campholyto lactone as well as trace of biphenyl were obtained.



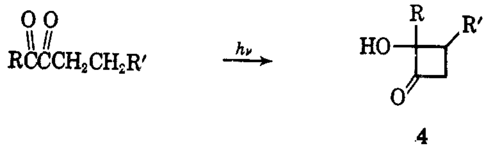
i

(5) (a) G. Ciamician and P. Silber, *Ber.*, **43**, 1340 (1910). (b) R. Srinivasan, *J. Am. Chem. Soc.*, **81**, 2604 (1959).

yielding α-campholenic aldehyde (**1**) and 3,3,4-trimethyl-4-acetylcyclopentene (**2**), in addition to traces of carbon monoxide. Mercury-photosensitized[6] decomposition of camphor afforded a complex mixture including the product of decarbonylation, 1,6,6-trimethylbicyclo[2.1.1]hexane (**3**), and carbon monoxide.



Except for a considerable body of work on photochemical reactions of biacetyl- and acetylpropionyl,[7] the only nonenolic α-diketones whose photochemistry has been investigated are a series of long chains of α-diketones,[8,9] in which the carbon atoms γ to the carbonyl groups bear hydrogen atoms. These underwent efficient intramolecular hydrogen abstraction (quantum yield *ca.* unity) affording cyclobutane derivatives (**4**) in a manner analogous to that observed with simple ketones.[10] The intramolecular process proceeded to the exclusion of intermolecular hydrogen abstraction except in the case of 3,4-hexanedione. Irradiation of this dione in propionaldehyde solution afforded 23% of hydroxycyclobutane (**4**, R = CH_3CH_2, R′ = H), 23% of 4-hydroxy-3-hexanone, and 54% of 4-oxo-3-hexanol propionate. It might also be noted that photochemical reactions of *o*-quinones have been investigated extensively.[1a,11] This report describes the results obtained upon photoirradiation of CQ in solutions of *o*- or *p*-xylene.



Exposure of a solution of CQ (Scheme I) in *p*-xylene under nitrogen in a Pyrex vessel either directly to light from a high-pressure mercury vapor lamp or to light filtered to remove radiation below 4000 A[12] led to a mixture of four products, separable by chromatography on Florisil. The two major products of the reaction, DL-3-*endo*-(*p*-methylbenzyl)-3-*exo*-hydroxy-2-bornanone (**6a**, mp 110°, 45%) and DL-2-*endo*-(*p*-methylbenzyl)-2-*exo*-hydroxy-3-bornanone (**7a**, mp 90°, 20%), were isomeric 1:1 adducts of CQ and *p*-xylene as shown by their mass spectral molecular weights and nmr spectra. On the basis of hydroxyl absorption at 2.8 and carbonyl absorption at 5.75 μ, it was assumed that the two isomers were products of 1,2 addition of the elements of *p*-xylene across one of the carbonyl groups of CQ. This was confirmed by synthesis of **6a** (41%) and **7a** (10%) *via* addition of excess *p*-methylbenzylmagnesium chloride to CQ.[13] Grignard additions to camphor have been shown[14] to involve addition from the *endo* side of the bicyclic system and it seems reasonable to assume that similar stereochemistry applies with CQ.

Each isomer was reduced with sodium borohydride in methanol; the products were separated by chromatography on silica gel G. From **6a** there were obtained two isomeric diols, DL-3-*endo*-(*p*-methylbenzyl)-2-*exo*-3-*exo*-dihydroxybornane (**8a**), mp 108° (63%), and DL-3-*endo*-(*p*-methylbenzyl)-2-*endo*-3-*exo*-dihydroxybornane (**9a**), mp 100° (27%), and from **7a** two additional diols, 2-*endo*-(*p*-methylbenzyl)-2-*exo*-3-*exo*-dihydroxybornane (**10a**), mp 127° (45%), and 2-*endo*-(*p*-methylbenzyl)-2-*exo*-3-*endo*-dihydroxybornane (**11a**), mp 115° (43%). Each of the four diols could be reconverted to the precursor ketone by oxidation. The configurations of each pair could be assigned from their infrared and nmr spectra.[15] Thus the *cis*-diols **8a** and **10a**, where strong intramolecular hydrogen bonding is possible, exhibited a single band at about 2.75 μ and each of the *trans*-diols **9a** and **11a** showed a pair of bands in the region 2.6–2.9 μ indicating the presence of bonded and nonbonded hydroxyl protons. In the case of **8a** and **9a**, nmr spectra provided further confirmation of configuration. For the hydrogen bonded isomer, **8a**, the C-2 proton and the *gem*-hydroxyl proton appeared as doublets at τ 6.70 and 7.58 (J = 6 cps), respectively, while in **9a**, where the usual rapid exchange of the hydroxyl proton occurs, the C-2 proton appeared as a singlet at τ 6.33.

The formation of two diols in each of these reductions supports the assignment of *endo* configuration to the *p*-methylbenzyl group. If this group were *exo*, it appears most probable[14b] that only the *exo* alcohol, resulting from approach of borohydride from the *endo* side of the adducts, would be formed. With the *endo* substituent, however, the specificity conferred by the 8-methyl group is counterbalanced and borohydride attack is not specific.

Sodium periodate cleavage of the crude diol mixture, or of the individual pure diols **8a** and **9a**, derived from **6a**, yielded 1,2,3-trimethyl-3-(*p*-methylphenylacetyl)-cyclopentanecarboxaldehyde (**12a**) whose aldehyde proton resonance at τ 0.3 appeared as a sharp singlet

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(6) R. Srinivasan, *J. Am. Chem. Soc.*, **83**, 4923 (1961).

