Photolysis of 2-Keto-2,3-dihydrobenzofurans, *o*-Hydroxystyrenes, and 1-(*o*-Hydroxyphenyl)-1,5-hexadienes

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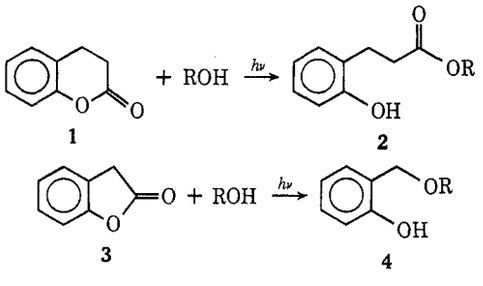
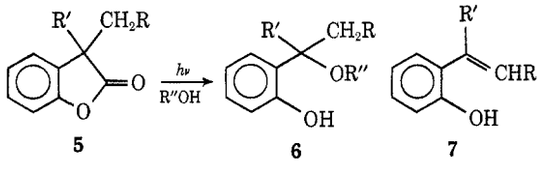
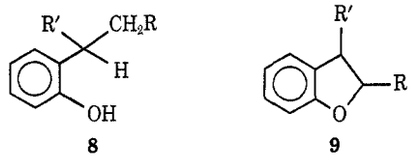
In continuation of earlier work in which it had been demonstrated that the photolysis of a methanol solution of 2-keto-2,3-dihydrobenzofuran yields methyl 2-hydroxybenzyl ether, the photolysis of several 3,3-disubstituted 2-keto-2,3-dihydrobenzofurans (**5**) has been studied. It has been found that, in addition to the ethers (**6**), the product mixture may also include olefins (**7**), reduction products (**8**), and dihydrobenzofurans (**9**) and that its composition is a function of the substituents at the C-3 position of **5**, the solvent, the concentration, and the incidence of secondary photolysis processes. To explain the results it is suggested that (a) the initially formed product from **5** is a quinonemethide, (b) the quinonemethide can react with alcohol, *via* a Michael addition, to form the ether and/or undergo intramolecular hydrogen transfer to form the olefin, (c) the olefin upon excitation can revert to the quinonemethide, cyclize to the dihydrobenzofuran, and/or react with the solvent to form reduction product. In support of this hypothesis it has been shown that (a) photolyses of the olefin (**7**) in methanol solution leads to product mixtures similar to those obtained from the 2-keto-2,3-dihydrobenzofurans and (b) photolyses of 2-keto-3-trideuteriomethyl-3-phenylbenzofuran (**5e**) and 1-phenyl-1-(*o*-hydroxyphenyl)-2,2-dideuterioethylene (**7e**) yield products in which some deuterium exchange has occurred. A chemical application of the Förster–Weller effect was sought in the photolysis of three 1-(*o*-hydroxyphenyl)-1,5-hexadienes which, it was hoped, would yield the cyclopentyl or cyclohexyl compounds **14–16**. Instead, however, the products parallel those obtained from the photolysis of the analogous *o*-hydroxystyrenes.

Whereas photolyses of alcohol solutions of 3,4-dihydrocoumarin (**1**) yield alkyl β-(2-hydroxyphenyl)-propionates (**2**), similar treatment of 2-keto-2,3-dihydrobenzofuran (**3**) yields 2-hydroxybenzyl ethers (**4**).[1] Further study has now revealed that ethers are







a, R = H; R′ = CH_3
b, R = CH_3; R′ = C_2H_5
c, R = H; R′ = C_6H_5
d, R = CH_3; R′ = C_6H_5
e, CH_2R = CD_3; R′ = C_6H_5

but one of several products that can be formed in the latter case and that the outcome can be affected by the substituents at C-3 of the 2-keto-2,3-dihydrobenzofuran, the solvent, the concentration, and the extent to which secondary photolysis takes place. The present paper is concerned with a discussion of these several factors.

Photolysis Products from 3,3-Disubstitued 2,3-Dihydrobenzofurans.—Employing alcohols and hydrocarbons as solvents, irradiations were carried out with 2-keto-2,3-dihydrobenzofurans substituted at C-3 with two methyl groups (**5a**), two ethyl groups (**5b**), one methyl and one phenyl group (**5c**), and one ethyl and one phenyl group (**5d**). The products obtained from these photolyses include ethers (**6**), olefins (**7**), reduction compounds (**8**), and dihydrobenzofurans (**9**), as shown in Table I. Inspection of this table reveals that (a) compounds **5a**, **5c**, and **5d** all yield ethers (**6**) as a major product in methanol solution, whereas compound **5b** yields the olefin (**7**), (b) the extent of ether formation in all cases diminishes as the solvent is changed from methanol to ethanol to 2-propanol, (c) the ratio of ether to reduction compound produced from **5c** decreases as the concentration of **5c** decreases, and (d) the olefins (**7**), formed at least in trace amounts in almost all cases, become the exclusive products in hydrocarbon solvents.

Photolysis Products from *o*-Hydroxystyrenes.—The substituted styrenes **7a–d**, which are the exclusive products from the photolysis of **5a–d** in hydrocarbon solvents, are also formed when the photolyses are carried out in alcohol solution. This suggests the possibility of a precursor role for the olefin with respect to the ether; to test this hypothesis methanol solutions of the olefins **7a–d** were irradiated. The results from these experiments, listed in Table II, show that (a) olefins **7a**, **7c**, and **7d** yield product mixtures qualitatively identical with and quantitatively similar to those obtained by photolysis of **5a**, **5c**, and **5d** in methanol; (b) olefin **7b** undergoes no change except a cis–trans isomerization; and (c) the ratio of ether to reduction produced from **7c** decreases as the concentration of **7c** decreases.

The photoinduced alcoholsis of 3,4-dihydrocoumarin to alkyl β-(2-hydroxyphenyl)propionates has been rationalized in terms of a spiro diketone intermediate[1] and a ketene intermediate,[2] the latter having been shown

(1) C. D. Gutsche and B. A. M. Oude-Alink, *J. Amer. Chem. Soc.*, **90**, 5855 (1968).

(2) D. A. Plank, PhD. Thesis, Purdue University, 1966.

TABLE I

PHOTOLYSIS OF 3,3-DISUBSTITUTED 2-KETO-2,3-DIHYDROBENZOFURANS

Starting compd							Product, % yield				
	R	R′	Solvent	Concn, mmol/l.	Time, hr	Apparatus[a]	5	6	7	8	9
5a	H	CH_3	MeOH	96.0	9	A	47	38	8	7	
			2-PrOH	37.7	2.5	A	53.5	6.5	40	3.5	
			Pentane	12.3	1	A	27.5		72.5		
5b	CH_3	C_2H_5	MeOH	97.5	13	A	56.5	4.5	39		
			2-PrOH	27.2	4	A	33		47		
			Pentane	18.1	1	A	57		43		
5c	H	C_6H_5	MeOH	25.0	18	B	11	68.5	4.1	13.7	
				12.0	18	B		57.6	4.6	21.2	
				7.9	9	B		21.4	24.1	18.8	
				4.1	18	B		32.8		36.2	
			EtOH	25.0	18	B	17	50	9	14.5	
			2-PrOH	25.0	18	B	25	29	18	9	
			Hexane	25.0	18	B	72		10		
5d	CH_3	C_6H_5	MeOH	25.0	18	B	33	30	13		27
			EtOH	25.0	18	B	36	28	10.5		26
			2-PrOH	25.0	18	B	47	18	9		22
			Hexane	25.0	18	B	69		28		

[a] A, 300-ml quartz immersion well 450-W Hg lamp; B, 600-ml Rayonet Model RPR-100 reactor with Hg lamps.

TABLE II

PHOTOLYSIS OF *o*-HYDROXYSTYRENES IN METHANOL SOLUTION

Starting compd						Product, % yield			
	R	R′	Concn, mmol/l.	Time, hr	Apparatus[a]	7	6	8	9
	H	H	52.8	18	B	12.5	56.3		
7a	H	CH_3	93.3	18	B	9.9	81.8	4.3	
7b	CH_3	C_2H_5	7.5	1.5	A	92			
7c	H	C_6H_5	56.6	18	B	3	93	4	
			27.3	18	B	6.8	57	15	
			19.3	18	B	4.6	50.6	18.4	
			14.3	18	B		51.2	24.0	
			8.84	18	B		40.7	32.6	
			5.48	18	B		33.2	36.6	
			3.73	0.33	A		28.5	42.5	
			2.82	18	B		17.0	43.7	
7d	CH_3	C_6H_5	16.4	18	B	6.2	35.9		47.6
			4.02	0.25	A		42.2		57.8

[a] A, 300-ml quartz immersion well with 450-W Hg lamp; B, 600-ml Rayonet Model RPR-100 reactor with Hg lamps.

quite conclusively, on the basis of low-temperature spectral observations and deuterium incorporation experiments, to account for at least part of the product.[3,4] Either of these intermediates would be more difficult to generate from 2-keto-2,3-dihydrobenzofurans, *i.e.*, the spiro diketone because of increased ring strain and the ketene because of a less accessible hydrogen for intramolecular transfer. Rather than following either of these pathways, therefore, the photoexcited 2-keto-2,3-dihydrobenzofuran loses carbon monoxide to yield a species which can be formulated as an *o*-quinonemethide.[5]

o-Quinonemethides react rapidly with nucleophiles, but alternative pathways may be followed if nucleophiles are not present. For example, the quinonemethides **10a–d** can rearrange, by intramolecular hydrogen transfer, to the corresponding *o*-hydroxystyrenes **7a–d**. This process, which is the exclusive one in hydrocarbon solvents, may also take place in protic solvents, and the olefins **7a–d** have been shown to be possible progenitors of the ethers **6a–d**. The immediate precursor to the ethers, however, is considered to be the *o*-quinonemethide (whether it be formed from the 2-keto-2,3-dihydrobenzofurans or from the *o*-hydroxystyrenes), which reacts with alcohol *via* nucleophilic attack (Michael addition) at the benzyl carbon atom.[6] The diminishing yield of ether with increasing size of the nucleophile (methanol to ethanol to 2-propanol) is in accord with the known sensitivity of Michael addi-

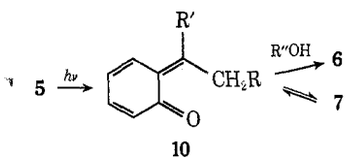
(3) O. H. Chapman and C. L. McIntosh, *J. Amer. Chem. Soc.*, **91**, 4309 (1969).

