

gave retention time 4.8 min. Analysis of the total methylation product (oil from benzene extract) by gas chromatography suggested that the ratio of monomethyl ether 2 to dimethyl ether of 1 formed in the reaction was 2:1 (by estimation of relative peak areas). No recovered diol 1 was detected.

**2,5-Di-*t*-pentyl-1,4-cyclohexanediol (3), M.p. 97–98°.**—2,5-Di-*t*-pentylhydroquinone (Brothers Chemical Co., practical grade 2,5-di-*t*-amylhydroquinone, recrystallized in a nitrogen atmosphere from 7 ml. of boiling glacial acetic acid plus 2.5 ml. of boiling water per 1.0 g., colorless crystals after four recrystallizations, m.p. 185.5–186.5°; reported<sup>29</sup> m.p. 185°) was hydrogenated as above.<sup>26</sup> To 5.00 g. (0.0200 mole) of 2,5-di-*t*-pentylhydroquinone in 150 ml. of acetic acid (reagent grade) was added 1.23 g. of platinum dioxide catalyst. At 25° and 2–3 atm. hydrogen pressure, hydrogenation stopped within 70 hr. after 60% of the calculated amount of hydrogen had reacted. Isolation of the crude product (as above for 1) by concentration and precipitation gave 4.78 g. of white solid, m.p. 67–83°. The crude products from five hydrogenations were combined and crystallized from 30 ml. of acetonitrile to give 9.45 g. of white crystals, m.p. 118–156°. From this solid, a hexane-soluble fraction was obtained, 4.71 g. of solid, which was dissolved in 10 ml. of benzene and was chromatographed on a 30-mm. i.d. column packed with 400 g. of alumina (Fisher A-540). Elution with anhydrous benzene, ether–benzene mixtures, and methanol–ether mixtures, gave 58 fractions. The solids obtained from selected fractions were analyzed by infrared spectroscopy in 0.004 *M* solutions in carbon tetrachloride. Fractions 28–42, which showed intense absorption at 3480 cm.<sup>-1</sup>, were combined (1.30 g.) and recrystallized twice from acetonitrile to give 1.05 g. (4%) of crystals, m.p. 95–96.5°. Twelve recrystallizations from acetonitrile gave the analytical sample, m.p. 97–98°.

(29) W. Koenigs and C. Mai, *Ber.*, **25**, 2649 (1892).

*Anal.* Calcd. for C<sub>16</sub>H<sub>32</sub>O<sub>2</sub>: C, 74.94; H, 12.58. Found: C, 75.33; H, 12.75.

***cis*-2,5-Di-*t*-pentyl-1,4-cyclohexanediol.**—The procedure previously reported for the analogous Jones oxidation of diol 1 to *cis*-2,5-di-*t*-butyl-1,4-cyclohexanediol was employed.<sup>16</sup> To 0.400 g. (1.56 mmoles) of diol 3 dissolved in 25 ml. of acetone (reagent grade, redistilled from potassium permanganate) and cooled to 5° in a 50-ml. erlenmeyer flask was added dropwise during 3 min. 1.56 ml. (50% excess) of 2.67 *M* chromium trioxide solution while the mixture, cooled in an ice–water bath, was stirred vigorously. The product mixture was immediately combined with 75 ml. of water containing 0.33 g. of sodium hydrogen sulfite, and was extracted with two 35-ml. portions of ether. The ether extract was washed with two 25-ml. portions of 10% aqueous ammonium chloride followed by two 25-ml. portions of 6% sodium bicarbonate. The ether solution was dried with anhydrous sodium sulfate and was evaporated (at ca. 20 mm.). The resulting white solid, 0.38 g., after three recrystallizations from 95% ethanol, gave the diol, 0.18 g. (46%), m.p. 75–75.5°.

*Anal.* Calcd. for C<sub>16</sub>H<sub>32</sub>O<sub>2</sub>: C, 76.14; H, 11.18. Found: C, 75.99; H, 11.21.