(7) *Inter alia:* W. A. Noyes, Jr., G. B. Porter, and J. E. Jolley, *Chem. Rev.*, **56**, 49 (1956); L. S. Forster, *J. Am. Chem. Soc.*, **77**, 1417 (1955); W. A, Noyes, Jr., W. A. Mulac, and M. S. Matheson, *J. Chem. Phys.*, **36**, 880 (1962); N. Padnos and W. A. Noyes, Jr., *J. Phys. Chem.*, **68**, 464 (1964); P. Jolly and P. de Mayo, *Can. J. Chem.*, **42**, 170 (1964); R. S. H. Liu, N. J. Turro, Jr., and G. S. Hammond, *J. Am. Chem. Soc.*, **87**, 3406 (1965). The principal course of reaction of biacetyl in solution appears to be abstraction of a hydrogen atom from solvent by photoexcited biacetyl followed by appropriate reactions of the resulting pair of radicals.

(8) W. H. Urry and D. J. Trecker, *J. Am. Chem. Soc.*, **84**, 118 (1962).

(9) W. H. Urry, D. J. Trecker, and D. A. Winey, *Tetrahedron Letters*, 609 (1962).

(10) *Cf.* P. Ausloos and R. E. Rebbert, *J. Am. Chem. Soc.*, **83**, 4897 (1961), and references contained therein.

(11) (a) C. H. Krauch, F. Samir, and G. O. Schenck, *Chem. Ber.*, **98**, 3102 (1965). (b) For a general summary, see A. Schönberg, Präparative Organische Photochemie, Springer-Verlag, Berlin, 1958.

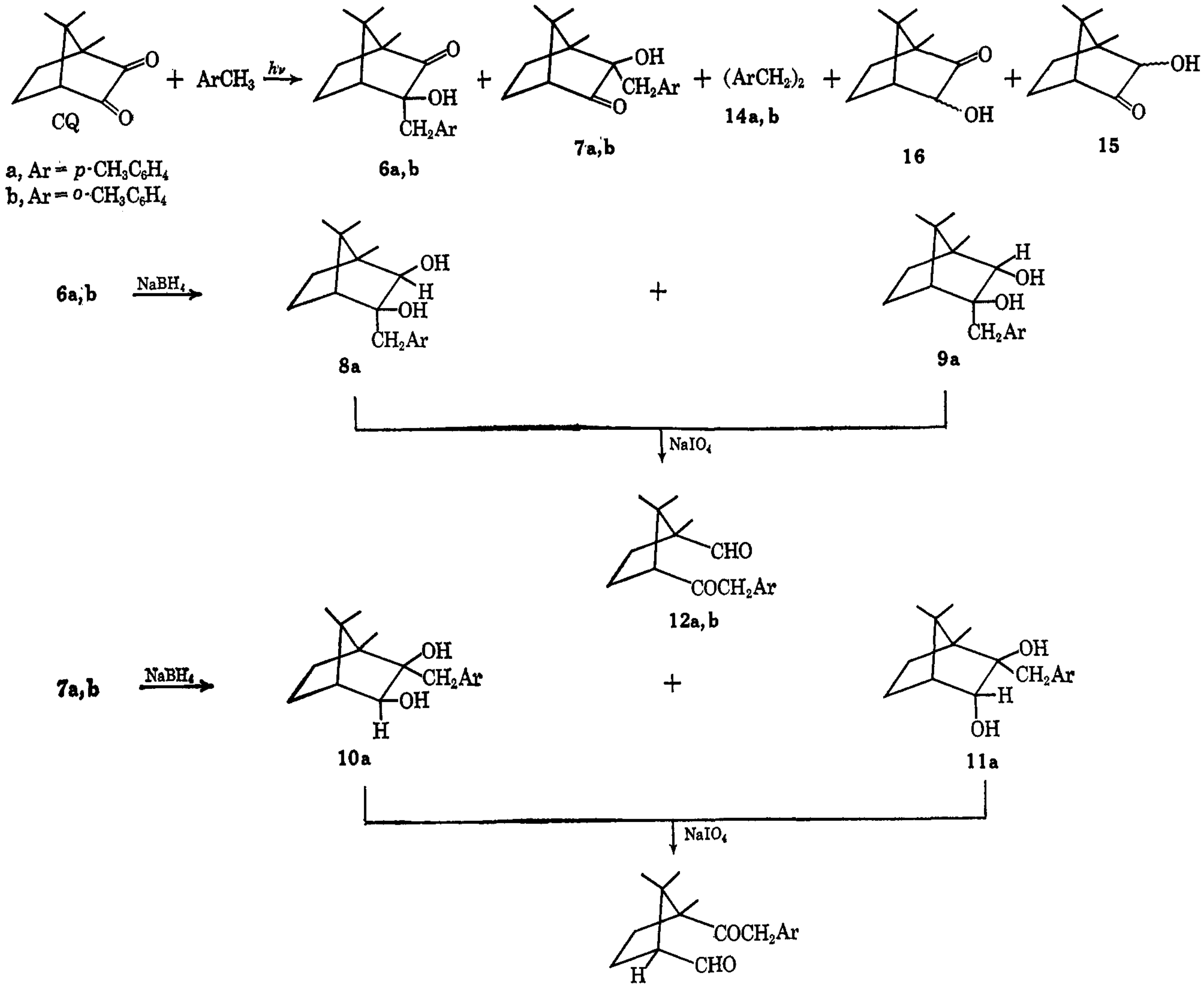
(12) The long wavelength maximum of CQ in *p*-xylene appears at 4700 A (ϵ 40).

(13) Reactions of Grignard reagents with CQ have been reported to lead to mixtures of products resulting from addition of only 1 equiv of reagent leaving one of the two carbonyl groups in CQ intact. The only reported exception is methylmagnesium iodide: J. Palmen, *Ann. Acad. Sci. Fennicae*, **29A**, 3 (1927); J. Gripenberg, *Suomen Kem.*, **18B**, 53 (1945); J. Gripenberg, *ibid.*, **19B**, 46 (1946).

(14) (a) P. Mälkönen, *Ann. Acad. Sci. Fennicae*, **128AII**, 1 (1964). (b) W. F. Erman and T. J. Flautt, *J. Org. Chem.*, **27**, 1526 (1962). (c) M. L. Capmau, W. Chodkiewicz, and P. Cadiot, *Tetrahedron Letters*, 1619 (1965).

