[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

The Competitive Oxidation of Cumene and Tetralin[1,2]

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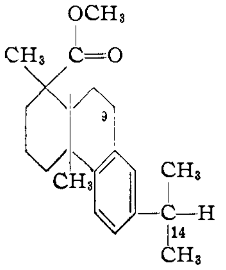
The peroxide-catalyzed reaction of oxygen with liquid cumene, tetralin and mixtures of the two has been studied from a viewpoint of products and rate. Hydroperoxides are the major products formed in the initial stage of the reaction at 90° in the presence of oxygen at pressures of about 730 mm. By making use of the absolute rate constants reported for the oxidation of pure cumene and tetralin the rate constants for the reaction of cumylperoxy radicals with tetralin, tetralylperoxy radicals with cumene, and cumylperoxy radicals with the tetralylperoxy radicals have been estimated. Tetralin was found to be 16–23 times as reactive as cumene toward the tetralyl- or cumylperoxy radicals at 90°. Mixtures of cumene and tetralin, containing only small amounts of tetralin, are peroxidized at rates considerably below the rate observed for the oxidation of either of the pure hydrocarbons. The decrease in the rate of oxidation observed when a small amount of the more reactive tetralin is added to cumene stems from the fact that a relatively high concentration of tetralylperoxy radicals is formed in solutions containing mostly cumene. Under these conditions tetralylperoxy radicals terminate much more readily than cumylperoxy radicals and a lower rate of oxidation is observed for the mixture than for pure cumene because of the lowered steady-state concentration of peroxy radicals. Small amounts of other reactive hydrocarbons that produce a secondary peroxy radical, such as indan, dibenzyl ether, styrene and cyclohexene, also retard the oxidation of cumene.

It has been reported that the oxidation of methyl dehydroabietate by molecular oxygen produces much more of the 9- than of the 14-hydroperoxide.[3] From the results cited it can be calculated that a hydrogen atom in the 9-position of methyl dehydroabietate is about 8 times as reactive as a hydrogen in the 14-position toward a peroxy radical at 80° (assuming that the 9- and 14-peroxy radicals have similar selectivities). Although this result is not unreasonable, it has been shown that the relative reactivities of similar α-hydrogen atoms of cumene (isopropylbenzene) and tetralin (1,2,3,4-tetrahydronaphthalene) toward the trichloromethyl radical are nearly equal at 91.5°.[4] As the predominant formation of the 9-hydroperoxide in the oxidation of methyl dehydroabietate can result from either an intrinsic difference in the reactivity of the two types of hydrogen atoms or from some other influence connected with the complex structure of this molecule, it appeared of interest to determine the relative reactivities of the α-hydrogen atoms of cumene and tetralin toward peroxy radicals by measuring the products resulting from competitive oxidations. During the course of this work some interesting observations on the rate of oxidation of mixtures of cumene and tetralin led to a complete kinetic analysis of this system.



Results

Products of the Reaction.—The peroxidation of hydrocarbons has been established to be a free radical process involving the rapid reaction of oxygen with an alkyl-free radical and the much slower reaction of a peroxy radical with the hydrocarbon as the chain-propagation steps.[5] The competitive peroxidation of two hydrocarbons is a more complex affair and a total of six propagation steps must be considered. In the case of the competitive oxidation of cumene (R_cH) and tetralin (R_tH) the following reactions of alkyl and peroxy radicals are involved in the formation of cumene hydroperoxide (R_cO_2H) and tetralin hydroperoxide (R_tO_2H).