A second crop of crystals, 0.10 g., m.p. 72–73°, was isolated from the combined filtrates.

**Infrared Spectra of 1–3.**—A Perkin–Elmer Model 421 DG spectrophotometer was used to record infrared spectra in the region 2500–4000 cm.<sup>-1</sup> by use of stoppered Beckman near-infrared silica cells of path length 1.00 and 5.00 cm. The frequencies were calibrated by recording atmospheric water vapor absorption with each spectrum. The accuracy of the frequencies reported is believed to be ±2 cm.<sup>-1</sup> near 3620 and ±4 cm.<sup>-1</sup> near 3500 cm.<sup>-1</sup>. The absorbance reported is a measure of the peak intensity. Data recorded for solutions in dried "Spectranalyzed" carbon tetrachloride are presented above (see Discussion and Results).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KANSAS, LAWRENCE, KAN.]

## Dialkyl Peroxide-Induced Reductions of Aromatic Ketones<sup>1</sup>

BY EARL S. HUYSER AND DOUGLAS C. NECKERS<sup>2</sup>

RECEIVED JULY 10, 1963

Decomposing di-*t*-butyl peroxide at 130° in a solution of benzophenone in 2-butanol reduced the ketone to benzhydrol and oxidized the 2-butanol to 2-butanone. In a similar reaction, acetophenone is reduced to a mixture of *meso*- and *rac*-2,3-diphenyl-2,3-butanediol. A mechanism involving reaction of 1-hydroxyalkyl radical with the carbonyl function of the ketone is proposed to account for these reductions. Competition reactions involving *m*- and *p*-substituted acetophenones show that the reactivity of the carbonyl function toward reaction with a 1-hydroxyalkyl radical follows a  $\log k/k_0 = \rho\sigma$  correlation with  $\rho = +1.59$ . The nature of this polar effect is discussed in terms of possible mechanisms for the reaction of the 1-hydroxyalkyl radical with the carbonyl function.

Although numerous examples of reactions involving the interaction of free radicals with a carbon–carbon unsaturated linkage are known, comparatively few radical reactions have been reported that involve the interaction of a free radical with carbonyl functions. The proposed mechanism for the formation of *meso*-dihydrobenzoin dibenzoate by the reaction of di-*t*-butyl peroxide with benzaldehyde requires the addition of a benzoyl radical to the carbonyl function of benzaldehyde.<sup>3</sup> A similar reaction is suggested to explain the formation of 4-(benzoyloxybenzyl)pyridine in the di-*t*-butyl peroxide-induced reaction of benzaldehyde with pyridine.<sup>4</sup> The photochemically-induced reactions of aromatic aldehydes with phenanthraquinone and chloranil yield products which suggest the addition of a radical to a carbonyl function.<sup>5</sup> The action of quinones as free radical vinyl polymerization inhibitors

(1) This work was supported in part by a research grant (A-5620) from the National Institutes of Health.

(2) National Science Foundation Cooperative Fellow, 1962–1963. Taken in part from the thesis submitted by D. C. N. in partial fulfillment of the requirements for the Ph.D. degree, University of Kansas, 1963.

(3) F. F. Rust, F. H. Seibold, and W. E. Vaughan, *J. Am. Chem. Soc.*, **70**, 5258 (1948).

(4) M. S. Kharasch, D. Schwartz, M. Zimmermann, and W. Nudenberg, *J. Org. Chem.*, **18**, 1051 (1953).

(5) R. F. Moore and W. A. Waters, *J. Chem. Soc.*, 238 (1953); other examples are given by A. Schönberg and A. Mustafa, *Chem. Rev.*, **40**, 181 (1947).