(15) For a recent summary of applications of infrared and nmr spectroscopy to hydrogen-bonding studies, see A. I. Cohen, B. T. Keeler, E. J. Becker, and P. A. Diassi, *J. Org. Chem.*, **30**, 2175 (1965).

SCHEME I



($W_{1/2}$ = 1 cps) indicating that the aldehyde group was attached to a quaternary carbon. Therefore, the carbonyl group in **6a** must have been at C-2, adjacent to the quaternary carbon at C-1, and the complete structure of **6a** is thus established. Corresponding cleavage of either the crude diol mixture, or the individual pure diols, **10a** and **11a**, derived from **7a** afforded 2,2,3-trimethyl-3-(*p*-methylphenylacetyl)cyclopentanecarboxaldehyde (**13a**). As expected, the aldehyde proton resonance of **13a** at τ 0.30 appeared as a doublet (J = 2.5 cps) indicating the presence of a hydrogen on the carbon atom bearing the aldehyde group. Accordingly, the keto group of **7a** must have been adjacent to C-4 in the adduct. The formation of two different aldehydes clearly requires that **6a** and **7a** cannot be epimeric about a single carbon atom.

In addition to **6a** and **7a**, chromatography of the photoirradiation mixture afforded 4% of 1,2-di(*p*-tolyl)ethane (**14a**) and a semicrystalline mixture (6%) of ketols presumed to contain the isomeric 2-hydroxy-3-bornanones (**15**) and 3-hydroxy-2-bornanones (**16**). The latter mixture, eluted from the Florisil column with ethyl acetate, exhibited hydroxyl and cyclopentanone bands in the infrared, the appropriate mass spectral and osmometric molecular weights, and was oxidized by chromic acid to CQ.

In addition to the four products described above, a weak band at 5.55 μ was observed in the infrared spectrum of one of the chromatographic fractions from the photoirradiation. Such a band might be expected of the product of decarbonylation of CQ, 1,6,6-trimethylbicyclo[2,1,1]-5-hexanone[16] (**17**). While the absence of **17** cannot be positively established, it appears likely that the 5.55-μ absorption reflects the formation of a small amount of DL-camphoric anhydride (**18**) produced by photochemical reaction of CQ with traces of oxygen present.[17] In fact, when CQ was irradiated while bubbling air through the *p*-xylene solution (*cf.* ref 4b), the only products obtained were **18** and DL-camphoric acid[18] (**19**). Gas chromatographic analysis of the total product from irradiation of CQ with careful exclusion of oxygen showed the complete absence of **18**; corresponding analysis of total product

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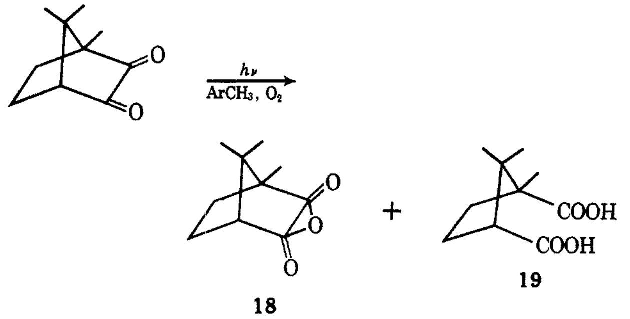
[16] J. Meinwald, A. Lewis, and P. J. Gassman [*J. Am. Chem. Soc.*, **84**, 977 (1962)] report carbonyl absorption at 5.61 μ for **17**.

[17] Exposure of an ether solution of CQ to sunlight has been reported to lead to conversion to **18**: M. Bredt-Salvelsberg, *Ber.*, **65**, 1 (1932).

[18] It seems probable that **19** arose from reaction of the anhydride **18** with traces of water present in the reaction mixture. However, the mechanism of this photooxidation is obscure at present. For a discussion of the photooxidation of biacetyl, see D. E. Hoare and G. S. Peterson, in "Advances in Photochemistry," W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr., Ed., Interscience Publishers Inc., New York, N. Y., 1964, pp 107 ff.

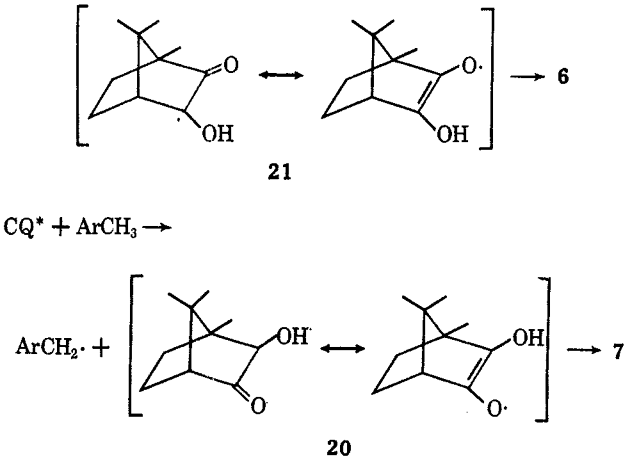


from irradiations in the presence of air indicated that none of the adducts **6a** and **7a** was present.

Irradiation of CQ in *o*-xylene proceeded in a manner completely analogous to that observed with *p*-xylene. In addition to 1,2-bis(*o*-tolyl)ethane (**14b**) and the hydroxybornanone mixture (**15**, **16**) previously observed, two isomeric adducts, DL-3-*endo*-(*o*-methylbenzyl)-3-*exo*-hydroxy-2-bornanone (**6b**, 44%) and DL-2-*endo*-(*o*-methylbenzyl)-2-*exo*-hydroxy-3-bornanone (**7b**, 18%), were obtained. Their structures were assigned on the basis of physical properties and the borohydride reduction followed by periodate cleavage scheme (see Experimental Section) utilized with the *p*-xylene adducts. It is noteworthy that the presence of the *o*-methyl group did not change the proportions of the two adducts appreciably.