$$R_t\cdot + O_2 \xrightarrow{\text{very fast}} R_tO_2\cdot$$

$$R_c\cdot + O_2 \xrightarrow{\text{very fast}} R_cO_2\cdot$$

$$R_tO_2\cdot + R_tH \xrightarrow{k_1} R_tO_2H + R_t\cdot$$

$$R_tO_2\cdot + R_cH \xrightarrow{k_2} R_tO_2H + R_c\cdot$$

$$R_cO_2\cdot + R_cH \xrightarrow{k_3} R_cO_2H + R_c\cdot$$

$$R_cO_2\cdot + R_tH \xrightarrow{k_4} R_cO_2H + R_t\cdot$$

The products of a competitive oxidation of two hydrocarbons are determined by the concentrations of the hydrocarbons and the values of the four propagation rate constants (k_1 to k_4). Although it is difficult to measure these rate constants directly, the ratios k_1/k_2 and k_3/k_4 can be determined from a knowledge of the products formed in the competitive oxidations of mixtures having different initial hydrocarbon concentrations by use of the copolymerization equation.[6]

$$\frac{d[R_tH]}{d[R_cH]} = \frac{d[R_tO_2H]}{d[R_cO_2H]} = \frac{[R_tH]}{[R_cH]}\,\frac{(k_1/k_2[R_tH] + [R_cH])}{(k_3/k_4[R_cH] + [R_tH])} \quad (1)$$

This technique has been applied previously in oxida-

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[1] Directive Effects in Aliphatic Substitutions. VI. Paper V, G. A. Russell and H. C. Brown, THIS JOURNAL, **77**, 4578 (1955).

[2] Presented before the Division of Organic Chemistry at the New York Meeting of the American Chemical Society, September, 1954.

[3] P. F. Ritchie, T. F. Sanderson and L. F. McBurney, THIS JOURNAL, **75**, 2610 (1953).

[4] E. C. Kooyman, *Disc. Faraday Soc.*, **10**, 163 (1951).

[5] (a) J. L. Bolland and G. Gee, *Trans. Faraday Soc.*, **42**, 236, 244 (1946); J. L. Bolland, *Proc. Royal Soc.* (*London*), **186A**, 218 (1946); (b) J. L. Bolland, *Trans. Faraday Soc.*, **44**, 669 (1948); (c) J. L. Bolland, *Quart. Revs.* (*London*), **3**, 1 (1949); L. Bateman, *ibid.*, **8**, 147 (1954).

[6] (a) F. R. Mayo and F. M. Lewis, THIS JOURNAL, **66**, 1594 (1944); F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 191 (1950); (b) C. Walling and E. A. McElhill, THIS JOURNAL, **73**, 2927 (1951); T. A. Ingles and H. W. Melville, *Proc. Royal Soc.* (*London*), **218A**, 163 (1953).

tion systems to determine the relative reactivities of aldehydes toward peroxy radicals.[6b]

Tetralin, cumene and mixtures of the two were oxidized at 90–110° in the presence of small amounts of *t*-butyl perbenzoate by vigorously shaking the hydrocarbon in the presence of oxygen at about 730 mm. Under these conditions hydroperoxides are produced in nearly quantitative yields during the initial stage of the oxidation (Table I). It has been demonstrated previously that only attack on the α-hydrogen atoms occurs in the low temperature oxidation of cumene[7] and tetralin.[8]

TABLE I

PRODUCTS OF THE OXIDATION OF CUMENE AND TETRALIN IN THE PRESENCE OF 0.02 *M* *t*-BUTYL PERBENZOATE

Mole fraction Cumene	Mole fraction Tetralin	Temp., °C.	Mole % oxidation	Oxygen, mole Absorbed	Oxygen, mole Found
	1.000	90	8.5	0.0294	0.0290
0.680	0.320	90	0.5	.0095	.0098
.680	.320	100	3.6	.0121	.0123
.680	.320	110	3.5	.0117	.0120
.915	.085	90	2.9	.0097	.0095
1.000		90	2.6	.0086	.0084