(4) On the basis of *apparent* nonincorporation of deuterium into **2** when a sample of **1** was irradiated in CH_3OH solution, the present authors favored the spiro diketone mechanism.[1] More recent work by Chapman and McIntosh,[3] however, has shown that a significant amount of deuterium *is* incorporated into **2**. The difference between these two sets of experiments is in the method of product assay that was employed, *viz.*, nmr in our case and mass spectra by Chapman and McIntosh. A recheck of our data showed that, although the purified sample of methyl β-(2-hydroxyphenyl)-propionate appeared to contain no carbon-bound deuterium, as indicated by a ratio of 1.0 for the CH_2/ArH resonance in the nmr, the crude photolysis product showed a CH_2/ArH ratio of only 0.89, corresponding to a 45% incorporation of deuterium into a methylene group. Repetition of the experiment produced a sample of the ester which has been shown by mass spectral analysis to contain 31% $C_{10}H_{12}O_3$, 48% $C_{12}H_{11}DO_3$, and 21% $C_{12}H_{10}D_2O_3$ (as C-bound deuterium), in accord with the findings of Chapman and McIntosh.

(5) Using low-temperature methods [*cf.* O. L. Chapman and J. D. Lassila, *J. Amer. Chem. Soc.*, **90**, 2449 (1968); L. L. Barber, O. L. Chapman, and J. D. Lassila, *ibid.*, **90**, 5933 (1968); **91**, 531 (1969)], Chapman and coworkers have detected *o*-quinonemethide as a product from the photolysis of **3** (O. L. Chapman, private communication).

(6) A. B. Turner, *Quart. Rev.*, **18**, 347 (1964).

tions to steric factors;[7] the higher yield of ether from **7c** and **7d** is in accord with the stabilization of the quinonemethide by the phenyl group at C-3; the failure of **5b** to yield ether and its propensity to simply undergo cis–trans isomerization, although surprising, can be attributed to the lack of resonance stabilization of the quinonemethide (*i.e.*, no phenyl group at C-3) and to the increased steric hindrance arising from two ethyl groups at C-3.



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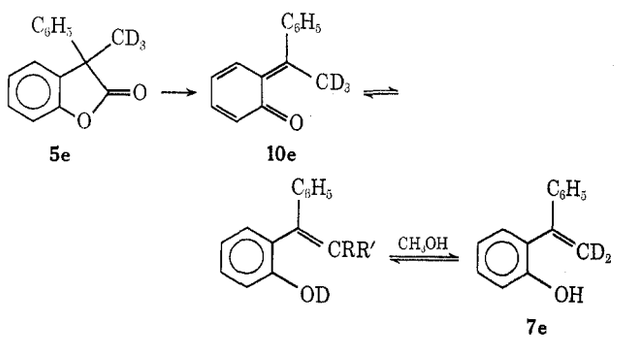
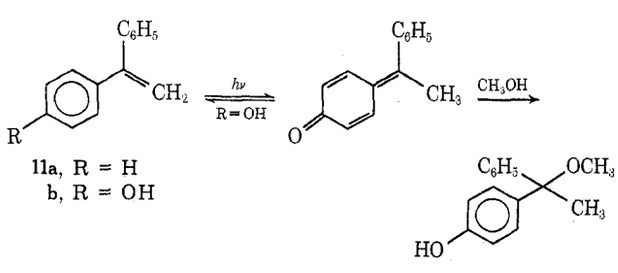
Experiments with deuterium-labeled compounds suggest that part of the ether may be formed directly from the 2-keto-2,3-dihydrobenzofuran, presumably *via* the quinonemethide, and that at least part must be formed *via* cycling through the olefin. Starting with the trideuterio compound **5e**, ether containing 2.65 C-bound deuterium atoms was obtained; starting with olefin containing 1.78 deuterium atoms in the vinyl positions, ether containing 1.54 C-bound deuterium atoms was obtained. If the ether from **5e** had its origin only from directly formed **10e**, the deuterium content should be



R, R' = D
R = D; R' = H
R, R' = H

3.00 atoms; if, on the other hand, cycling between the *o*-quinonemethide and the olefin precedes ether formation, the deuterium content should fall below 3.00 atoms and could approach zero. The results indicate that such cycling must take place, although in the absence of quantitative data for the rate of interconversion of *o*-quinonemethide to olefin and the rate of hydrogen transfer from olefin to methanol an accurate assessment of the fraction of ether formed in this manner cannot be made.



11a, R = H
b, R = OH

12

(7) E. D. Bergmann, D. Ginsburg, and R. Pappo, *Org. React.*, **10**, 179 (1959).

The necessity that a phenolic group be present if the ether is to be a product is shown by the failure of 1,1-diphenylethylene (**11a**) to undergo any reaction whatsoever under the conditions that convert its hydroxylated analog **7c** to the ether **6c**. It is not essential, however, that the hydroxyl function be in the ortho position, for 1-phenyl-1-*p*-hydroxyphenylethylene (**11b**) also forms an ether (**12**), although at a considerably slower rate. A quinonemethide intermediate can, of course, be invoked in this case also,[8] but an intermolecular rather than an intramolecular pathway would seem to be necessary for its formation.

A working hypothesis for rationalizing these four different reaction pathways asserts, albeit with little hard evidence, that (a) the ether arises from the *o*-quinonemethide, and the reduction product and benzofuran arise from the *o*-hydroxystyrene; (b) the formation of *o*-quinonemethide from the *o*-hydroxystyrene is the result of an intramolecular hydrogen transfer from the phenolic hydroxyl group to the β carbon of the styrene, and the reduction product and benzofuran are the result of intramolecular hydrogen transfer from the phenolic hydroxyl group to the α carbon of the styrene; and (c) the partitioning of hydrogen between the α and β positions is sensitive to structure, conformation, solvent, and concentration. The chromophore in the *o*-hydroxystyrenes that is responsible for initiating these events is uncertain. The studies of Förster and Weller[9] showing enhanced acidity of phenols in the electronically excited state, along with the recently reported photochemical conversions of 2-allylphenols to 2,3-dihydrobenzofurans,[10] support the possibility that the phenolic moiety is the essential chromophore and that the hydrogen is transferred as a proton. That photochemical additions, including reductions, can involve ionic intermediates has been demonstrated by the work of Marshall[11] and Kropp.[12] Activation *via* the styrene chromophore and the involvement of radicals cannot be discounted, however; reduction products from the somewhat analogous system, spiro[2.5]octa-4,7-dien-6-one, have, for instance, been explained in terms of radical intermediates.[13] It should be emphasized that these proposals are meant to be nothing more than tentative working hypotheses. Other schemes, intermediates, and mechanistic pathways can, of course, be envisaged, and additional experiments clearly are required to substantiate or refute the ideas embodied in the present scheme. See Scheme I.

Photolysis Products from 1-(*o*-Hydroxyphenyl)-1,5-hexadienes.—In continuation of a quest for a chemical application of the Förster–Weller effect,[9] three 1-(*o*-hydroxyphenyl)-1,5-hexadienes (**13**) have been prepared and irradiated in methanol solution in the hope that the cyclization products **14–16** might be observed. This expectation was not realized, however, and the

(8) The irradiative conversion of 1-(*p*-hydroxyphenyl)propene to the corresponding *p*-quinonemethide has been demonstrated by means of flash photolysis by G. Leary, *Chem. Commun.*, 688 (1971).

(9) T. Förster, *Z. Elektrochem.*, **54**, 42 (1950); A. Weller in "Progress in Reaction Kinetics," Vol. 1, G. Porter, Ed., Pergamon Press, Oxford, 1961, p 187; *cf.* E. L. Wehry and L. B. Rogers, *J. Amer. Chem. Soc.*, **87**, 4234 (1965), for a list of other pertinent references for this phenomenon.

(10) W. H. Horspool and P. L. Pauson, *Chem. Commun.*, **4**, 195 (1967); G. Frater and H. Schmid, *Helv. Chim. Acta*, **50**, 255 (1967).