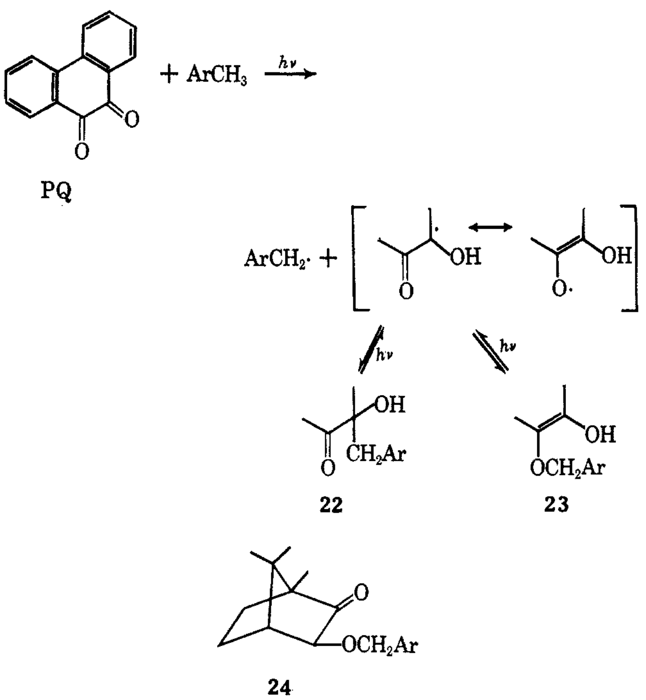
The observation of diarylethane and the hydroxybornanone mixture as products of these photochemical reactions is suggestive of a free-radical process. This might involve abstraction of a hydrogen atom from the xylene by photoexcited CQ leading to formation of a benzyl radical and either radical **20** or **21** (Scheme II) derived from CQ. Combination of the benzyl radical with **20** would produce **7**.[19] Alternatively, the CQ derived radicals might abstract a second hydrogen atom to give the hydroxybornanone mixture[20] and benzyl radicals could dimerize to diarylethane. The absence of a radical chain process is suggested by the low quantum yield, 0.07 ± 0.01, for disappearance of CQ upon irradiation at 4360 A in carefully degassed solution. The quantum yield for the photooxidation of CQ at the same wavelength was at least 0.16 ± 0.01.[21] These quantum yields are significantly lower than the value of unity reported[9b] for the intramolecular cyclization of long-chain α-diketones.

SCHEME II



The mechanism suggested above for the photoadditions parallels the mechanism proposed[1a] for the photoaddition of substituted toluenes to 9,10-phenanthrenequinone (PQ). The experimental results, however, are not completely parallel. Firstly, additions to PQ result in formation of both 1,2 (**22**) and 1,4 (**23**) adducts (Scheme III), the relative proportions of the two depending on the nature of substituents present. No evidence for formation of a keto ether such as **24** could be obtained in CQ reactions. Secondly, the PQ adducts **22** and **23** were photochemically interconvertible at wavelengths below 4000 A and underwent slow reversal to PQ upon irradiation in benzene solution. Although the carbonyl absorptions of **6a** and **7a** appeared at 308–309 mμ (ϵ 110–120), irradiation of solutions of either compound in a Pyrex vessel resulted only in recovery of unchanged starting materials. The results observed with PQ were explained in terms of a series of equilibria involving a semiquinone and benzyl radical as common intermediates; the divergences in results obtained with CQ may be due to differences in the relative magnitudes of the equilibrium constants in these cases. Further investigations of the mechanisms of these and other CQ photoreactions are in progress. In any event, it appears clear that the primary photochemical process in reactions of CQ as well as long-chain α-diketones involves hydrogen abstraction by a photoexcited carbonyl group in a manner very similar to the process observed in reactions of the $n \rightarrow \pi^*$ excited state of simple ketones.

SCHEME III



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[19] The relative proportions of **6** and **7** must then be determined by the relative rates of hydrogen abstraction by the two carbonyl oxygens. Presumably the preponderance of **6** over **7** reflects the steric influence of the bridgehead methyl group.

[20] The pinacols resulting from dimerization of **20** or **21** were not observed.

[21] This represents a minimum value since an oxygen-saturated solution was not maintained during the determination.

Experimental Section[22]

Photoirradiation of DL-Camphorquinone in *p*-Xylene Solution.—A solution of 3.02 g of CQ[4] in 600 ml of *p*-xylene was irradiated with a Hanovia 200-w immersion lamp in a Pyrex well. A nitrogen atmosphere was maintained by evacuating and filling with nitrogen four times and then closing off the system. After 9 hr the yellow color of CQ had disappeared and excess *p*-xylene was removed under reduced pressure with a rotary evaporator. A sample (0.35 g) of the residual oil was set aside and the remainder dissolved in 15 ml of hexane and left in the refrigerator for 2 days. Filtration and washing with hexane afforded 1.04 g (23%) of DL-3-*endo*-(*p*-methylbenzyl)-3-*exo*-hydroxy-2-bornanone (**6a**), mp 104–107°. Crystallization from hexane afforded the analytical sample of **6a**: mp 110°; $\lambda_{max}^{CH_2Cl_2}$ 2.83 and 5.75 μ; $\lambda_{max}^{CH_3OH}$ 253 (180), 259 (270), 265 (350), 273 (320), and 308 mμ (110); nmr, τ = 2.79 (d, J = 8 cps, 2 H), 2.83 (d, J = 8 cps, 2 H), 7.15 (2 H), 7.68 (4 H), complex absorption 7.9–8.6, 8.94 (3 H), 9.02 and 9.05 ppm. Crystallization of a sample from acetone–deuterium oxide afforded material with an identical nmr spectrum except for a reduction in the relative intensity of the 7.68 line to *ca*. three protons.

Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88; mol wt, 272. Found: C, 79.43; H, 8.88; mass spectrum no. 272.

The filtrate was then chromatographed on 130 g of Florisil. Elution with hexane afforded 0.16 g (4%) of crystalline 1,2-bis(*p*-tolyl)ethane (**14a**) whose identity was established by comparison with an authentic sample.