The products of two of the competitive oxidations (0.32 and 0.085 mole fraction of tetralin) were reduced with lithium aluminum hydride after removal of most of the unreacted hydrocarbons, and the alcohols formed analyzed by infrared absorption. This procedure was especially attractive since not only are hydroperoxides quantitatively reduced to the corresponding alcohols by lithium aluminum hydride,[9] but any α-tetralone formed in the oxidation also would have been reduced to the alcohol. Infrared spectra of the reduction products were obtained in dilute cumene solution and the absorption at 10.00 and 8.52 μ used for the analysis of α-tetralol and 2-phenyl-2-propanol. Cumene had only a slight absorbance at these wave lengths and dilute solutions of tetralin in cumene were found to have the same absorbance as pure cumene. α-Tetralol and 2-phenyl-2-propanol both absorb at 8.52 μ, whereas 2-phenyl-2-propanol absorbs only slightly at 10.00 μ. Plots of absorbance as a function of concentration were prepared for the alcohols and used to calculate the concentrations of the alcohols in the unknown samples. The method of analysis was checked on prepared samples of the pure alcohols.

Oxidation of the mixture of cumene and tetralin containing 0.68 mole fraction of cumene with 1.5 mole % of oxygen thus was found to have produced tetralyl hydroperoxide and cumyl hydroperoxide in the ratio of 7.7 to 1 at 90° and 6.5 to 1 at 110° while the mixture containing 0.915 mole fraction of cumene produced the hydroperoxides in the ratio of 1.15 to 1 at 90° (2.87 mole % oxidation). The results at 90° were transformed into relative reactivities by use of the integrated form of equation 1.[6a] The values of 16 and 0.043 thus were obtained for the ratios k_1/k_2 and k_3/k_4, respectively. These ratios indicate that an α-tetralylperoxy radical attacks a tetralin molecule 16 times as readily as it attacks a cumene molecule, while a cumylperoxy radical attacks a tetralin molecule 23 times as readily as a cumene molecule. Within experimental error the relative reactivities of tetralin and cumene are the same toward the two peroxy radicals. These values reflect not only the differences in the reactivities of each α-hydrogen atom of cumene and tetralin but also the fact that tetralin has four times as many α-hydrogen atoms as cumene.

Kinetics of the Oxidation.—The formation of a hydroperoxide from the reaction of a hydrocarbon with oxygen in the presence of a catalyst at relatively low temperatures (0–80°) and high oxygen pressures (>100 mm.) has been shown to involve only the following steps.[5]

$$\text{Catalyst} \xrightarrow{k_{\text{i}}} 2\text{R}'\cdot \xrightarrow[\text{O}_2 + \text{RH}]{\text{RH or}} 2e\text{R}\cdot$$

$$\text{R}\cdot + \text{O}_2 \xrightarrow{\text{very fast}} \text{RO}_2\cdot$$

$$\text{RO}_2\cdot + \text{RH} \xrightarrow{k_{\text{p}}} \text{RO}_2\text{H} + \text{R}\cdot$$

$$2\ \text{RO}_2\cdot \xrightarrow{k_{\text{t}}} \text{non-radical products}$$

The number e represents the efficiency of the initiation process and may vary from 0 to 1.

The kinetic expression obeyed when only the above reactions are involved in the oxidation is

$$-\text{d}[\text{RH}]/\text{d}t = k_{\text{p}}k_1^{-1/2}[\text{RH}](2ek_{\text{i}}[\text{Cat.}])^{1/2} \quad (2)$$

If the oxygen pressure is low the lifetime of an alkyl radical may be long enough that termination between two alkyl radicals or between a peroxy and an alkyl radical competes with the termination of two peroxy radicals.[5,10] When this occurs the kinetics are more complex and the rate of oxidation is no longer independent of the oxygen pressure.[5,10] In general, the rate of oxidation of olefins has been found to be independent of the oxygen pressure above about 100 mm.[5c] Moreover, it has been shown that the rate of oxidation of cumene at 65°, catalyzed by the decomposition of 1,1′-azobis-1-cyanocyclohexane, is independent of the oxygen pressure above about 250 mm.[11] and that in the presence of benzoyl peroxide the rate of oxidation of tetralin is independent of the oxygen pressure above 50 mm. at 45°.[12] The oxidation of diphenylmethane at 115° also involves the termination of only peroxy radicals above oxygen pressures of 400 mm.[12a]

The rate of oxidation of cumene, tetralin and mixtures of the two have been measured under a variety of conditions by shaking the hydrocarbons in an oxygen atmosphere at a controlled temperature. In the presence of a catalyst stable enough that its concentration can be considered to be constant, the amount of oxygen absorbed was proportional to time during the initial stage of the oxidation. In Table II are summarized data on the rates of oxida-

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[7] (a) H. Hock and S. Lang, *Ber.*, **77**, 257 (1944); (b) G. P. Armstrong, R. N. Hall and D. C. Quin, *J. Chem. Soc.*, 666 (1950).