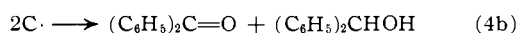
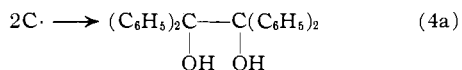
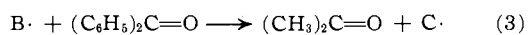
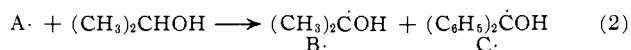
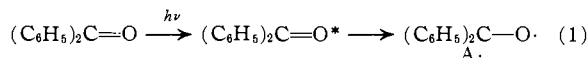
is proposed to involve the addition of polymer radicals to a carbonyl function.<sup>6</sup> The di-*t*-butyl peroxide-induced additions of alkanes to formaldehyde, a reaction leading to the formation of primary alcohols, very likely proceeds by addition of an alkyl radical which attacks the carbon atom of the carbonyl function.<sup>7</sup>

Of particular interest relating to the work reported in this paper is the reaction of a 1-hydroxyalkyl radical with benzophenone producing a benzhydrol radical (reaction 3) suggested by Pitts and co-workers in their mechanism for the photochemical reduction of benzophenone to benzpinacol in 2-propanol.<sup>8</sup> In this mechanism, the 1-hydroxyalkyl radical B· is produced by abstraction of a hydrogen from the alcohol molecule by the benzophenone diradical A, a species which results from the photochemical excitation of benzophenone. The benzpinacol is produced by the radical coupling reaction of two benzhydrol radicals C, half of the C· formed in reaction 2, and half in reaction 3. If the benzhydrol radical C· is indeed produced in a reaction such as 3, it should be possible to reduce benzophenone using 1-hydroxyalkyl radicals such as B·

(6) J. W. Breitenback and A. J. Renner, *Can. J. Research*, **28B**, 509 (1950).

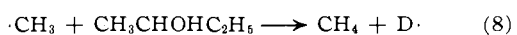
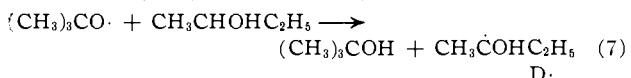
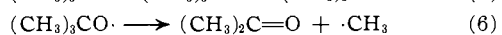
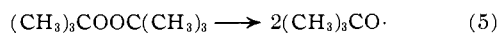
(7) G. Fuller and F. F. Rust, *J. Am. Chem. Soc.*, **80**, 6148 (1958).

(8) J. N. Pitts, R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald, and R. B. Martin, *ibid.*, **81**, 1068 (1959).



produced in some other manner. The work described in this article is concerned with such reactions.

A facile method of producing 1-hydroxyalkyl radicals from primary and secondary alcohols is by decomposing di-*t*-butyl peroxide in the alcohol, the  $\alpha$ -hydrogen of the alcohol being very labile to attack by the *t*-butoxyl or methyl radicals produced by the thermal decomposition of the peroxide. The reactions involved are shown in eq. 5-8 for the reaction of 2-butanol with di-*t*-butyl peroxide.



We found that heating a solution consisting of equimolar amounts of di-*t*-butyl peroxide and benzophenone in a 6 *M* excess of 2-butanol at 130° produced the products shown in Table I. The amounts of the volatile components were determined by gas chromatographic methods and the benzhydrol by means of its n.m.r. spectrum. The benzhydrol is most likely produced by a disproportionation reaction of two benzhydrol radicals C· (reaction 5)<sup>9</sup> which resulted from interaction of benzophenone with 2-butanol radicals in a reaction similar to 3.

TABLE I

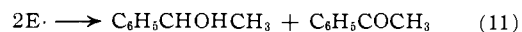
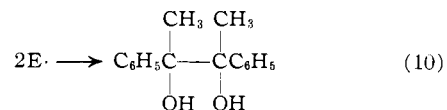
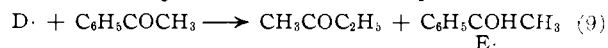
REACTIONS OF AROMATIC KETONES WITH 2-BUTANOL INDUCED BY DI-*t*-BUTYL PEROXIDE AT 130°