Elution with 50, 60, and 70% benzene in hexane afforded 0.78 g of crystalline DL-2-*endo*-(*p*-methylbenzyl)-2-*exo*-hydroxy-3-bornanone (**7a**) which was crystallized from hexane to give 0.58 g, mp 89–90°. The analytical sample was obtained by further crystallization from hexane: mp 90–91°; $\lambda_{max}^{CH_2Cl_2}$ 2.82 μ and 5.75 μ; $\lambda_{max}^{CH_3OH}$ 253 (230), 260 (270), 265 (320), 274 (290), and 309 mμ (120); nmr, τ = 2.87 (4 H), 7.20 (2 H), 7.70 (3 H), 7.75 (1 H), complex absorption 7.9–8.6, 8.94 (3 H), 9.04 (3 H), and 9.18 (3 H) ppm. Exchange with deuterium oxide resulted in disappearance of the line at τ 7.75. This compound exhibited retention times identical with those of **6a** in gas chromatographic experiments using SF-96, SE-30, QF-1, Apiezon L, or NPGS as stationary phases.

Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88; mol wt, 272. Found: C, 79.17; H, 8.94; mass spectrum no., 272.

Elution with 80% benzene in hexane afforded 0.29 g of oil containing equal amounts of **6a** and **7a** on the basis of infrared and tlc analysis (silica gel G, benzene developer). Total yield of **7a** was 0.92 g (20%).

Elution with 90% benzene in hexane and pure benzene gave 0.51 g of pure **6a**. The following fraction eluted with 5% ethyl acetate in benzene weighed 0.77 g and contained at least 50% of **6a** by infrared and tlc. In addition to the carbonyl maximum of **6a** at 5.75 μ, the mixture exhibited a weak (*ca.* 20% of 5.75-μ intensity) band at 5.55 μ. Total yield of **6a** was 2.13 g (45%).

Finally, elution with pure ethyl acetate afforded 0.42 g (6%) of a semisolid mixture of 2-hydroxy-3-bornanones (**15**) and 3-hydroxy-2-bornanones (**16**): λ_{max} 2.89, 2.90, and 5.75 μ; nmr, τ = 3.7 (br, 1 H), 5.77, 5.85, 6.15 (total 5.77, 5.85, 6.15 intensity = 1 H), complex absorption 7.7–8.8 (5.2 H), 8.95, 9.00, 9.05, and 9.10 ppm. The material reacted very slowly with sodium periodate in aqueous methanol.

Anal. Calcd for $C_{10}H_{16}O_2$: mol wt, 168. Found: mass spectrum no., 168; vapor pressure osmometer, 181.

A mixture of very similar composition was obtained when a solution of CQ in *p*-xylene under helium was irradiated in a Pyrex vessel with light from a 1000-w General Electric high-pressure mercury vapor lamp (AH-6) filtered through a Corning 3-73 color glass filter (<0.5% transmission at 3910 A).

Irradiation of solutions containing 30 mg of **6a** or **7a** in 7 ml of benzene in a Pyrex vessel with unfiltered light from the 1000-w lamp for 2 hr resulted in quantitative recovery of starting material.

Oxidation of Hydroxybornanone Mixture (15, 16) to CQ.—A solution of 150 mg of the mixture **15**, **16** in 0.5 ml of acetone was treated with a few drops of 8 N chromic acid solution[23] at room temperature. A few drops of methanol were added to the resulting green solution after 2 min and the mixture then diluted with water. Extraction with ethyl acetate followed by drying and concentration afforded 140 mg of yellow semisolid material which exhibited λ_{max}^{hexane} 470 mμ. Sublimation at 50° and 1 mm yielded 25 mg of yellow solid, mp 193–195°, identical with CQ.

Reaction of DL-Camphorquinone and *p*-Methylbenzylmagnesium Chloride.—The Grignard reagent prepared from 8.5 ml of freshly distilled *p*-methylbenzyl chloride and 1.44 g of magnesium in 35 ml of anhydrous ether was filtered from excess magnesium, and a solution of 2.5 g of DL-camphorquinone in 35 ml of anhydrous ether was added to the magnetically stirred solution as rapidly as the exothermic nature of the reaction permitted. After the addition was completed, the dark solution was stirred for 1.25 hr and poured onto iced sulfuric acid which was extracted twice with 100-ml portions of ethyl acetate, washed with saturated sodium bicarbonate solution, water, and saturated sodium chloride solution. The ethyl acetate layer was dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure to give 6 g of oily solid. Crystallization from 15 ml of hexane gave 1.98 g of 1,2-bis(*p*-tolyl)ethane (**14a**), mp 78–80°. Chromatographic separation as described above afforded an additional 1.0 g of **14a**, 1.20 g (41%) of **6a**, 0.59 g of CQ, 0.28 g (10%) of **7a**, and 0.85 g of the mixture **15**, **16**.

Reduction of DL-3-*endo*-(*p*-methylbenzyl)-3-*exo*-hydroxy-2-bornanone (6a) with Sodium Borohydride.—A solution of 1.00 g of **6a** in 15 ml of methanol was treated with 556 mg of sodium borohydride for 2.5 hr at room temperature. This was then neutralized with acetic acid and the colorless solution added to 200 ml of a 1:1 mixture of ethyl acetate and saturated salt solution. The ethyl acetate layer was separated and washed with saturated sodium bicarbonate solution, water, and saturated salt solution and then dried over anhydrous sodium sulfate and concentrated to dryness on the steam bath under reduced pressure to give 1.3 g of cloudy oil. This oil was chromatographed on 60 g of silica gel G. Elution with 75% benzene in hexane gave 637 mg (63%) of DL-2-*endo*-(*p*-methylbenzyl)-2,3-*exo*,*exo*-dihydroxybornane (**8a**). The analytical sample was obtained by crystallization from hexane: mp 107–108.5°; $\lambda_{max}^{CCl_4}$ 2.75 μ; nmr, τ 2.95, 6.70 (d, J = 6 cps), 7.20, 7.58 (d, J = 6 cps), 7.76, complex absorption 8.3–8.7, 8.91, 9.14, and 9.22 ppm. Addition of D_2O and redetermination of the spectrum gave an identical result except that the 6.70 doublet (C-2 H) collapsed to a singlet at 6.71, the 7.58 doublet disappeared, and intensity of higher field absorption decreased slightly.