[8] A. Robertson and W. A. Waters, *ibid.*, 1574, 1578, 1585 (1948); *Trans. Faraday Soc.*, **42**, 201 (1946).

[9] G. A. Russell, THIS JOURNAL, **75**, 5011 (1953)

[10] L. Bateman and A. L. Morris, *Trans. Faraday Soc.*, **49**, 1026 (1953).

[11] H. W. Melville and S. Richards, *J. Chem. Soc.*, 944 (1954).

[12] C. H. Bamford and M. J. S. Dewar, *Proc. Royal. Soc.* (*London*), **198A**, 252 (1949).

[12a] D. D. K. Grant and C. F. H. Tipper, *J. Chem. Soc.*, 640 (1955).

tion obtained from the slopes of the plots of oxygen absorbed as a function of time. The data were obtained at essentially constant hydrocarbon and catalyst concentrations during the reaction of less than one mole % of oxygen with the hydrocarbon. Most of the measurements were made at a shaking rate of 150 cycles min.$^{-1}$. However, changing the shaking rate to 90 or 250 cycles min.$^{-1}$ did not alter the observed rate of oxidation.

The results demonstrate that at 90° in the presence of 0.005–0.02 *M* *t*-butyl perbenzoate, equation 2 is obeyed during the initial stage of the oxidation of cumene or tetralin. Furthermore, the rate of oxidation was independent of the oxygen pressure between about 200 and 760 mm. As evidenced by the constancy of the values of $k_p k_t^{-1/2}(2ek_i)^{1/2}$ in the right-hand column of Table II, the rate of oxidation of tetralin or cumene is proportional to the hydrocarbon concentration and the square root of the catalyst concentration as demanded by equation 2. It therefore is concluded that under the conditions employed only peroxy radicals are involved in the termination reaction.

TABLE II

THE RATE OF OXIDATION OF CUMENE AND TETRALIN AT 90° IN THE PRESENCE OF 0.02 *M* *t*-BUTYL PERBENZOATE[a]

Hydrocarbon concn. Tetralin	Hydrocarbon concn. Cumene	Cat. concn.	Oxygen pressure[b] mm.	Rate, mole l.$^{-1}$ hr.$^{-1}$	Rate/[RH][Cat]$^{1/2}$ mole$^{-1/2}$ l.$^{1/2}$ hr.$^{-l}$
6.91		0.02	281	0.203	0.21
6.91		.02	500	.210	.22
6.91		.02	760	.210	.22
6.91		.05	760	.291	.19
6.91		.008	760	.159	.26
4.88[c]		.02	760	.160	.23
3.32[c]		.02	760	.079	.21
	6.65	.02	260	.067	.071
	6.65	.02	460	.066	.070
	6.65	.02	760	.065	.069
	6.65	.01	760	.047	.071
	6.65	.002	760	.021	.071
	5.18[c]	.02	760	.047	.064
4.64	2.21	.02	760	.145	
2.15	4.61	.02	760	.083	
2.15	4.61	.02	760	.084	
0.58	6.14	.02	760	.032	
0.19	6.50	.02	760	.023	

[a] All concentrations in moles l.$^{-1}$. [b] Uncorrected for the vapor pressure of the hydrocarbon. [c] Bromobenzene diluent.

Rate of Oxidation of Mixtures of Cumene and Tetralin.—The most interesting feature of the competitive oxidation of cumene and tetralin is the effect of concentration on rate. The addition of small amounts of tetralin to cumene reduces the over-all rate of oxidation even though tetralin is oxidized much easier than cumene. As the concentration of tetralin is increased the rate passes through a minimum at about 98 mole % cumene (Table II).