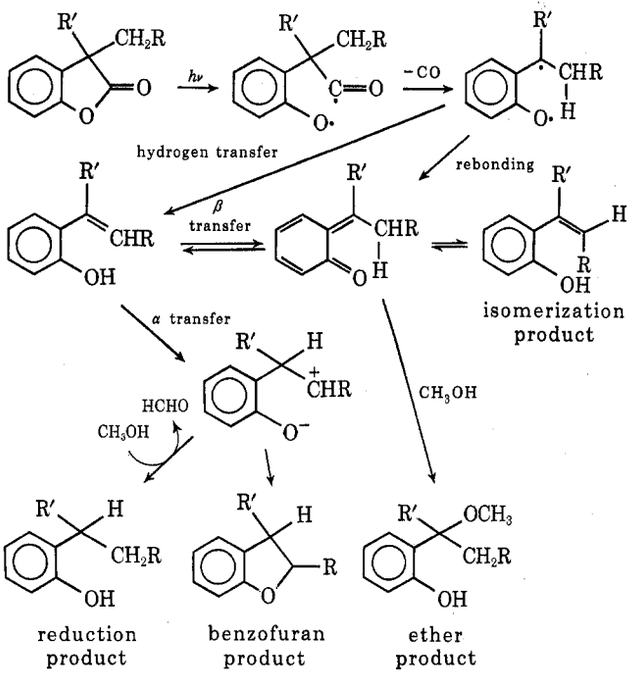
(11) J. A. Marshall, *Accounts Chem. Res.*, **2**, 33 (1969).

(12) P. J. Kropp and H. J. Krauss, *J. Amer. Chem. Soc.*, **91**, 7466 (1969).

(13) D. I. Schuster and C. J. Polowczyk, *J. Amer. Chem. Soc.*, **88**, 1722 (1966).

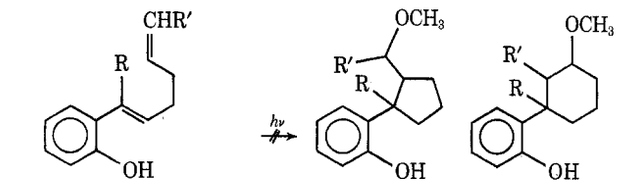
SCHEME I

PHOTOLYSIS PATHWAYS FOR 2-KETO-2,3-DIHYDROBENZOFURANS



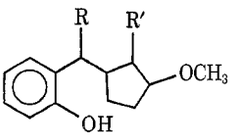
products proved to be similar to those obtained from the analogous *o*-hydroxystyrenes.

Compounds **13a** and **13b** were prepared by the action of 2 molar equiv of the appropriate Grignard reagent



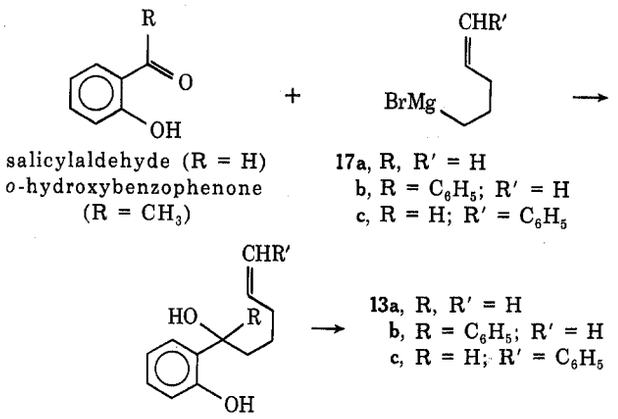
13a, R, R′ = H
b, R = C_6H_5; R′ = H
c, R = H; R′ = C_6H_5

14 **15**



16

on salicylaldehyde and *o*-hydroxybenzophenone, respectively, followed by dehydration of the initially formed alcohol. In the case of salicylaldehyde and 1-pentenylmagnesium bromide, the alcohol **17a** was isolable and, in fact, required a vapor-phase pyrolysis to effect conversion to the diene **13a**. With *o*-hydroxybenzophenone and 1-pentenylmagnesium bromide, on the other hand, the alcohol **17b** was not isolated, and the diene **13b** was obtained directly from the acidified Grignard mixture. The action of 1-phenyl-1-pentenylmagnesium bromide on salicylaldehyde yielded the alcohol **17c**, but attempts to dehydrate it to the diene **13c** furnished a compound which is thought to be 4-phenyl-1,2,3,3a,4,9b-hexahydrocyclopenta[*c*][1]benzopyran (**19**). The elemental analysis and nmr spectrum of the compound are compatible with this formulation, and the action of sodium and pyridine cleaves **19** to the

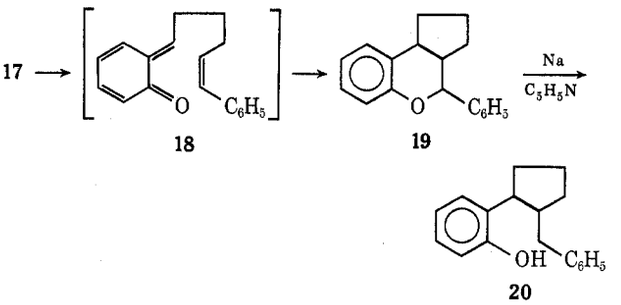


salicylaldehyde (R = H)
o-hydroxybenzophenone (R = CH_3)

17a, R, R′ = H
b, R = C_6H_5; R′ = H
c, R = H; R′ = C_6H_5

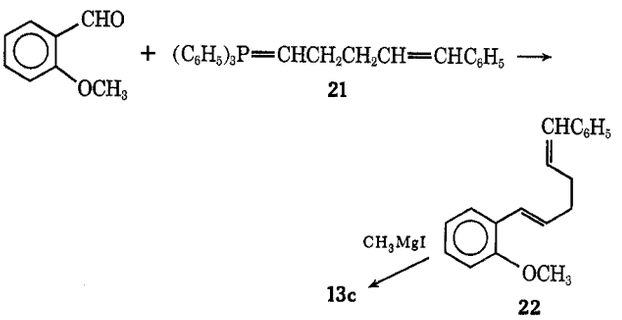
13a, R, R′ = H
b, R = C_6H_5; R′ = H
c, R = H; R′ = C_6H_5

phenol **20**. A plausible mechanism for the formation of **19** from **17** involves a prior conversion to the quinonemethide **18** followed by an intramolecular Diels–Alder



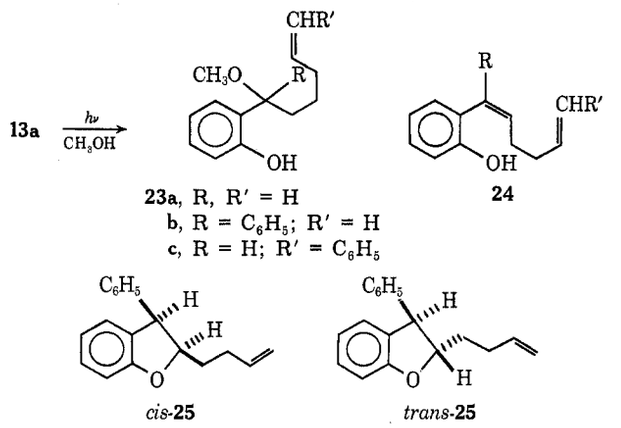
18 **19** **20**

reaction. Other routes to the synthesis of **13c** were investigated, and the one that proved to be successful involves the formation of the diene **22** (by the action of the Wittig reagent **21** on 2-methoxybenzaldehyde) followed by demethylation to the desired diene.



21 **13c** **22**

Irradiation of a 10^{-2} *M* solution of **13a** in methanol yielded a mixture which was shown to contain some of the ether **23a** along with larger amounts of the starting material **13a** and its cis isomer **24**. Aliquots removed



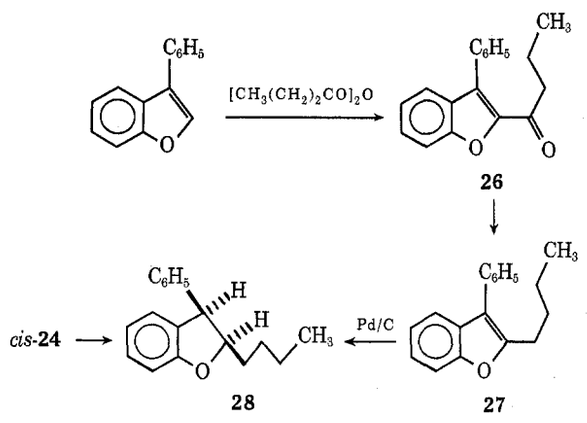
23a, R, R′ = H
b, R = C_6H_5; R′ = H
c, R = H; R′ = C_6H_5

24

cis-**25** *trans*-**25**

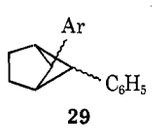
from the photolysis mixture at various times showed that the cis:trans ratio increases to a maximum of 82:18 after 2 hr and then recedes slightly to *ca.* 75:25 after 4 hr. The decrease is attributed to the formation of more **23a** in the longer photolysis and its subsequent thermal decomposition to **13a** during the glc analysis of the product. Analogous results have been noted in the *o*-hydroxystyrene series, where *o*-hydroxystyrene yields the ether as the major product, but 3-(*o*-hydroxyphenyl)-2-butene undergoes cis–trans isomerization. Irradiation of **13a** in cyclohexane rather than methanol solution results in cis–trans isomerization and polymerization.

Irradiation of a 10^{-2} *M* solution of **13b** in methanol yields a mixture which contains the cis and trans isomers of 2-(3-butenyl)-3-phenyldihydrobenzofuran (**25**) as the major components along with a small amount of the ether **23b**. The isomers of **25** were separated by column chromatography, and the assignments of stereochemistry[14] were made on the basis of a comparison with the cis-dihydro compound **28**, which was prepared by the conversion of 3-phenylbenzofuran to 2-butanoyl-3-phenylbenzofuran (**26**), Huang-Minlon reduction of **26** to 2-butyl-3-phenylbenzofuran (**27**), and catalytic reduction of **27** to *cis*-2-butyl-3-phenyldihydrobenzofuran (**28**). The formation of **25** from **13b** finds its



analog in the photolysis of 1-(*o*-hydroxyphenyl)-1-phenyl-1-propene (**7d**), where the dihydrobenzofuran is the sole product.