Anal. Calcd for $C_{18}H_{26}O_2$: C, 78.79; H, 9.55. Found: C, 78.99; H, 9.70.

Elution with 1% ethyl acetate in benzene gave 270 mg (27%) of DL-3-*endo*-(*p*-methylbenzyl)-2-*endo*-3-*exo*-dihydroxybornane (**9a**). The analytical sample was prepared by crystallization from hexane: mp 99.5–100.5°; $\lambda_{max}^{CCl_4}$ 2.65 and 2.87 μ; nmr, 3.00, 6.33, 7.27, 7.74, 7.79, complex absorption 8.05–8.7, 9.14, and 9.18 ppm.

Anal. Calcd for $C_{18}H_{26}O_2$: C, 78.79; H, 9.55; mol wt, 274. Found: C, 78.59; H, 9.65; mass spectrum no., 274.

Oxidation of **8a** or **9a** with chromic acid solution as described above for oxidation of **15**, **16** furnished **6a**.

Reduction of DL-2-*endo*-(*p*-Methylbenzyl)-2-*exo*-hydroxy-3-bornanone (7a) with Sodium Borohydride.—Reaction of 540 mg of **7a** in 10 ml of methanol with 300 mg of sodium borohydride as described above gave 700 mg of cloudy oil which was chromatographed on 55 g of silica gel G. Elution with benzene gave 247 mg (45%) of DL-2-*endo*-(*p*-methylbenzyl)-2,3-*exo*,*exo*-dihydroxybornane (**10a**). The analytical sample was obtained by crystallization from hexane: mp 126.5–127.5°; $\lambda_{max}^{CCl_4}$ 2.73 μ; nmr, τ = 2.92, 6.69 (d, J = 6 cps), 7.25, 7.74, 7.76, 8.3, 8.91, 9.14, and 9.23 ppm.

Anal. Calcd for $C_{18}H_{26}O_2$: C, 78.79; H, 9.55; mol wt, 274. Found: C, 78.92; H, 9.71; mass spectrum no 274.

Elution with 1% ethyl acetate in benzene gave 231 mg (43%) of DL-2-*endo*-(*p*-methylbenzyl)-2-*exo*-3-*endo*-dihydroxybornane (**11a**). The analytical sample was obtained by crystallization from hexane: mp 114–115.5°; $\lambda_{max}^{CCl_4}$ 2.65 and 2.88 μ, nmr, τ = 3.00, 6.34 (m), 7.21, 7.27, 7.76, 7.85, complex absorption 8.1–9.2 with intense lines protruding at 8.90, 9.15, and 9.20

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[22] Solvents used in photoirradiations were distilled and either freshly boiled or purged with helium before use. Melting points are corrected. Nmr spectra were determined at 60 Mc in deuteriochloroform using tetramethylsilane (TMS) as internal standard. Hexane refers to a commercial petroleum fraction (Skellysolve B) of bp 62–70°.

[23] K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, **39** (1946); C. Djerassi, R. R. Engle, and A. Bowers, *J. Org. Chem.*, **21**, 1547 (1956).

ppm. Oxidation of **10a** or **11a** with chromic acid solution as described above furnished **7a**.

Anal. Calcd for $C_{18}H_{26}O_2$: C, 78.79; H, 9.55; mol wt, 274. Found: C, 78.70; H, 9.57, mol wt, 274.

DL-1,2,2-Trimethyl-3-(*p*-methylphenylacetyl)cyclopentanecarboxaldehyde (12a). A. From 8a.—A solution of 188 mg of **8a** in 10 ml of methanol was mixed with a solution of 275 mg of sodium metaperiodate in 5 ml of distilled water. After 16 hr the solution, containing a mass of white needles, was diluted with 50 ml of saturated salt solution and 50 ml of ethyl acetate. The layers were separated, the aqueous layer was washed with ethyl acetate, and the combined organic layers were washed with saturated sodium chloride solution, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to give 181 mg of clear oil which could not be induced to crystallize. The analytical sample of DL-1,2,2-trimethyl-3-(*p*-methylphenylacetyl)cyclopentane carboxaldehyde (**12a**) was prepared by three crystallizations from hexane at Dry Ice–acetone temperature; the resulting colorless product was liquid at room temperature; $\lambda_{\max}^{\mathrm{CH_2Cl_2}}$ 3.65 μ and 5.84 μ; nmr, $\tau = 0.30$ ($W_{1/2} = 1$ cps), complex absorption 2.8–3.3, broad envelope 7.0–9.25 with lines protruding at 7.14, 7.75, 8.89, 9.09, and 9.16 ppm.

Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88. Found: C, 79.10; H, 8.70.

B. From 9a.—Similar treatment of 130 mg of **9a** gave 138 mg of clear oil whose nmr and infrared spectra were identical to those of the above.

Reaction of the crude mixture obtained by borohydride reduction of compound **6a** with sodium periodate gave identical results.

DL-2,2,3-Trimethyl-3-(*p*-methylphenylacetyl)cyclopentanecarboxaldehyde (13a). A. From 10a.—Similar sodium metaperiodate cleavage of 75 mg of **10a** gave 78 mg of clear oil which could not be induced to crystallize. The analytical sample of DL-2,2,3-trimethyl-3-(*p*-methylphenylacetyl)cyclopentanecarboxaldehyde (**13a**) was prepared by three crystallizations from hexane at Dry Ice–acetone temperature; the colorless product was liquid at room temperature; $\lambda_{\max}^{\mathrm{CH_2Cl_2}}$ 3.67 μ and 5.85 μ; nmr, $\tau = 0.30$ (d, $J = 2.5$ cps), 3.67, 5.85, 7.71, 8.64, 8.82, and 9.15 ppm.

Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88. Found: C, 79.12; H, 8.76.

B. From 11a.—Similar treatment of 82 mg of **11a** gave 93 mg of clear oil whose nmr and infrared spectra were identical with those of the above.

Reaction of the crude mixture obtained by borohydride reduction of compound **7a** with sodium periodate gave identical results.