The effect of small amounts of tetralin on the rate of oxidation of cumene undoubtedly is connected with the fact that a relatively high concentration of tetralylperoxy radicals is formed in these solutions because tetralin is much more reactive than cumene toward peroxy radicals. In order to determine whether tetralin is unique in this respect or it is a general phenomenon for reactive hydrocarbons capable of producing a secondary peroxy radical, cumene and several other more reactive hydrocarbons have been competitively peroxidized. Styrene, which previously has been reported to retard the rate of oxidation of cumene,[7b] cyclohexene, indan and dibenzyl ether were chosen as compounds known to be more easily oxidized than cumene and which yield secondary peroxy radicals. α-Methylstyrene, a substance that should be much more reactive toward peroxy radicals than cumene and which yields a tertiary peroxy radical also was competitively oxidized with cumene.

Both cyclohexene[13] and dibenzyl ether[14] are known to react with oxygen to produce the hydroperoxides in nearly quantitative yields by the same reaction path that is involved in the oxidation of cumene and tetralin. Styrene and α-methylstyrene react with oxygen in a similar manner except that in these cases the propagation steps involve the addition of a peroxy radical to the double bond and the product is a polymeric peroxide instead of a hydroperoxide.[15]

In Table III are summarized data which demonstrate that tetralin is not unique in its property of retarding the rate of oxidation of cumene. Styrene, indan, dibenzyl ether and cyclohexene, all sub-

TABLE III

THE RATE OF OXIDATION OF MIXTURES OF CUMENE AND HYDROCARBONS IN THE PRESENCE OF 0.02 *M* *t*-BUTYL PERBENZOATE AT 90°

Hydrocarbon	Concentration, moles l.$^{-1}$ Cumene	Concentration, moles l.$^{-1}$ Hydrocarbon	Rate, moles l.$^{-1}$ hr.$^{-1}$
	6.65		0.067
Styrene	6.52	0.19	.042
	6.07	0.72	.034
	4.40	2.69	.110
	2.22	5.37	.245
		8.04	.400
α-Methylstyrene	6.57	0.12	.068
	6.01	0.71	.092
	4.44	2.41	.201
	2.21	5.02	.379
		7.23	.575
Dibenzyl ether	6.60	0.055	.011
	6.23	.33	.012
	5.68	.75	.018
	4.54	1.61	.052
	2.92	2.82	.108
		4.98	.325
Indan	6.40	0.25	.032
	5.26	0.74	.043
	2.91	4.32	.086
		7.64	.129
Cyclohexene	6.56	0.19	.032

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(13) (a) L. Bateman, *Trans. Faraday Soc.*, **42**, 266 (1946); L. Bateman and J. L. Bolland, *Proc. Intern. Congr. Pure and Appl. Chem. (London)*, **11**, 325 (1947); L. Bateman and G. Gee, *Proc. Royal Soc. (London)*, **195A**, 376, 391 (1948); (b) J. L. Bolland, *Trans. Faraday Soc.*, **46**, 358 (1950).

(14) L. Debiais, M. Niclause and M. Letort, *Compt. rend.*, **239**, 539, 1040 (1954); L. Debiais, P. Horstmann, M. Niclause and M. Letort, *ibid.*, **239**, 587 (1954).

(15) A. A. Miller, Abstracts of Papers, 124th Meeting of the American Chemical Society, Chicago, Ill., Sept., 1953, p. 35-O.

stances that are oxidized more easily than cumene and which involve secondary peroxy radicals in their oxidation, retard the oxidation of cumene. α-Methylstyrene which also is oxidized more readily than cumene but which yields a tertiary peroxy radical does not retard the rate of oxidation when added to cumene. These results suggest that the low rate observed for the oxidation of certain mixtures of cumene and tetralin occurs because of the formation of relatively high concentrations of secondary peroxy radicals in a solution that is mainly cumene.