Reactants (amounts in mmoles)	Products
Benzophenone reaction	
Benzophenone (3.30)	2-Butanone (5.54)
Di- <i>t</i> -butyl peroxide (4.75)	<i>t</i> -Butyl alcohol (7.98)
	Acetone (1.36)
2-Butanol (24.3)	Benzhydrol (0.76)
Acetophenone reaction	
Acetophenone (240)	2-Butanone (146)
Di- <i>t</i> -butyl peroxide (96)	<i>t</i> -Butyl alcohol (159)
2-Butanol (820)	Acetone (40)
	$\alpha$ -Phenylethanol (10)
	<i>meso</i> - and <i>rac</i> -2,3-diphenyl-2,3-butanediol (41)

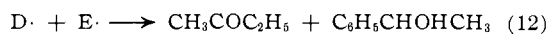
Acetophenone yielded a diol and  $\alpha$ -phenylethanol as reduction products in a reaction with di-*t*-butyl peroxide in 2-butanol (Table I). The volatile products listed in the table were identified and their amounts determined by gas chromatographic techniques. The diol was isolated by removal of the volatile products by distillation and proved to be an almost equimolar mixture of *meso*- and *rac*-2,3-diphenyl-2,3-butanediol. The formation of this diol and the  $\alpha$ -phenylethanol in this reaction can be explained by the following reactions

(9) At temperatures above 100°, the photochemical reduction of benzophenone produces mostly benzhydrol. The benzhydrol radicals apparently do not couple at higher temperatures but only undergo disproportionation in bimolecular processes involving two benzhydrol radicals or a reaction between a benzhydrol radical and a 1-hydroxyalkyl radical such as B·. E. S. Huyser and D. C. Neckers, unpublished work.

involving formation of the  $\alpha$ -phenylethanol radical by interaction of a 2-butanol radical (D·) derived from the reaction sequences 5-8 with acetophenone.



OR



Examination of the quantitative data for the reactions shown in Table I reveals that the peroxide used can be accounted for as *t*-butyl alcohol and acetone, two moles of these fragmentation products for each mole of peroxide. Although 2-butanone is not an unexpected product in the reaction of di-*t*-butyl peroxide with 2-butanol, the ketone being formed by disproportionation reactions between two 1-hydroxyalkyl radicals (D·) or a 1-hydroxyalkyl radical and a *t*-butoxyl radical from the peroxide, the amount is greater than might be expected. The stoichiometry of the reaction of 2-butanol with di-*t*-butyl peroxide is that shown in eq. (13) and only one mole of 2-butanone can be formed from one mole of peroxide.<sup>10</sup> As our data clearly show, more (CH<sub>3</sub>)<sub>3</sub>COOC(CH<sub>3</sub>)<sub>3</sub> + CH<sub>3</sub>CHOHC<sub>2</sub>H<sub>5</sub> → [(CH<sub>3</sub>)<sub>3</sub>COH + CH<sub>3</sub>COCH<sub>3</sub>] + CH<sub>3</sub>COC<sub>2</sub>H<sub>5</sub> + CH<sub>4</sub> (13) total, 2 moles

2-butanone is formed than can be accounted for from eq. 13. In each case the amount of 2-butanone in excess of that expected from the stoichiometry shown in (13) is equivalent to the amount of reduction experienced by the aromatic ketone. Such a result is consistent with the mechanism suggested for these reactions, namely that 1-hydroxyalkyl radicals are interacting with the aromatic ketone as shown in eq. 3 and 9. The 2-butanone produced in such a reaction results from a process that is unimolecular in radicals and if all the peroxide fragments produced 1-hydroxyalkyl radicals, all of which reacted with the aromatic ketone, twice as much 2-butanone as peroxide that reacted should be formed. The aromatic ketone reduction products, on the other hand, are produced in bimolecular radical reactions. Thus the total number of moles of 2-butanone produced in reactions such as 3 and 9 must be twice that of the aromatic ketone reduction products. The acetophenone data in Table I can be used to illustrate this point. The formation of 0.04 mole of the 2,3-diphenyl-2,3-butanediols required 0.08 mole of  $\alpha$ -phenylethanol radicals, and 0.01 mole of  $\alpha$ -phenylethanol required 0.02 mole of  $\alpha$ -phenylethanol radicals.<sup>11</sup> Thus a total of 0.10 mole of 2-butanone was produced in reaction 9. If the 0.10 mole of 1-hydroxyalkyl radicals required for this reaction had undergone disproportionation, only 0.05 mole of 2-butanone would have been produced. This amount plus the 2-butanone that cannot be assumed to be formed in reaction 12 (0.046 mole) is equal to the amount of peroxide. The benzophenone data, when treated in this fashion, show that the amount of 2-butanone formed in excess of the amount of peroxide