In the photolysis of **13a** and **13b** there is no evidence for any involvement of the terminal double bond, the products being analogous to those observed in the corresponding *o*-hydroxystyrene series. That it was, perhaps, naive to have expected such involvement is indicated by attempts to induce an acid-catalyzed cyclization of **13b**. The action of hydrobromic acid–acetic acid as well as that of refluxing methanol containing concentrated sulfuric acid on **13b** were both without effect, and aqueous methanolic sulfuric acid led to decomposition products. In the thought that a phenyl group attached to the terminal double bond might increase the possibility of interaction with the conjugated double bond, **13c** was next investigated. Irradiation of a 10^{-2} *M* solution of **13c** in methanol resulted in the disappearance of starting compound and the formation of a mixture containing *ca.* 40% of volatile material. The ir spectrum of the volatile product showed a strong hydroxyl absorption, and the nmr spectrum indicated the absence of vinyl protons, the absence of methoxyl protons, and the presence of a pair of benzylic protons. These data are compatible with structure **29**, which would be the result of an intra-



29

molecular cycloaddition of the two styrene moieties.[15] Further efforts to substantiate this structure were not undertaken, however, for a glc analysis of the silyl derivative of the crude product indicated that at least four components were present, none of which appeared to be compounds of the type **14–16**.

Experimental Section[16]

Synthesis of 2-Keto-2,3-dihydrobenzofurans. 2-Keto-2,3-dihydrobenzofuran (3).—Following published procedures, *o*-methoxybenzaldehyde was converted to its cyanohydrin[17] in 72% yield, the cyanohydrin was hydrolyzed to *o*-hydroxyphenylacetic acid in 57% yield,[18] and the acid was lactonized to afford **3** in 85% yield as a colorless solid: uv max (95% EtOH) 271 nm (ε 1225) and 277 (1210); ir (liquid) 1800 and 1775 cm^{-1} (C=O); nmr (CCl_4) δ 4.54 (s, 2, $ArCH_2$) and 6.80–7.40 ppm (m, 4, ArH).

2-Keto-3,3-dimethyl-2,3-dihydrobenzofuran (5a).—A solution of 30 g of 2-keto-2,3-dihydrobenzofuran in 50 ml of dimethylformamide was added, dropwise over a period of 30 min, to a stirred and cooled suspension of 19 g of sodium hydride in 125 ml of dimethylformamide. Stirring and cooling were continued until the evolution of hydrogen ceased (*ca.* 20 min), and 150 g of methyl iodide was then added. The reaction mixture was stirred for 20 hr at room temperature and then processed in the usual fashion to yield 24 g of a colorless oil, bp 79–82° (0.08 mm), which was shown by glc analysis to contain product and starting material in an 85:15 ratio. Distillation through a spinning band column achieved only partial separation, whereas passage through a glc column afforded 16.0 g (44%) of pure material: bp 43° (0.05 mm); uv max (95% EtOH) 270 nm (ε

(14) The magnitude of the H_2–H_3 coupling constant provides an uncertain guide for the specification of the stereochemistry in these compounds. In the case of 2,3-dialkyl-2,3-dihydrobenzofuran [E. C. Hayward, D. S. Tarbell, and L. D. Colebrook, *J. Org. Chem.*, **33**, 399 (1968)], 2-phenyl-3-hydroxy-2,3-dihydrobenzofuran [S. P. Pappas, R. D. Zehr, and J. E. Alexander, *J. Heterocycl. Chem.*, **7**, 1215 (1970)], and 2-methyl-3-hydroxy-2,3-dihydrobenzofuran [M. P. Mertes and L. J. Powers, *Chem. Commun.*, 620 (1970)], J_{23} is greater for the cis isomer than for the trans isomer. In the case of 2-isopropyl-3-hydroxy-2,3-dihydrobenzofuran [L. H. Zalkow and M. Ghosal, *Chem. Commun.*, 922 (1967)] and 2-methyl-3-acetoxy-5-nitro- (and 7-nitro-) 2,3-dihydrobenzofuran [M. P. Mertes, L. J. Powers, and E. Shefter, *J. Org. Chem.*, **36**, 1805 (1971)], however, J_{23} is greater for the trans than for the cis isomer. The third alternative is observed in 2-phenyl-3-methyl-2,3-dihydrobenzofuran [M. Gregson, W. D. Ollis, R. T. Redman, and I. O. Sutherland, *Chem. Commun.*, 1394 (1968)] where J_{23} is the same for the cis and trans isomers, in close correspondence with the observations in the present instance where J_{23} for the cis isomer is 7.9 Hz and that for the trans isomer is 7.6 Hz.

(15) R. Srinivasan, *J. Phys. Chem.*, **67**, 1367 (1963); *J. Amer. Chem. Soc.*, **85**, 819 (1963); K. J. Crowley, *Proc. Chem. Soc.*, 17 (1964); *J. Amer. Chem. Soc.*, **86**, 5692 (1964); J. K. Crandall and C. F. Mayer, *J. Org. Chem.*, **35**, 3049 (1970).

(16) Melting points and boiling points are uncorrected. The infrared spectra were recorded on a Perkin-Elmer Infracord spectrometer; the ultraviolet spectra were recorded on Cary Model 11 and Model 14 spectrometers; the nuclear magnetic resonance spectra were recorded on Varian A-60A instruments, and the resonances are stated in parts per million downfield shift from tetramethylsilane used as an internal reference. Glc analyses were performed on units containing thermistor detectors and using the following columns: column 1, a 0.25 in. × 16 ft column packed with 15% w/w neopentylglycol sebacate polymer on 40–50 mesh type ABS Anakrom (a product of Analytical Engineering Laboratory, Inc., Hamden, Conn.); column 2, 0.25 in. × 6 ft column packed with 5% w/w Dow No. 710 silicone oil on a 40–50 mesh type ABS Anakrom. Microanalyses were performed by Mikroanalytisches Laboratorium, Vienna, Austria.

(17) Levine, T. E. Eble, and H. Fischbach, *J. Amer. Chem. Soc.*, **70**, 1930 (1948).

(18) S. Czaplicki, St. v. Kostanecki, and V. Lampe, *Chem. Ber.*, **42**, 827 (1909).

1225) and 276 (1160); ir (liquid) 1800 cm^{-1} (C=O); nmr (CCl_4) δ 1.47 (s, 6, CH_3) and 7.08–7.68 ppm (m, 4, ArH).

Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.21. Found: C, 74.02; H, 6.61.

2-Keto-3,3-diethyl-2,3-dihydrobenzofuran (5b).—Following the procedure described above, 40.2 g of 2-keto-2,3-dihydrobenzofuran yielded 32 g (57%) of **5b** as a colorless oil: bp 68–70° (0.07 mm); uv max (95% EtOH) 270 nm (ϵ 1235) and 277 (1180); ir (liquid) 1800 cm^{-1} (C=O); nmr (CCl_4) δ 0.69 (t, 6, J = 7.3 Hz, CH_2CH_3), 1.94 (q, 2, J = 6.9 Hz, CH_2CH_3), 1.96 (q, 2, J = 7.7 Hz, CH_2CH_3), 7.08–7.68 ppm (m, 4, ArH).

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.96; H, 7.56.

2-Keto-3-phenyl-2,3-dihydrobenzofuran.—Following a published procedure[19] a 114-g sample of (*R,S*)-mandelic acid was heated with 81.5 g of phenol and 225 ml of 73% sulfuric acid to yield, after two recrystallizations from 95% ethanol, 45 g (35%) of colorless needles: mp 117–118° (lit. mp 113–114°); uv (95% EtOH) 272 nm (ϵ 1515), 279 (1420), and 318 (200, arising from the enol form and absent when 1,2-dichloroethane is the solvent); ir (KBr) 1805 cm^{-1} (C=O); nmr ($CDCl_3$) δ 4.86 (s, 1, ArCH) and 7.00–7.50 ppm (m, 9, ArH).

Anal. Calcd for $C_{14}H_{12}O_2$; C, 79.98; H, 4.79. Found: C, 80.05; H, 4.94.

2-Keto-3-methyl-3-phenyl-2,3-dihydrobenzofuran (5c).—A 15.75-g sample of 2-keto-3-phenyl-2,3-dihydrobenzofuran in 20 ml of dimethylformamide was added to a cooled and stirred mixture of 3.3 g of sodium hydride in 90 ml of dimethylformamide. After hydrogen evolution ceased (*ca.* 15 min), 13.8 g of methyl iodide was added, and the reaction mixture was stirred for 20 hr at room temperature. The product was obtained in the usual fashion and was distilled to yield 14.2 g (85%) of **5c** as a colorless, heavy oil: bp 130–135° (0.04 mm); uv mas (95% EtOH) 271 nm (ϵ 1360) and 277 (1240); ir (liquid) 1805 cm^{-1} (C=O); nmr (CCl_4) δ 1.82 (s, 3, CH_3) and 6.82–7.50 ppm (m, 9, ArH).

Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.34; H, 5.29. Found: C, 80.61; H, 5.53.

2-Keto-3-trideuteriomethyl-3-phenyl-2,3-dihydrobenzofuran (5e).—Using trideuteriomethyl iodide in the procedure described above, **5e** was obtained as a colorless oil: uv max (95% EtOH) 271 nm (ϵ 1260) and 277 (1200); ir (liquid) 1800 cm^{-1} (C=O); nmr (CCl_4) δ 6.82–7.50 (m, 9, ArH).