Photoirradiation of DL-Camphorquinone in *o*-Xylene.—A solution of 300 mg of DL-camphorquinone in 7 ml of *o*-xylene in Pyrex was irradiated with a 1000-w high pressure mercury vapor lamp using a Corning 3-73 filter until the yellow color had disappeared (15 hr). Removal of excess *o*-xylene under reduced pressure gave 370 mg of clear oil. Crystallization from hexane gave 117 mg (32%) of white solid, DL-3-*endo*-(*o*-methylbenzyl)-3-*exo*-hydroxy-2-bornanone (**6b**). The analytical sample was obtained by crystallization from hexane: mp 132–133.5°; $\lambda_{\max}^{\mathrm{CH_2Cl_2}}$ 2.76 μ and 5.74 μ; nmr, τ = complex absorption 2.5–3.1, 7.13 (1.9 H), 7.75 (3 H), complex absorption 7.8–8.6, 8.94, 9.00, and 9.07 ppm; addition of deuterium oxide caused a reduction in intensity of the τ 7.8–8.6 absorption.

Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88; mol wt, 272. Found: C, 79.18; H, 8.66; mass spectrum no., 272.

The mother liquor was chromatographed on 15 g of Florisil. Elution with 150 ml of hexane gave 2.5 mg (1%) of 1,2-bis(*o*-tolyl)ethane (**14b**), mp 64–66°, lit.[24] 66°.

Elution with 30% benzene in hexane gave 65 mg (18%) of white solid, DL-2-*endo*-(*o*-methylbenzyl)-2-*exo*-hydroxy-3-bornanone (**7b**). The analytical sample was obtained by crystallization from hexane: mp 89–90.5°; $\lambda_{\max}^{\mathrm{CH_2Cl_2}}$ 2.78 μ and 5.74 μ; nmr, τ = complex absorption 2.8–3.1, 7.17 (d, $J = 3$ cps, 2 H), 7.76, complex absorption 7.8–8.6 with a sharp line at 7.96, 8.96, 9.02, and 9.07 ppm; addition of deuterium oxide resulted in disappearance of the line at 7.96.

Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88; mol wt, 272. Found: C, 79.20; H, 8.69; mass spectrum no., 272.

Elution with 60% benzene in hexane gave an additional 47 mg (13%, total yield 44%) of **6b**. Elution with ethyl acetate gave 41 mg (11%) of a white, oily solid, a mixture of **15** and **16**, mp 108–131°.

Reduction and Cleavage of DL-3-*endo*-(*o*-Methylbenzyl)-3-*exo*-hydroxy-2-bornanone (6b).—A solution of 30 mg of **6b** in 3 ml of methanol was treated with 17 mg of sodium borohydride for 2.5 hr at room temperature. Work-up as described for **6a** gave 29 mg of clear oil which exhibited no absorption at 5.5–6.0 μ. This was dissolved in 3 ml of methanol and treated with a solution of 41 mg of sodium metaperiodate in 2 ml of water. After 13 hr. the solution containing white needles was worked up as described above to give 31 mg of 1,2,2-trimethyl-3-(*o*-methylphenylacetyl)cyclopentane carboxaldehyde (**12b**) as an oil: $\lambda_{\max}^{\mathrm{CH_2Cl_2}}$ 3.65 μ and 5.83 μ; nmr, $\tau = 0.3$ (singlet, $W_{1/2} = 0.7$ cps), complex absorption 2.55–2.75, 6.23, 7.77, and complex absorption 8.7–9.15 ppm.

Reduction and Cleavage of DL-2-*endo*-(*o*-Methylbenzyl)-2-*exo*-hydroxy-3-bornanone (7b).—A solution of 25 mg of **7d** in 3 ml of methanol was treated with 15 mg of sodium borohydride for 3 hr at room temperature. Work-up as described above gave 27 mg of a clear oil which was dissolved in 3 ml of methanol and treated with a solution of 38 mg of sodium metaperiodate in 2 ml of water. After 24 hr, the mixture, which contained white needles, was worked up as described above to give 21 mg of 2,2,3-trimethyl-2-(*o*-methylphenylacetyl)cyclopentane carboxaldehyde (**13b**) as a clear oil: $\lambda_{\max}^{\mathrm{CH_2Cl_2}}$ 3.63 and 5.82 μ; nmr, $\tau = 0.32$ (d, $J = 2.5$ cps), complex absorption 2.7–3.0, 7.14, 7.75, complex absorption 7.8–8.8, 8.82, 8.88, and 8.93 ppm.

Photooxidation of DL-Camphorquinone with Air.—A solution of 700 mg of DL-camphorquinone in 7 ml of *p*-xylene was irradiated for 10 hr while air was continuously bubbled through the solution. The excess *p*-xylene was removed to give 750 mg of light yellow solid. This was dissolved in 100 ml of ether and extracted three times with 30-ml portions of 10% aqueous sodium hydroxide. The neutral fraction was washed with water, dried over anhydrous sodium sulfate, and concentrated on the steam bath to give 500 mg of a yellow white solid. Crystallization from hexane gave 270 mg of DL-camphoric anhydride (**18**), mp 221–223° (lit.[25] 220°), $\lambda_{\max}^{\mathrm{CH_2Cl_2}}$ 5.52 μ and 5.65 μ. The infrared spectrum was identical with that of an authentic sample of camphoric anhydride and a mixture melting point showed no depression.

The acidic fraction was neutralized with 10% hydrochloric acid and extracted twice with 75-ml portions of ethyl acetate. The combined ethyl acetate extracts were washed with water and saturated salt solution, dried over anhydrous sodium sulfate, and concentrated under reduced pressure on the steam bath to give 113 mg of camphoric acid (**19**), mp 201–202.5° (lit.199–200°), $\lambda_{\max}^{\mathrm{CH_2Cl_2}}$ 5.86 μ. The infrared spectrum was identical with that of authentic sample and a mixture melting point showed no depression.