(10) Evidence for an interaction of 1-hydroxyalkyl radicals with the peroxide is available and will be reported later. However, the stoichiometry of the reaction between alcohols and peroxide is not changed although the ketone does arise in part from another reaction.

(11) Some of the  $\alpha$ -phenylethanol may have been formed by reaction 12. This does not change the argument since this reaction produces a molecule of 2-butanone which would have been produced in the formation of the other  $\alpha$ -phenylethanol radical required for the bimolecular reaction of two such radicals.

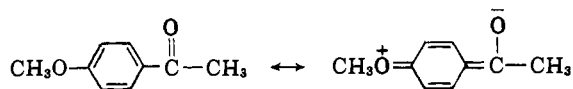
used can be assumed to arise from the reaction of 1-hydroxyalkyl radicals with benzophenone producing benzhydryl radicals which disproportionate in a bimolecular radical process yielding benzhydryl.

Competitive reactions involving substituted acetophenones showed that the lability of the acetophenone carbonyl toward reaction with a 1-hydroxyalkyl radical is influenced by the substituents. The relative reactivities of the substituted acetophenones with respect to acetophenone are shown in Table II. Electron-

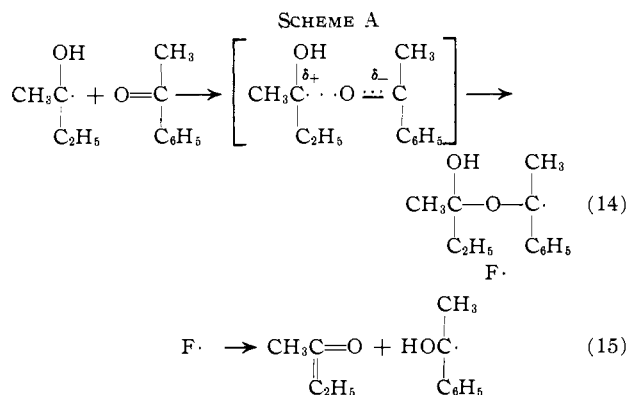
TABLE II  
RELATIVE REACTIVITIES OF SUBSTITUTED ACETOPHENONES  
TOWARD REACTION WITH 2-BUTANOL  
(Di-*t*-butyl peroxide induced at 125°)

Substituent	No. of runs	$k/k_0$	Av. deviation
<i>m</i> -CF <sub>3</sub>	2	4.85	0.50
<i>p</i> -Cl	3	3.01	.23
H	..	1.00	..
<i>m</i> -Me	2	0.85	0.01
<i>p</i> -Me	5	.59	.06
<i>p</i> -OMe	2	.17	.01
2,4-Dimethyl	5	.18	.10
2,4,6-Trimethyl	6	.05	.03

releasing groups in the *m*- and *p*-position decrease the reactivity of the carbonyl of acetophenone toward reaction with the 1-hydroxyalkyl radical, whereas electron-withdrawing groups increase the reactivity. Plotting  $\log k/k_0$  against the Hammett  $\sigma$ -values (Fig. 1) gives a  $\rho$  of 1.59 by a least-squares plot with a correlation factor of 0.92 if the values of *m*-CF<sub>3</sub>, *p*-Cl, H, *m*-CH<sub>3</sub>, and *p*-CH<sub>3</sub> are used for the calculation. A probable explanation for the failure of the *p*-OCH<sub>3</sub> to correlate well with the other substituents in this treatment is that resonance factors increasing the electron density at the carbonyl are greater than might be expected.