2-Keto-3-ethyl-3-phenyl-2,3-dihydrobenzofuran (5d).—Following the procedure described above with ethyl bromide in place of methyl iodide, **5d** was obtained in 88% yield as colorless crystals: mp 69–70°; uv max (95% EtOH) 271 nm (ϵ 1550) and 278 (1395); ir (KBr) 1805 cm^{-1} (C=O); nmr (CCl_4) δ 0.75 (t, 3, J = 7 Hz, CH_2CH_3), 2.25 (q, 1, J = 7 Hz, CH_2CH_3), 2.33 (q, 1, J = 7 Hz, CH_2CH_3), 6.50–7.60 (m, 9, ArH).

Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.60; H, 6.01.

Synthesis of *o*-Hydroxystyrenes. 2-Hydroxyphenylethylene was prepared by decarboxylation of *o*-hydroxycinnamic acid according to a published procedure[20] and obtained as a colorless oil: bp 92–95° (11 mm); nmr (CCl_4) δ 5.24 (doubled doublet, 1, J = 1.6 and 11 Hz, =CH_2), 5.68 (doubled doublet, 1, J = 1.6 and 17 Hz, =CH_2), 6.19 (s, 1, OH), 6.91 (doubled doublet, 1, J = 11 and 17 Hz, =CH) 6.50–7.65 ppm (m, 4, ArH); uv and ir identical with published data.[21]

2-(2-Hydroxyphenyl)propene (7a).—A 40-g sample of *o*-hydroxyacetophenone in 100 ml of dry ether was treated with 250 ml of a 3 *M* solution of methylmagnesium chloride in tetrahydrofuran. The carbinol was dehydrated by heating for 10 min at 180°, and the resulting product was twice distilled under reduced pressure to yield 35 g of **7a** as a colorless oil: bp 50–52° (0.7 mm); uv max (95% EtOH) 240 sh (ϵ 5000) and 282 (2460); ir (liquid) 3550 cm^{-1} (OH); nmr (CCl_4) δ 2.05 (s, 3, CH_3), 5.08 (broad d, 1, =CH_2), 5.22 (d, 1, =CH_2), 5.73 (s, 1, OH), and 6.50–7.30 ppm (m, 4, ArH).

Anal. Calcd for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.62; H, 7.75.

1-Phenyl-1-(2-hydroxyphenyl)ethene (7c).—Starting with 25 g of *o*-hydroxybenzophenone and following the procedure described above, 20 g of **7c** was obtained as a viscous oil: bp 102–103° (0.05 mm); uv max (95% EtOH) 281 nm (ϵ 3420); ir (liquid) 3600 cm^{-1} (OH); nmr (CCl_3) δ 6.02 (s, 1, OH), 5.32 (d, 1, =CH_2), 5.74 (d, 1, =CH_2), and 6.63–7.58 ppm (m, 9, ArH).

Anal. Calcd for $C_{14}H_{12}O$: C, 85.68; H, 6.16. Found: C, 85.68; H, 6.21.

1-Phenyl-1-(2-hydroxyphenyl)-2,2-dideuterioethene (7e).—A 6.0-g sample of **7c** was dissolved in 3.5 ml of methanol-d_1, the methanol was removed by distillation, and the residue was heated at 180–185° for 10 min in a stream of nitrogen. This process was repeated several times to yield a product, bp 101° mm), which was shown by nmr analysis to contain 1.78 deuterium atoms at the 2 position.

1-Phenyl-1-(2-hydroxyphenyl)propene (7d).—Starting with 25 g of *o*-hydroxybenzophenone and using ethylmagnesium bromide in the procedure described above, 15.5 g of **7d** was obtained as a colorless oil: bp 102–105° (0.05 mm); ir (liquid) 3600 cm^{-1} (OH); nmr (CCl_4) δ 1.60 (d, 2.1, CH_3 of *E* isomer), 1.77 (d, 0.9, CH_3 of *Z* isomer), 5.25 (s, 1.0, OH), 5.87 (q, 0.3, =C*H* of *Z* isomer), 6.26 (q, 0.7, =C*H* of *E* isomer), 6.50–7.50 ppm (m, 9, ArH). The nmr intensities indicate that the product is a mixture containing *ca.* 5 parts of the *E* isomer and 2 parts of the *Z* isomer. Confirmation of the structure was achieved by conversion to 2-methyl-3-dihydrobenzofuran (**9d**).

1-Phenyl-1-(4-hydroxyphenyl)ethene (11b) was prepared from *p*-hydroxybenzophenone by procedures described above and obtained as an extremely viscous oil: bp 125–126° (0.1 mm); ir (liquid) 3600 cm^{-1} (OH); nmr ($CDCl_3$) 5.35 (m, 2, =CH_2), 6.23 (s, 1, OH), 6.62–7.67 ppm (m, 9, ArH).

Synthesis of 1-(*o*-Hydroxyphenyl)-1,5-dienes. 1-(*o*-Hydroxyphenyl)-1,5-hexadiene (13a).—5-Bromo-1-pentene[22] was converted to the Grignard reagent, and a 0.1-mol portion in 50 ml of dry ether cooled in an ice bath and maintained under a nitrogen atmosphere was treated, dropwise, with 6.0 g of salicylaldehyde in 25 ml of dry ether over a period of 10 min. The thick, brown-yellow mixture was refluxed for 24 hr, cooled, treated with a saturated solution of ammonium chloride, and worked up to yield a crude product which was dissolved in benzene and chromatographed on a column containing 300 g of silica gel. Elution with a mixture of ether, benzene, and carbon tetrachloride (2:5:8) yielded a middle fraction consisting of 5.5 g (57% based on salicylaldehyde) of **17a** as a yellow oil: bp 100–102° (0.1 mm); nmr (CCl_4) δ 1.0–2.3 (m, 6, CH_2), 4.2 (s, 1, OH), 4.48–5.22 (m, 3, CHO and =CH_2), 5.35–6.12 (m, 1, =CH), 6.53–7.4 (m, 4, ArH), 8.3 (s, 1, ArOH). Samples of this oil, *ca.* 0.3 ml at a time, were injected through a serum cap into a 0.625 in. × 1 ft pyrolysis tube filled with type 110–5005 Superbrite glass beads (product of Minnesota Mining and Manufacturing Co.), maintained at 280–300°, and evacuated to *ca.* 0.1–0.3 mm of pressure. From 5.5 g of crude alcohol there was obtained, by this batchwise procedure allowing 5–10 min between injections, a total of 4.5 g (48–50% overall from salicylaldehyde) of crude product which, upon chromatography on alumina followed by distillation, yielded **13a** as a colorless oil, mp 78–79° (0.07 mm).

Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.81, H, 8.06.

Purification *via* glc yielded (a) 9 parts of the trans isomer of **13a** [ir (liquid) 972 cm^{-1} (trans CH=CH); uv max (95% EtOH) 285 nm (ϵ 7700), 262.5 (shoulder, 12,000), 255 (14,000), and 214 (14,700)] and (b) 1 part of the cis isomer of **13a** [uv max (95% EtOH) 290 nm (ϵ 4100), 242.5 (11,700), and 215 (17,000)].

1-(*o*-Hydroxyphenyl)-1-phenyl-1,5-hexadiene (13b).—A solution of 0.2 mol of Grignard reagent from 5-bromo-1-pentene[22] in 100 ml of ether was treated, as described above, with 9.3 g of *o*-hydroxybenzophenone in 20 ml of ether. The reaction mixture was refluxed for 24 hr and worked up to give a crude product which, after chromatography on alumina [eluted with ether–heptane (1:9)] and distillation, yielded 6.6 g (52% based on benzophenone) of **13b** as a colorless oil: bp 126–127° (0.25 mm); uv max (95% EtOH) 210 nm (ϵ 15,600), 250 (8460), and 282.5 (shoulder, 2400); ir (liquid) 3600 (ArOH), 922 (=CH_2), 760 (1,2-disubstituted Ar), and 697 cm^{-1} (monosubstituted Ar); nmr (CCl_4) δ 1.72–2.42 (m, 4, CH_2), 4.69–5.17 (m, 3, =CH_2 and OH), 5.30–6.45 (m, 2, =CH and Ar_2C=CH), and 6.60–7.35 ppm (m, 9, ArH).

Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 85.71; H, 7.16.

1-(*o*-Hydroxyphenyl)-6-phenyl-1,5-hexadiene (13c).—Equimolar amounts of triphenylphosphine and 5-bromo-1-phenyl-1-

(19) A. Bistryzycki and J. Flatau, *Chem. Ber.*, **30**, 124 (1897).

(20) K. Fries and G. Fickewirth, *Ber.*, **41**, 367 (1908).

(21) H. E. Hennis, Ph.D. Dissertation, University of Missouri, 1956.