Discussion

It is clear that the oxidation of methyl dehydroabietate gives preponderantly the 9-hydroperoxide in preference to the 14-hydroperoxide because of an intrinsic difference in the reactivities of the two types of hydrogen atoms toward peroxy radicals, since at 90° an α-hydrogen atom of tetralin is 4–6 times as reactive as an α-hydrogen atom of cumene toward a peroxy radical. Furthermore, a peroxy radical appears to be more selective (*i.e.*, less reactive) than a trichloromethyl radical because at 91.5° a trichloromethyl radical attacks a hydrogen atom of tetralin and cumene with equal ease.[4] It is not surprising that a peroxy radical is more selective than a trichloromethyl radical since the bond dissociation energy of the carbon–hydrogen of chloroform is $\geq$89.5 kcal. mole^{-1} [16] whereas the oxygen–hydrogen bond strength of a hydroperoxide has been estimated to be only 80 kcal. mole^{-1}.[17]

The observation that a peroxy radical abstracts a hydrogen atom to give a secondary benzyl-type radical (tetralyl) in preference to a tertiary benzyl-type radical (cumyl) is puzzling. It usually is observed that secondary aliphatic hydrogen atoms are less reactive than tertiary hydrogen atoms toward free radicals, the relative reactivity varying with the activity of the attacking radical. Thus in photochemical chlorination it has been shown that a tertiary hydrogen atom is about 1.5 times as reactive as a secondary hydrogen atom at 25°[18] while in the photobromination reaction a tertiary hydrogen atom is far more reactive (at least 20 times) than a secondary hydrogen atom.[19] This difference in the reactivity of secondary and tertiary hydrogen atoms usually is associated with differences in the bond dissociation energies of the carbon–hydrogen bonds involved[20]; a secondary carbon–hydrogen bond is on the average about 3–4 kcal. mole^{-1} weaker than a tertiary carbon–hydrogen bond.[21]

The unusually high reactivity noted for the secondary hydrogen atoms of tetralin toward peroxy radicals probably is connected with the fact that the α-hydrogen atoms of tetralin are attached to carbon atoms contained in a six-membered ring possessing unsaturation. Thus cyclohexene is peroxidized much more readily than 1-octene because the attack of a cyclohexenylperoxy radical on cyclohexene involves an activation energy 2.8 kcal. mole^{-1} less than that observed in the attack of an octenylperoxy radical on 1-octene.[14c] A similar increased reactivity of hydrogen atoms attached to an unsaturated six-membered ring has been noted by Kooyman,[4,22] who found that hydrogen atom abstraction by the trichloromethyl radical occurs much more readily for cyclohexene, tetralin and 9,10-dihydroanthracene than for 3-heptene, ethylbenzene and diphenylmethane, respectively. Thus, the possibility exists that the high reactivity observed in peroxidation for the α-hydrogen atoms of tetralin relative to the α-hydrogen atoms of cumene may be explained by a difference in the bond dissociation energy of the two types of hydrogen atoms.

In support of this view are the energies of activation reported for the oxidation of cumene and tetralin which indicate that the higher reactivity observed for tetralin results from a difference in the energy of activation for the two propagation reactions. Tetralylperoxy radicals are reported to attack tetralin with an energy of activation of 4.5 kcal. mole^{-1},[12] whereas the attack of a cumylperoxy radical on cumene involves an energy of activation slightly less than 6.7 kcal. mole^{-1}.[11] If these values are correct it appears that the bond strength of an α-carbon–hydrogen bond of tetralin must be at least 2.2 kcal. mole^{-1} less than the tertiary carbon–hydrogen bond strength of cumene.

It has been demonstrated for homolytic reactions similar to the propagation step in the oxidation reaction that differences in the energies of activation are related to differences in the strengths of the bonds being broken by the relationship $\Delta E_{\text{act}} = \alpha \Delta H$ where α is a number between 0 and 1.[21a,23] This relationship has been assumed to hold for the propagation step in the oxidation reaction and a value of α of 0.39 has been obtained from several sources.[14b] Using this value of α the benzyl-type carbon–hydrogen bond of tetralin is calculated to be 5.6 kcal. mole^{-1} weaker than the tertiary carbon–hydrogen bond of cumene.