The positive  $\rho$  indicates that the 1-hydroxyalkyl radical prefers reacting at a site of low electron density. This observation is consistent with two possible modes of attack of the 1-hydroxyalkyl radical on the carbonyl. In Scheme A, the 1-hydroxyalkyl radical adds to the carbonyl forming a hemiacetal radical F<sup>•</sup> which could decompose yielding the arylethanol radical E<sup>•</sup> and the observed 2-butanone.



A polar factor involving the 1-hydroxyalkyl radical acting as an electron donor may be important in this reaction. Since a donor radical requires a site to donate its negative charge as indicated in the transition state drawn for this reaction, this might be expected to be accomplished more readily at a site that is deficient in electrons. Thus, electron-releasing substituents

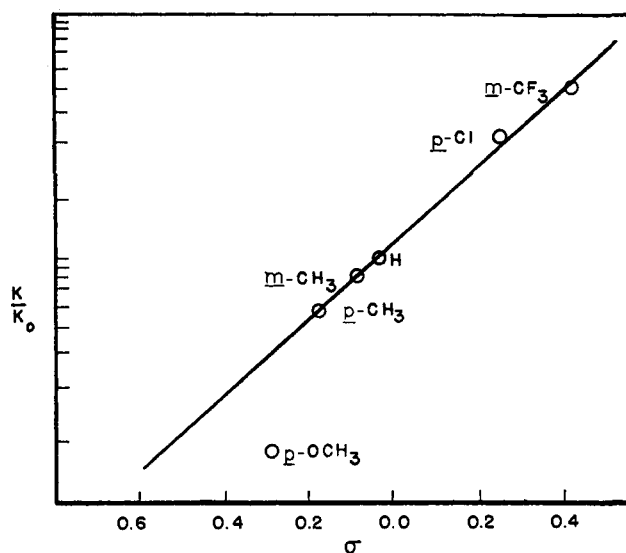
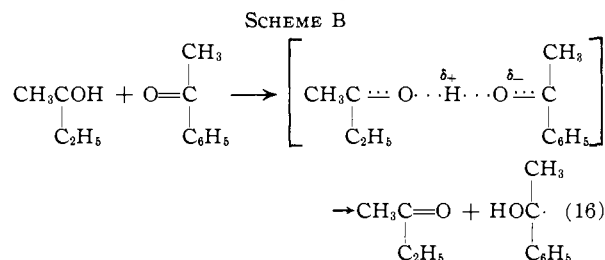


Fig. 1.—Correlation between  $\log k/k_0$  and  $\sigma$ -values of substituents.

would lower the contribution of the polar factor to the transition state and electron-withdrawing groups would increase this contribution.

In reaction Scheme B, the 1-hydroxyalkyl radical transfers a hydrogen atom directly to the carbonyl of the acetophenone, and the arylethanol radical and 2-butanone are formed in one step.

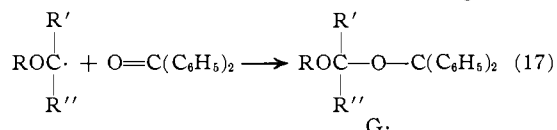


The hydrogen atom should also be expected to be an electron donor and prefer to react at a site where the electron density is low. The observed order of the reactivities of the substituted acetophenones is consistent with this proposal.

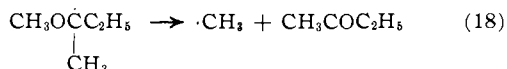
The relative reactivities of 2,4-dimethylacetophenone and 2,4,6-trimethylacetophenone (see Table II) indicate that the reactivity of the carbonyl is influenced to some extent by steric factors. Although *o*- and *p*-methyl groups should lower the reactivity for the polar reasons cited previously, the decrease in the reactivity of the 2,4,6-trimethylacetophenone is somewhat greater than can be attributed to this factor alone. The steric effect observed in these reactions, however, is not great enough to make reaction Scheme B preferable to A for two reasons. (1) The reaction is taking place on the oxygen of the carbonyl function and this atom is not sufficiently hindered to exclude attack by the larger 1-hydroxyalkyl radical. (2) The steric effect may be one which involves inhibition of resonance in that the  $\alpha$ -arylethanol radical cannot make its fullest resonance contribution to the transition state since it cannot lie planar with the aromatic ring in the reaction with 2,4,6-trimethylacetophenone.