Quantum Yield Determinations.—Quantum yields were determined at 4360 A (Mazda 125-w medium-pressure lamp, Corning glass color filters 3-73 and 5-58) using ferrioxalate actinometry.[26] Distilled *p*-xylene was degassed by the freeze–thaw method and distilled in a vacuum line into a 10-mm square quartz cell containing 10.34 mg of CQ and the cell was then sealed off. The photochemical reaction was monitored by the decrease in optical density at 4700 A, the long wavelength maximum of CQ. The quantum yield, measured over initial 10% reaction, was 0.07 ± 0.01. The quantum yield in the presence of oxygen was determined using 3 ml of a solution containing 3.445 mg of CQ/ml of distilled *p*-xylene placed in a standard, loosely stoppered 1-cm quartz cell. No attempt was made to maintain an air-saturated solution. The value obtained for initial 10% of reaction was 0.16 ± 0.01.

Both reactions were allowed to proceed to about 80% completion and then the solutions removed from the cells and evaporated to dryness. Each residue was dissolved in a small volume of ethyl acetate and analyzed by gas chromatography (6 ft × 0.25 in. column, 20% SF-96 on firebrick, 195°, 45 psi of helium pressure). In addition to the solvent peak, the degassed sample exhibited peaks with retention times of 3.0 (CQ), 14.0 (**14a**), and 49.0 min (**6a** and **7a**). The sample irradiated in the presence of air showed peaks at 3.1 (CQ) and 5.5 min (**18**).

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Rearranged Products from the Reaction of Benzenesulfonic Acids with Caustic

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It has been demonstrated that the isomeric benzenedisulfonic acids and phenolsulfonic acids do not form rearranged, phenolic products when treated with molten caustic. These results are contrary to the generally accepted belief that molten caustic reacts with either benzene-1,2-disulfonic acid or benzene-1,4-disulfonic acid to form substantial amounts of the rearranged product, resorcinol. The most plausible explanation for this lack of agreement appears to be that the previous investigators incorrectly identified the sulfonic acids employed or employed sulfonic acids containing isomeric impurities.

A number of current organic chemistry books contain statements to the effect that a substantial amount of the rearranged product, resorcinol, is formed by the reaction of caustic with benzene-1,2-disulfonic acid and benzene-1,4-disulfonic acid. Statements relative to the formation of rearranged products from analogous reactions employing the phenolsulfonic acids are less common and no publications claiming the formation of catechol or hydroquinone by the reaction of caustic with benzene-1,3-disulfonic acid were found. It has been implied that the formation of rearranged products involves a benzyne intermediate[1] which would be consistent with the benzyne chemistry of substituted chlorobenzenes.[2]

Most of the experimental data relative to the formation of rearranged products by reactions of caustic with benzenedisulfonic acids or phenolsulfonic acids are very old and the reliability of these data has been questioned.[1] The literature contains numerous examples of lack of agreement between investigators, incorrect identification of reactants and products, and sketchy experimental details. Even in the case of the more recent literature, there are inconsistencies and the establishment of the isomeric purity of the sulfonic acids employed was not reported.

The conversion of benzenedisulfonic acids to dihydroxybenzenes involves the replacement of two sulfonate groups. It is thus possible that rearranged products are formed during the formation of the intermediate phenolsulfonic acids, during the conversion of the phenol sulfonic acid to the dihydroxybenzene, or during both reactions. The literature was reviewed in an attempt to determine at what stage rearrangement occurs.

Disulfonic Acids to Phenolsulfonic Acids.—Experimental details were not found for the conversion of benzene-1,2-disulfonic acid with molten caustic to a phenolsulfonic. Nearly a hundred years ago Barth and Senhofer[3] reported that both benzene-1,3-disulfonic acid and the 1,4 isomer produced nearly quantitative yields of phenol-3-sulfonic acid when allowed to react with caustic at intermediate temperatures. The conversion of benzene-1,3-disulfonic acid to phenol-3-sulfonic acid was verified by Willson and Meyer;[4] however, no subsequent report of the formation of phenol-3-sulfonic acid from benzene-1,4-disulfonic acid was found.

Phenolsulfonic Acids to Dihydroxybenzenes.—In 1867 Kekule[5] reported that the reaction of phenol-3-sulfonic acid with potassium hydroxide yielded the rearranged product, catechol, containing a substantial amount of resorcinol. Kekule's procedure for the preparation of what he reported to be phenol-3-sulfonic acid was later reported by Barth and Senhofer[3] as well as Degener[6] to yield phenol-2-sulfonic acid. Furthermore, these later investigators were unable to detect the presence of resorcinol in the product from the reaction of phenol-2-sulfonic acid with molten caustic. Other than the report by Kekule, no references claiming the formation of rearranged products by the reaction of phenol-3-sulfonic acid with caustic were found.

Kekule[5] also reported that the reaction of phenol-4-sulfonic acid with potassium hydroxide resulted in the formation of the rearranged product, resorcinol. A short time later Barth and Senhofer,[3] Degener,[6] and Lincke[7] all reported that neither resorcinol nor hydroquinone was formed by this reaction.

In 1942 Fierz-David and Stamm[8] stated "it is known that considerable amounts of hydroquinone are formed by treatment of phenol-4-sulfonic acid with aqueous alkali particularly in the presence of copper or a copper salt." These authors further stated that this reaction produced resorcinol in up to 9.5% yield. A search of the literature failed to uncover any experiments in which copper or its salts were used to catalyze the reaction of sulfonic acids with caustic or any experimental evidence for the formation of hydroquinone from phenol-4-sulfonic acid. The reliability of the report by Fierz-David and Stamm is rendered more questionable by their own statement in a later portion of this paper that "phenol-4-sulfonic acid yields practically no resorcinol when treated with molten caustic."

Benzenedisulfonic Acids to Dihydroxybenzenes.—Statements can be found in books and journal articles to the effect that the rearranged product, resorcinol, is formed by the reaction of caustic with benzene-1,2-disulfonic acid; however, published experimental

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(2) See ref 1 for leading references.

(3) L. Barth and C. Senhofer, *Ber.*, **8**, 1477 (1875); **9**, 969 (1876).

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(8) H. E. Fierz-David and G. Stamm, *Helv. Chim. Acta*, **25**, 364 (1942).