It is difficult to compare the rates of oxidation of mixtures of hydrocarbons if the rates of initiation are unknown or not maintained at a constant value. Thus the rates of oxidation of mixtures of cumene and tetralin were measured at a constant catalyst concentration of 0.02 M *t*-butyl perbenzoate. However, a constant catalyst concentration is not assurance of a constant rate of initiation since the rate constant for the decomposition of peroxide catalysts and the efficiency of radicals produced by the catalyst in initiating oxidation chains are not necessarily independent of the solvent.[24] It is known that in the absence of oxygen that *t*-butyl perbenzoate can undergo an induced radical decomposition and that its rate of decomposition is not completely independent of the solvent or concentration.[25] However, measurements of the rate of decomposition of

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(16) J. H. Sullivan and N. Davidson, *J. Chem. Phys.*, **19**, 143 (1951).

(17) W. E. Vaughan, *Disc. Faraday Soc.*, **10**, 314 (1951).

(18) H. B. Hass, E. T. McBee and P. Weber, *Ind. Eng. Chem.*, **27**, 1190 (1935); **28**, 333 (1936).

(19) G. A. Russell and H. C. Brown, THIS JOURNAL, **77**, 4025 (1955).

(20) H. Steiner and R. H. Watson, *Disc. Faraday Soc.*, **2**, 88 (1947); G. A. Russell and H. C. Brown, THIS JOURNAL, **77**, 4031 (1955).

(21) (a) E. T. Butler and M. Polanyi, *Trans. Faraday Soc.*, **39**, 19 (1943); (b) J. S. Roberts and H. A. Skinner, *ibid.*, **45**, 339 (1949).

(22) E. C. Kooyman and A. Strang, *Rec. trav. chim.*, **72**, 329 (1953).

(23) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **34**, 11 (1938); M. G. Evans, *Disc. Faraday Soc.*, **2**, 271 (1947).

(24) L. Bateman and A. L. Morris, *Trans. Faraday Soc.*, **48**, 1149 (1952).

(25) A. T. Blomquist and A. F. Ferris, THIS JOURNAL, **73**, 3408 (1951).

t-butyl perbenzoate in cumene and tetralin solutions in the absence of oxygen showed that for periods up to 10 hours the rate of decomposition was the same in both solvents. Furthermore, it is not certain that a chain reaction leading to the decomposition of an acyl peroxide can occur in the presence of oxygen.[5b]

Variations in the efficiency of initiation are more difficult to detect. Since the rate of oxidation involves the efficiency to the one-half power (equation 2) a small change in the efficiency of initiation has a relatively minor effect on the rate of oxidation. Although a constant rate of initiation and in particular a constant efficiency has not been proven for *t*-butyl perbenzoate in cumene–tetralin solutions, it does not seem at all possible that a variation in the rate of initiation could account for the minimum in the rate of oxidation observed as tetralin is added to cumene.

The decrease in the rate of oxidation that occurs when small amounts of tetralin, indan, dibenzyl ether, styrene or cyclohexene are added to cumene is evidently a phenomenon connected with some difference between tertiary and secondary peroxy radicals. In the case of tetralin, and presumably for the other hydrocarbons also, a relatively high concentration of secondary peroxy is formed in a solution containing mostly cumene. In view of this, several possible explanations of the effect of the addition of these hydrocarbons to cumene are available.

In general, the decrease in the rate of oxidation may be explained as either a decrease in the rate of propagation or an increase in the rate of termination. Two secondary peroxy radicals or a secondary peroxy radical and a tertiary peroxy radical may terminate much more readily than two tertiary peroxy radicals. If this is the case the addition of small amounts of tetralin and similar hydrocarbons to cumene may cause a decrease in the rate of oxidation by lowering the steady-state concentration of peroxy radicals. Alternately, secondary peroxy radicals may be much less reactive toward cumene than a cumylperoxy radical. In this event the addition of a small amount of a hydrocarbon containing reactive secondary hydrogen atoms will create a high steady-state concentration of peroxy radicals and the rate of oxidation will be retarded because the increase in the concentration of peroxy radicals increases the rate of termination.