Support for the hydrogen atom transfer mechanism (Scheme B) can be found from the photochemical reduction of benzophenone by compounds other than alcohols. If the addition of a radical to the carbonyl did occur as shown in Scheme A, additions to form species more stable than the hemiacetal should lead to products other than a pinacol. Photochemical reduction of benzophenone in the presence of an ether

might be expected to produce a stable diketal derivative upon coupling of two adduct radicals such as G· which would be formed in the manner shown in eq. 17. In



the photochemical reduction of benzophenone in benzhydrolmethyl ether, Bergman and Fujise<sup>12</sup> reported finding only benzpinacol and benzpinacol dimethyl ether, the coupling products of both the benzhydrol radical and ether radicals, as products of the reaction. The energetics are admittedly not favorable for any interaction between a highly stabilized ether radical and benzophenone. For this reason, we performed essentially the same reaction using 2-methoxybutane. After 2 weeks illumination in sunlight, a solid reduction product separated from the reaction mixture. With no further purification other than drying, the material melted at 182–187° (recorded m.p. for benzpinacol, 185–187°) indicating very little, if any, material other than pinacol was formed. Some 2-butanone was also formed in this reaction. It very likely results from fragmentation of the ether radical. Since the frag-



mentation might compete with the addition reaction, a more definitive system will be required, however, to eliminate the addition reaction (Scheme A) from consideration.

### Experimental<sup>13</sup>

The following reagents were commercial materials, purified when necessary by distillation: di-*t*-butyl peroxide (Lucidol); 2-butanol (Eastman); acetophenone (Matheson Coleman and Bell); *p*-methoxyacetophenone (Matheson Coleman and Bell); *p*-methylacetophenone (Matheson Coleman and Bell); *p*-chloroacetophenone (Eastman), and benzophenone (Matheson). In each case, the material gave a single gas chromatographic peak before it was used. *m*-Methylacetophenone was prepared from *m*-toluic acid (Matheson) by the method described by Gilman and Nelson.<sup>14</sup> *m*-Trifluoromethylacetophenone was prepared by the oxidation of the corresponding  $\alpha$ -arylethanol which was obtained by the Grignard reaction of *m*-trifluoromethylphenylmagnesium bromide and acetaldehyde. The Grignard reagent was prepared from *m*-trifluoromethylbromobenzene (Pierce Chem. Co.) by the method described previously.<sup>15</sup> 2,4-Dimethylacetophenone was obtained by acetylation of *m*-xylene by the method of Perkin and Stone.<sup>16</sup> 2,4,6-Trimethylacetophenone was prepared by acetylation of mesitylene in the manner outlined by Noller and Adams.<sup>17</sup>

**Benzophenone, Di-*t*-butyl Peroxide, and 2-Butanol.**—A reaction mixture consisting of 0.60 g. (0.003 mole) of benzophenone, 0.69 g. (0.0047 mole) of di-*t*-butyl peroxide, and 1.80 g. (0.024 mole) of 2-butanol was sealed in a glass tube and heated at 125° for 24 hr. At the end of this period, all of the peroxide was consumed. The amounts of acetone, *t*-butyl alcohol, and 2-butanone were determined by gas chromatography using a weighed amount

of the reaction mixture containing a known quantity of ethyl acetate as an internal standard. A 15-ft. column packed with 5% E-600 (Dow Chemical Co.) on Chromasorb P at 60° was employed for the gas chromatographic analysis. The quantity of benzhydrol formed in the reaction was ascertained from the n.m.r. spectrum of the reaction mixture. The  $\alpha$ -hydrogen of the benzhydrol showed an absorption at 5.62 p.p.m. and its integrated area was compared with that of the total integrated area of the phenyl protons (centered at 7.22 p.p.m.). No benzpinacol was found in the reaction mixture.