(22) H. B. Wood and E. C. Horning, *J. Amer. Chem. Soc.*, **75**, 5511 (1953).

pentene in benzene were stirred and heated at reflux for 72 hr, cooled, washed with benzene, and dried to give an 80% yield of triphenyl-1-pentenylphosphonium bromide, mp 203–205°. A suspension of 24.3 g of this compound in 200 ml of dry ether was treated, dropwise, with phenyllithium from 1.9 g of lithium and 15.7 g of bromobenzene in 15 ml of dry ether. To the vigorously stirred solution was slowly added 6.7 g of *o*-methoxybenzaldehyde in 25 ml of ether. After 16 hr of refluxing, the mixture was worked up to give a crude product which was purified by chromatography on 300 g of alumina [product eluted with ether–heptane (1:1)] followed by distillation to yield 6.6 g (60%) of 1-(*o*-methoxyphenyl)-6-phenyl-1,5-hexadiene (**22**) as a colorless oil, bp 153–155° (0.05 mm), which solidified and was recrystallized from heptane: mp 38–40°; ir (liquid) 965 (trans CH=CH), 752 (1,2-disubstituted Ar), and 962 cm^{-1} (monosubstituted Ar); uv max (95% EtOH) 213 nm (ϵ 24,300), 255 (29,200), 285 (5830), 293 (6390), and 300 (5530); nmr (CCl_4) δ 1.90–2.73 (m, 4, CH_2),3.53 (s, 3, OCH_3), and 5.35–7.50 ppm (m, 13, ArH and =CH).

Anal Calcd for $C_{19}H_{20}O$: C, 86.32; H, 7.63. Found: C, 85.92; H, 7.71.

Following a literature procedure,[23] a 4.0-g sample of **22** was added dropwise to a solution prepared from 14.1 g of methyl iodide and 2.8 g of magnesium in 80 ml of ether. The ether was removed by distillation, and the residue was heated for 2.5 hr at 155–160° and then treated with an ammonium chloride solution. Extraction with ether afforded a pale yellow oil which was chromatographed on 50 g of alumina. Elution with heptane–ether (3:1) followed by methanol–ether (1:6) yielded 3.0 g (75%) of **13c** containing only a trace of the benzopyran **19**. Recrystallization from heptane yielded 2.4 g of colorless crystals: mp 73–75°; ir (Nujol) 3680 (OH), 980 and 973 (trans CH=CH), 752 (monosubstituted and 1,2-disubstituted Ar), and 695 cm^{-1} (monosubstituted Ar); uv max (95% EtOH) 255 nm (ϵ 30,900), 285 (5400), 293 (6700), and 301 (6260); nmr (CCl_4) δ 1.85–2.70 (m, 4, CH_2), 5.22 (s, 1, OH), 5.60–7.50 ppm (m, 14, ArH and =CH).

Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.21; H, 7.39.

4-Phenyl-1,2,3,3a,4,9b-hexahydrocyclopenta[*c*][1]benzopyran (19).—A solution of 0.1 mol of Grignard reagent from 5-bromo-1-phenyl-1-pentene in 75 ml of ether was treated, as described above, with 5.5 g of salicylaldehyde. Chromatography of the crude product on silica gel using carbon tetrachloride–benzene–ether (8:5:2) as eluent yielded 1-phenyl-1-pentene in the first fraction, salicylaldehyde in the second fraction, and 7.0 g (60%) of the alcohol **17c** in the third fraction: nmr (CCl_4) δ 0.98–2.37 (m, 6, CH_2), 3.78 (s, 1, OH), 4.64 (t, 1, ArCHCH), 5.71–6.50 (m, 2, CH=CH), 6.55–7.35 (m, 9, ArH), and 8.21 ppm (s, 1, ArOH). Pyrolysis of a 5-g sample of this material under the conditions described above yielded 3.5 g of solid, mp 57–60° which was distilled [bp 141–143° (0.1 mm)] and recrystallized from methanol to give **19** as colorless, transparent plates: ir (Nujol) 756 (1,2-disubstituted Ar) and 700 cm^{-1} (monosubstituted Ar); uv max (95% EtOH) 220 nm (ϵ 9340), 260 (2710), 279.5 (3580), and 285 (3280); nmr (CCl_4) δ 1.00–2.93 (m, 8, CH and CH_2), 4.24 (d, J = 9.6 Hz) and 4.88 (d, J = 8.8 Hz) together account for 1 H (–OCHAr), and 6.56–7.51 ppm (m, 9, ArH).

Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.47; H, 7.28.

1-Benzyl-2-(*o*-hydroxyphenyl)cyclopentane (20).—Following a literature procedure[24] a solution of 0.25 g of **7** in 3 ml of dry pyridine was treated with 0.3 g of sodium metal, and the mixture was stirred and refluxed under a nitrogen atmosphere for 4 hr. Work-up gave 0.21 g of crude product which was distilled to yield 0.29 g (80%(of **8** as a viscous, pale yellow oil: bp 125° (0.1 mm); ir (liquid) 3600 cm^{-1} (ArOH); uv max (95% EtOH) 218 nm (ϵ 10,400), 270 (shoulder, 2300), 277 nm (2700), and 281 (shoulder, 2500); nmr (CCl_4) δ 1.08–3.58 (m, 10, CH_2), 4.58 (s, 1, OH), 6.35–7.44 (m, 9, ArH).

Anal. Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.35; H, 7.95.

***cis*-2-Butyl-3-phenyl-2,3-dihydrobenzofuran (28).**—Following published procedures, ω-phenoxyacetophenone[25] was converted to 3-phenylbenzofuran[26] and the latter was acylated.[27] A mixture of 4.0 g of 3-phenylbenzofuran, 4 ml of butyric anhydride, 3 ml of butyric acid, and 0.8 g of 85% phosphoric acid was stirred and heated at 100–105° for 44 hr. Chromatography of the crude product on alumina yielded 1 g of starting material and 2.6 g (64% based on recovered starting material) of 2-*n*-butyroyl-3-phenylbenzofuran (**26**) as a pale yellow oil, bp 146–148° (0.1 mm), which solidified on standing: mp 58–60° after recrystallization from heptane; ir (Nujol) 1685 cm^{-1} (C=O); uv max (95% EtOH) 208 nm (ϵ 14,300), 230 (15,200), and 300 (18,900); nmr (CCl_4) δ 0.92 (t, 3, CH_3), 1.30–2.05 (m, 2, CH_2), 2.83 (m, 2, CH_2), 6.90–7.79 ppm (m, 9, ArH).

Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.92; H, 6.24.

Huang-Minlon[28] reduction of a 5.5-g sample of **26** produced, after distillation, 4.5 g (86%) of 2-*n*-butyl-3-phenylbenzofuran (**27**) as a pale yellow oil which was chromatographed on alumina and distilled to give a colorless oil: bp 118–120° (0.1 mm); nmr (CCl_4) δ 0.63–2.05 (m, 7, CH_2 and CH_3), 2.76 [t, 2, –O(=C)-CH_2–], and 6.91–7.70 ppm (m, 9, ArH).

Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.14; H, 7.24.

A 1.8-g sample of **27** was mixed with 0.2 g of 10% palladium on charcoal catalyst and hydrogenated in 20 ml of absolute ethanol for 24 hr at 15 psi. Chromatography of the crude product on a column containing 200 g of alumina yielded starting material in the first fraction [eluted with heptane–ether (30:1)], a mixture of **25** and **27** in the middle fraction, and *cis*-2-butyl-3-phenyl-2,3-dihydrobenzofuran (**28**) in the last fraction (eluted with ether), obtained as 0.6 g of a colorless oil which solidified on standing: mp 63.5–64.5° after recrystallization from methanol; nmr (CCl_4) identical with that of the hydrogenation product from isomer B of **25** (see below).

Anal. Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.56; H, 8.03.

1-Phenyl-1-(*o*-hydroxyphenyl)hexane was prepared by reduction with hydrogen and 10% palladium on charcoal catalyst of 1-phenyl-1-(*o*-hydroxyphenyl)-1,5-hexadiene (**13b**) and was obtained as a colorless oil: bp 97–99° (0.1 mm); ir (liquid) 3600 cm^{-1} (ArOH); nmr (CCl_4) δ 0.59–1.00 (m, 3, CH_3), 1.00–2.36 (m, 8, CH_2), 4.21 (t, 1, J = 7.1 Hz, Ar_2CH), 4.75 (s, 1, OH), and 6.23–7.57 ppm (m, 9, ArH).

Anal. Calcd for $C_{18}H_{22}O$: C, 84.99; H, 8.72. Found: C, 84.49; H, 8.43.

Photolysis Experiments. Comparative Photolyses.—Samples of the 2-keto-2,3-dihydrobenzofurans or the *o*-hydroxystyrenes were dissolved in 400–500 ml of the specified solvent and were irradiated in a Rayonet Model RPR-100 reactor (product of Southern New England Ultraviolet Co., Middletown, Conn.) equipped with 2537-Å reactor lamps for 18 hr. The solvent was removed, and the crude product was analyzed by nmr to give the results recorded in Tables I and II.

The photolyses described below were carried out in an inert atmosphere in an apparatus of 300-ml capacity carrying a quartz immersion well containing a Hanovia 450-W medium-pressure lamp (product of Hanovia Co., Newark, N. J.).

Photolysis of 2-Keto-2,3-dihydrobenzofuran (3).—A 3.00-g sample of **3** in 280 ml of 2-propanol was irradiated for 5 hr, the 2-propanol was removed by distillation, the residue was distilled to yield 2.42 g of an oil, bp 46–49° (0.02 mm), and the oil was separated by glc (column 1) into unreacted starting material (55%) and isopropyl *o*-hydroxybenzyl ether (**4**, R = *i*-C_3H_7) (45%): uv max (95% EtOH) 275 nm (ϵ 2720); ir (liquid) 3400 cm^{-1} (OH); nmr (CCl_4) δ 1.17 [d, 6, J = 6.1 Hz, $CH(CH_3)_2$], 3.64 [septuplet, 1, J = 6.1 Hz, $CH(CH_3)_2$], 4.57 (s, 2, $ArCH_2$), and 7.56 ppm (s, 1, OH).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.18; H, 9.52.

Photolysis of 2-Keto-3,3-dimethyl-2,3-dihydrobenzofuran (5a). A. In Methanol.—A 4.20-g sample of **5a** in 279 ml of methanol was irradiated for 9 hr, during which time samples were withdrawn every hour to check the course of the reaction. The crude product consisted of 2.86 g of an oil, bp 54–57°, which was separated by glc (column 1; temperature 160°) into starting material (47%), product **a** (46%), and product **b** (7%). Product

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a was identified as 2-(*o*-hydroxyphenyl)propene (**7a**) by comparison with an authentic sample (see above). Product **b** was identified as *o*-isopropylphenol (**8a**): ir (liquid) 3450 cm^{-1} (OH); nmr (CCl_4) δ 1.22 [d, 6, $CH(CH_3)_2$], 3.18 [septuplet, 1, $CH(CH_3)_2$], 5.38 (s, 1, OH), and 6.50–7.26 ppm (m, 4, ArH).

Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.71; H, 9.05.

2-Methoxy-2-(*o*-hydroxyphenyl)propane (**6a**, R′ = CH_3), although not isolated in pure form, was shown to be present in 38% amount in the crude product on the basis of the nmr (CCl_4): δ 1.57 [s, $C(CH_3)_2$], 3.18 (s, OCH_3), 6.42–7.35 (m, ArH), and 8.35 ppm (s, OH).

B. In 2-Propanol.—Irradiation of 1.71 g of **5a** in 281 ml of 2-propanol for 2.5 hr yielded 1.50 g of crude product which was shown by nmr analysis to contain unreacted starting material (53.5%), 2-(2-hydroxyphenyl)propene (**7a**) (40%), and 2-isopropoxy-2-(2-hydroxyphenyl)propane [**6a**, R″ = $CH(CH_3)_2$] (6.5%). That *o*-isopropylphenol must also be present is shown by the composition of a pyrolysate of the crude reaction product which contains starting material (55.5%), 2-(2-hydroxyphenyl)-propene (40.5%), and *o*-isopropylphenol (**8a**) (3.5%).

C. In *n*-Pentane.—Irradiation of 0.60 g of **5a** in 300 ml of *n*-pentane (Spectrograde) for 1 hr gave 0.50 g of a crude product which was separated by glc into unreacted starting material and 2-(2-hydroxyphenyl)propene (**7a**). Nmr analysis of the crude product indicated that it is comprised only of these two materials, present to the extent of 27.5 and 72.5%, respectively.

Photolysis of 2-Keto-3,3-diethyl-2,3-dihydrobenzofuran (5b). A. In Methanol.—Irradiation of 5.00 g of **5b** in 270 ml of methanol for 13 hr yielded, after distillation of the crude product, 4.18 g of a colorless oil, bp 55–57° (0.05 mm), which was separated by glc (column 1; temperature 182°) into starting material and a fraction which, upon further glc separation (column 2; temperature 133°), was resolved into two fractions. One of these was identified as a 91:9 mixture of (*E*)- and (*Z*)-3-(2-hydroxyphenyl)pentene-2 (**7b**): uv max (95% EtOH) 214 nm (ϵ 7220) and 279 (1860); ir (liquid) 3600 cm^{-1} (OH); nmr (CCl_4) δ 0.85 (t, J = 7.47 Hz) and 1.00 (t, J = 7.40 Hz) for 3 H of CH_2CH_3, 1.47 (doubled triplet, J = 1.30 and 6.61 Hz) for 2.74 H of $-CHCH_3$, 1.76 (d, J = 6.80 Hz) for 0.29 H of $=CHCH_3$, 2.28 (q, J = 7.40 Hz) for 2 H of CH_2CH_3, 5.01 (s, 0.85, OH), 5.81–5.86 (broad, 0.11, OH), 5.71 (quartet of triplets, J = 1.40 and 6.61 Hz, 0.85, $=CHCH_3$), 6.56–7.30 ppm (m, 4, ArH).

Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.16; H, 8.65.

The other fraction was identified as a 42:58 mixture of (*E*)- and (*Z*)-**7b**. Nmr analysis of the crude distillate showed that it was comprised of starting material (56.4%), (*E*)-3-(2-hydroxyphenyl)pentene-2 (35%), 3-methoxy-3-(2-hydroxyphenyl)pentane (**6b**, R″ = CH_3) (4.4%), and (*Z*)-3-(2-hydroxyphenyl)-pentene-2 (4.2%).

B. In 2-Propanol.—Irradiation of 1.45 g of **7b** in 280 ml of 2-propanol for 4 hr yielded a crude product containing 47% of 3-(2-hydroxyphenyl)pentene-2 (**7b**). Distillation of the crude product afforded 1.17 g of a pale yellow oil, bp 60–65° (0.02 mm), which glc analysis (column 2; temperature 110°) showed to be comprised of starting material (33%), (*E*)-3-(2-hydroxyphenyl)-pentene-2 (41.5%), and (*Z*)-3-(2-hydroxyphenyl)pentene-2 (15.5%).

C. In *n*-Pentane.—Irradiation of 6.07 g of **5b** in 2340 ml (six separate runs) for 1 hr yielded, after distillation, 5.50 g of a colorless oil, bp 70–77° (0.1 mm), which was shown by nmr analysis to contain unreacted starting material (57%), (*E*)-3-(2-hydroxyphenyl)pentene-2 (23%), and (*Z*)-3-(2-hydroxyphenyl)pentene-2 (20%).

Photolysis of 2-Keto-3-methyl-3-phenyl-2,3-dihydrobenzofuran (5c).—A 4.48-g sample of **5c** in 260 ml of methanol was irradiated for 6 hr, during which time aliquots were withdrawn to follow the course of the reaction. Distillation of the crude product yielded 2.45 g, bp 110° (0.07 mm), which was separated by glc (column 2; temperature 180°) into starting material and two other compounds. One of these was identified as 1-(*o*-hydroxyphenyl)-1-phenylethene (**7c**) by comparison. The other was identified as 1-(*o*-hydroxyphenyl)-1-phenylethane (**8c**): uv max (95% EtOH) 275.5 nm (ϵ 2680); ir (liquid) 3600 cm^{-1} (OH); nmr (CCl_4) δ 1.54 (d, 3, J = 7.33 Hz, CH_3), 4.28 (q, 1, J = 7.33 Hz, Ar_2CHCH_3), 4.70 (s, 1, OH), and 6.30–7.30 ppm (m, 9, ArH).

Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.63; H, 7.02.

Nmr analysis of the distilled product, before glc separation, indicated it to contain starting material (20%), 1-(*o*-hydroxyphenyl)-1-phenylethene (58.3%), and 1-(*o*-hydroxyphenyl)-1-phenylethane (9.7%). 1-Methoxy-1-(*o*-hydroxyphenyl)-1-phenylethane (**6c**, R″ = CH_3), although not isolated in pure form, was shown to be present as the major component of the undistilled reaction product: nmr (CCl_4) δ 1.76 (s, 3, Ar_2CCH_3), 3.16 (s, 3, OCH_3), 6.43–7.40 (m, 9, ArH), and 8.17 ppm (s, 1, OH).

Photolysis of 2-Keto-3-ethyl-3-phenyl-2,3-dihydrobenzofuran (5d).—A 1.79-g sample of **5d** in 280 ml of methanol was irradiated for 6 hr to give, after distillation, 1.35 g of a colorless oil, bp 112–114° (0.05 mm), which was separated by glc (column 2; temperature 167°) into starting material and a fraction containing four components. Passage of the latter fraction through column 1 (temperature 184.5°) yielded two fractions, the first of which contained a 1:1 mixture of the cis and trans isomers of 2-methyl-3-phenyl-2,3-dihydrobenzofuran (**9d**): uv max (95% EtOH) 281.5 nm (ϵ 3820); ir (liquid) absence of OH and C=O; nmr (CCl_4) δ 0.95 (d, 1.15, J = 6.4 Hz, CH_3), 1.43 (d, 1.5, J = 6.0 Hz, CH_3), 3.88–5.10 (m, 2, ArCH and OCH), and 6.50–7.50 ppm (m, 4, ArH).

Anal. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.95; H, 6.91.

The second fraction contained a 5:2 mixture of the *E* and *Z* isomers of 1-phenyl-1-(*o*-hydroxyphenyl)propene-1 (**7d**), identified by comparison with an authentic sample (see above). Nmr analysis of the crude and distilled products showed their compositions to be identical, *viz.*, starting material (21.5%), 1-methoxy-1-phenyl-1-(2-hydroxyphenyl)propane (40%), (*Z*)-1-phenyl-1-(2-hydroxyphenyl)propene-1 (8.1%), (*E*)-1-phenyl-1-(2-hydroxyphenyl)propene-1 (7.8%), *cis*- (or *trans*-) 2-methyl-3-phenyl-2,3-dihydrobenzofuran (11.3%), and *trans*- (or *cis*-) 2-methyl-3-phenyl-2,3-dihydrobenzofuran (11.3%).

Photolysis Experiments. A. 1-(*o*-Hydroxyphenyl)-1,5-hexadiene (13a).—A solution of 0.90 g of **13a** in 180 ml of methanol was degassed by alternate evacuation and nitrogen flushing and then irradiated for 4.5 hr with a 550-W Hanovia arc contained in a quartz well. Aliquots removed at hourly intervals and analyzed by glc showed the following ratios of *cis*-**1a** to *trans*-**13a**: 1 hr, 61:39; 2 hr, 82:18, 3 hr, 78:22; 4 hr, 75:25. An nmr spectrum of the crude, undistilled product indicated it to consist of *ca.* two parts of olefin (*cis*- and *trans*-**13a**) and one part of the ether **23a**, the latter indicated by a singlet resonance at δ 3.25 (CH_3O) and a triplet resonance at 4.30 ppm (ArCH) with an intensity ratio of 3:1. Upon distillation, however, decomposition of **23a** to **13a** took place.