**Acetophenone, Di-*t*-butyl Peroxide, and 2-Butanol.**—A reaction mixture consisting of acetophenone (28.4 g., 0.24 mole), di-*t*-butyl peroxide (14.1 g., 0.096 mole), and 2-butanol (60.5 g., 0.82 mole) was heated at 140° in a stainless steel autoclave for 18 hr. After cooling, a weighed aliquot (*ca.* 1 g.) of the reaction mixture was subjected to gas chromatographic analysis in the manner described in the previous experiment. The quantities of acetone, *t*-butyl alcohol, and 2-butanone formed were determined in this manner. Another weighed aliquot (*ca.* 1 g.), with benzyl alcohol as an internal standard, was subjected to gas chromatographic analysis on a 10-ft. column packed with 5% L-699 (Nalco Chem. Co.) on Chromasorb P at 145° using helium as a carrier gas (40 p.s.i.g.) for the  $\alpha$ -phenylethanol determination. The remainder of the reaction mixture was distilled to remove the lower boiling components, leaving a high boiling residue (9.89 g.). The infrared spectrum and n.m.r. spectrum (see below) of the crude material were essentially the same as those of the pinacol obtained from the photochemical reduction of acetophenone in 2-propanol. The residue was recrystallized once from Skellysolve F and melted over a range of 85–110°. After several recrystallizations, *meso*-2,3-diphenyl-2,3-butanediol, m.p. 121–122° (reported<sup>18</sup> m.p. 122°), was obtained.

The n.m.r. spectrum of the crude residue showed three distinct absorptions: a split peak centered at 7.05 p.p.m. due to the phenyl protons of both the *racemic* and *meso* isomers; a split peak at 1.37 p.p.m. due to the methyl groups of both isomers; and two distinct peaks, one at 2.40 p.p.m. and one at 2.80 p.p.m., due to the hydroxy protons. The purified *meso*-2,3-diphenyl-2,3-butanediol showed only three absorptions, a singlet at 1.30 p.p.m., a singlet at 2.40 p.p.m., and a singlet at 7.12 p.p.m.

**Determination of Relative Reactivities of Substituted Acetophenones.**—Approximately equimolar quantities of acetophenone and the substituted acetophenone were weighed out into a 10-mole excess of 2-butanol. A quantity of di-*t*-butyl peroxide amounting to about one-half the total molar amount of the ketones was added. A weighed aliquot of this mixture was subjected to gas chromatography on the L-699 column under the conditions described above, using a weighed amount of iodobenzene as an internal standard. The peak areas of the two ketones were determined. The remainder of the reaction mixture was heated for 24 hr. in a 125° oil bath. After cooling, a weighed sample of the reaction mixture was mixed with a weighed amount of iodobenzene and the gas chromatographic peak areas again determined. From the areas of the ketone peaks before and after the reaction, the quantities of the two ketones remaining after reaction were calculated. These quantities were substituted in the equation where  $k/k_0$  is the relative reactivity ratio,  $A_0$  and  $B_0$  are quantities of the substituted acetophenone and acetophenone, respectively,

$$k/k_0 = \log(A_0/A) / \log(B_0/B)$$

before reaction, and  $A$  and  $B$  are the quantities of the two ketones after reaction. Two or more runs were performed in each case.

**Photochemical Reduction of Benzophenone in 2-Methoxybutane.**—A solution of benzophenone (10.0 g., 0.055 mole) in 2-methoxybutane (27.5 g., 0.31 mole) was placed in a Pyrex flask and illuminated in the sun for 18 days. At the end of this period, a solid material had separated out of the solution. The solid was filtered out and after drying under vacuum for 2 hr., the material melted at 182–187°. The recorded melting point for benzpinacol is 185–187°. The liquid portion of the reaction mixture showed the presence of 2-butanone on gas chromatographic analysis. No further work was done with this reaction mixture.

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