B. 1-(*o*-Hydroxyphenyl)-1-phenyl-1,5-hexadiene (13b).—A solution of 1.00 g of **13b** in 180 ml of methanol was degassed in the fashion described above and irradiated for 5.5 hr with a 550-W Hanovia arc contained in a quartz well. Removal of the solvent under vacuum at a temperature below 40° left a crude product which was shown by nmr spectral analysis to be lacking in starting material but to include some methoxyl-containing compound (presumably **23b**). Chromatography on alumina yielded 0.55 g of a colorless oil consisting of a mixture of *cis*- and *trans*-2-(4′-but-1-enyl)-3-phenyl-2,3-dihydrobenzofuran (**25**), bp 118° (0.05 mm).

Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.17; H, 7.14.

Rechromatography of **25** on alumina using heptane–ether (9:1) as the eluting solvent yielded isomer A of **25** in the first fraction and isomer B of **25** in the fourth fraction: nmr (CCl_4) of isomer A δ 1.60–2.73 (m, 4, CH_2), 4.16 [d, 1, J = 7.6 Hz, $(C_6H_5)_2CH$], 4.34–4.74 (m, 1, –OCH), 4.75–5.21 (m, 2, $=CH_2$), 5.43–6.13 (m, 1, CH=C), and 6.60–7.52 ppm (m, 9, ArH); nmr (CCl_4) of isomer B δ 1.00–1.59 (m, 2, CH_2), 1.78–2.45 (m, 2, CH_2), 4.42 [d, 1, J = 7.9 Hz, $(C_6H_5)_2CH$], 4.58–5.18 (m, 3, $=CH_2$ and –OCH), 5.32–6.07 (m, 1, CH=C), and 6.57–7.43 ppm (m, 9, ArH).

Hydrogenation of isomer A of **25** in the presence of 10% palladium on charcoal catalyst afforded 85% of the corresponding 2-*n*-butyl-3-phenyl-2,3-dihydrobenzofuran (**28**): nmr (CCl_4) δ 0.69–2.11 [m, 9, $-(CH_2)_3CH_3$], 4.13 [d, 1, J = 7.6 Hz, $(C_6H_5)_2CH$], 4.31–4.73 (m, 1, –OCH), and 6.53–7.57 ppm (m, 9, ArH).

Hydrogenation of isomer B of **25** under similar conditions afforded 85% of the corresponding 2-*n*-butyl-3-phenyl-2,3-dihydrobenzofuran (**28**), identical with the cis isomer of this compound (see above): nmr (CCl_4) δ 0.59–1.62 [m, 9, $-(CH_2)_3CH_3$], 4.40 [d, 1, J = 7.9 Hz, $(C_6H_5)_2CH$], 4.58–5.02 (m, 1, –OCH), 6.51–7.60 (m, 9, ArH). The detailed pattern of the

6.5–7.6-ppm region of isomer B is quite different from that of isomer A.

C. 1-(*o*-Hydroxyphenyl)-6-phenyl-1,5-hexadiene (13c).—A 0.55-g sample of pure, crystalline **13c** in 180 ml of methanol was degassed in the fashion described above and irradiated for 1.5 hr with a 550-W Hanovia arc contained in a quartz well. The solvent was then removed, and the thick, orange, oily crude product was chromatographed on 50 g of alumina. Elution with ether–heptane (1:3) yielded only a trace of material, and elution with ether–methanol (6:1) yielded a yellow oil which was distilled, bp *ca.* 150° (0.1 mm), to give 0.21 g of a viscous, yellow oil: ir (liquid) 3400 cm^{-1} (ArCH); nmr (CCl_4) δ 1.2–2.7 (broad, 7, CH and CH_2), 3.12 (d, *ca.* 1, J = 1.2 Hz, ArCH), 3.23 (d, *ca.* 1, J = 2 Hz), and 6.5–7.3 ppm (m, 9, ArH). A sample of this material was treated with trifluorohexamethylsilylacetamide, and the silylated product was shown by glpc analysis to contain four components.

Registry No.—**3**, 553-86-6; **4** (R = *i*-Pr), 33316-78-8; **5a**, 13524-76-0; **5b**, 39477-78-6; **5c**, 4355-42-4; **5d**, 4374-69-0; **5e**, 39477-81-1; **6a**, 39477-82-2; **7a**, 10277-93-7; *cis*-**7b**, 39477-84-4; *trans*-**7b**, 39477-85-5; **7c**, 39477-86-6; *cis*-**7d**, 39477-87-7; *trans*-**7d**, 39477-88-8; **7e**, 39477-89-9; **8a**, 88-69-7; **8c**, 4237-44-9; *cis*-**9d**, 38281-39-9; *trans*-**9d**, 38281-40-2; **11b**, 17256-00-7; *cis*-**13a**, 39477-93-5; *trans*-**13a**, 39477-94-6; **13b**, 39477-95-7; **13c**, 39477-96-8; **17a**, 38865-45-1; **17c**, 39477-98-0; **19**, 39477-99-1; **20**, 39478-00-7; **22**, 39478-01-8; *cis*-**25**, 39478-02-9; *trans*-**25**, 39478-03-0; **26**, 39478-04-1; **27**, 39478-05-2; *cis*-**28**, 39478-06-3; *trans*-**28**, 39478-07-4; 2-keto-3-phenyl-2,3-dihydrobenzofuran, 3117-37-1; *o*-hydroxyacetophenone, 118-93-4; *o*-hydroxybenzophenone, 117-99-7; *p*-hydroxybenzophenone, 1137-42-4; 5-bromo-1-pentene, 1119-51-3; salicylaldehyde, 90-02-8; triphenylphosphine, 603-35-0; 5-bromo-1-phenyl-1-pentene, 37464-87-2; triphenyl-1-pentenylphosphonium bromide, 39478-10-9; *o*-methoxybenzaldehyde, 135-02-4; 1-phenyl-1-(*o*-hydroxyphenyl)hexane, 39478-11-0.

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Quenching and Reduction of Photoexcited Benzophenone by Thioethers and Mercaptans[1]

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Reactions of thioethers (sulfides) with excited triplet benzophenones have been studied (1) by retardation by the sulfides of photoreduction by isoborneol, (2) by quenching by naphthalene of photoreduction by the sulfides, and (3) by quenching of phosphorescence of the ketone by the sulfides. Quenching rate constants, k_{ir}, are in the range 10^7–10^9 M^{-1} sec^{-1}. They are highest for aliphatic and lowest for aromatic sulfides, and values are decreased by α branching and by electronegative substituents, and higher in acetonitrile than in benzene. Benzophenone is photoreduced by sulfides containing α H. Quantum yields are low, $\varphi \sim 0.05$–0.2, and increase with decreasing values of k_{ir}. Quenching of phosphorescence of benzophenone by mercaptans shows values of k_q in the range 10^7–10^9 M^{-1} sec^{-1}, highest for aromatic, lowest for aliphatic thiols, decreased by electron-attracting substituents. Reversible hydrogen abstraction is not important in reactions of sulfides, while probably dominant in reactions of thiols. Quenching and photoreduction by sulfides may proceed *via* a common charge transfer complex, in which a full unit of charge separation is not developed. Contributions of charge transfer, hydrogen transfer, and polarizability in quenching and reduction of excited carbonyl compounds by alcohols, ethers, amines, sulfides, and mercaptans are discussed.

The photoreduction of benzophenone to benzopinacol by alcohols proceeds by abstraction of hydrogen by the excited ketone triplet[2] from the α carbon of the alcohol, eq 1, and reduction of ground-state benzophenone by

$$(C_6H_5)_2C{=}O(T_1) + RR'CHOH \longleftrightarrow (C_6H_5)_2\dot{C}OH + RR'\dot{C}OH \quad (1)$$

the alcohol derived radical, eq 2. Such photoreduc-

$$(C_6H_5)_2C{=}O + RR'\dot{C}OH \longrightarrow (C_6H_5)_2\dot{C}OH + RR'C{=}O \quad (2)$$

tions are inhibited by mercaptans or disulfides, present in low concentration, by hydrogen transfer reactions which, in effect, catalyze disproportionation of the initially formed radicals, eq 3 and 4. Ketone and alcohol are regenerated, while the sulfur compounds are regenerated in their alternate oxidation states and function repeatedly, each molecule of sulfur compound negating the effects of many quanta. Support for this mechanism was found in racemization of optically active alcohols[3] and in introduction of carbon-bound deuterium into alcohols[4] during the mercaptan-inhibited reaction, but not during uninhibited photoreduction. Mercaptans might also retard the photoreduction more directly if the excited ketone abstracted sulfhydryl hydrogen from S of mercaptan and the resulting radicals disproportionated, eq 4. At appropriate high concentrations of alcohol and low concentration of thiols the sequence of reactions, eq 1, 3, 4, can be shown to occur almost exclusively.[5]

$$RR'\dot{C}OH + ASH \longrightarrow RR'CHOH + AS\cdot \quad (3)$$

$$(C_6H_5)_2\dot{C}OH + AS\cdot \longrightarrow (C_6H_5)_2C{=}O + ASH \quad (4)$$

The borneols are effective photoreducing agents for benzophenone, leading to camphor and benzopinacol

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