The latter type of retardation will occur in the cumene–tetralin system when $k_3 \gg k_2$. This possibility can be excluded by the absolute rate constants reported for the oxidation of cumene and tetralin and the values of the ratios k_1/k_2 and k_3/k_4. Bamford and Dewar[12] report a value of 51 mole^{-1} l. sec.$^{-1}$ for k_1 (cor. to 90°), whereas Melville and Richards[11] report a value of 1.3 mole^{-1} l. sec.$^{-1}$ for k_3 (cor. to 90°). Since k_1/k_2 was found to be equal to 16, k_2 and k_3 are nearly equal. In fact these figures indicate that a tetralylperoxy radical attacks cumene somewhat more readily than a cumylperoxy radical attacks cumene.

The termination rate constants reported for the oxidation of cumene and tetralin indicate that at least a considerable portion of the decrease in the rate of oxidation observed when tetralin is added to cumene stems from the fact that tetralylperoxy radicals terminate about 500 times as readily as cumylperoxy radicals; tetralylperoxy radicals have a termination rate constant of 2.4×10^7 mole^{-1} l. sec.$^{-1}$ (cor. to 90°)[12] while cumylperoxy radicals have a termination rate constant of 4.2×10^4 mole^{-1} l. sec.$^{-1}$ (cor. to 90°).[11] Termination rate constants in the range of 10^6 mole^{-1} l. sec.$^{-1}$ have been reported for numerous other secondary peroxy radicals including cyclohexenylperoxy radicals.[26]

The value of the termination rate constant for the reaction between a tetralylperoxy radical and a cumylperoxy radical can be calculated from the available data. Under the conditions employed the only termination reactions of importance in the oxidation of mixtures of cumene and tetralin are[5,27]

$$\left.\begin{array}{r} 2\mathrm{R_tO_2}\cdot \xrightarrow{k_5} \\ 2\mathrm{R_cO_2}\cdot \xrightarrow{k_6} \\ \mathrm{R_cO_2}\cdot + \mathrm{R_tO_2}\cdot \xrightarrow{2k_7} \end{array}\right\} \text{non-radical products}$$

Since the rate of initiation (R_i) is equal to the rate of termination (R_t), the following equations apply under steady-state conditions.

$$R_i = R_t = k_5[\mathrm{R_tO_2}\cdot]^2 + k_6[\mathrm{R_cO_2}\cdot]^2 + 2k_7[\mathrm{R_tO_2}\cdot][\mathrm{R_cO_2}\cdot] \tag{3}$$

$$k_2[\mathrm{R_tO_2}\cdot][\mathrm{R_cH}] = k_4[\mathrm{R_cO_2}\cdot][\mathrm{R_tH}] \tag{4}$$

By solving (3) and (4) simultaneously and substituting into the expression for the rate of hydrocarbon disappearance (5)

$$-\mathrm{d}([\mathrm{R_tH} + \mathrm{R_cH}])/\mathrm{d}t = k_1[\mathrm{R_tO_2}\cdot][\mathrm{R_tH}] + k_2[\mathrm{R_tO_2}\cdot][\mathrm{R_cH}] + k_3[\mathrm{R_cO_2}\cdot][\mathrm{R_cH}] + k_4[\mathrm{R_cO_2}\cdot][\mathrm{R_tH}] \tag{5}$$

it is possible to obtain the expression

$$\frac{-\mathrm{d}([\mathrm{R_tH}] + [\mathrm{R_cH}])}{\mathrm{d}t} = \frac{\{[\mathrm{R_tH}]^2 k_1/k_2 + 2[\mathrm{R_tH}]\,[\mathrm{R_cH}] + [\mathrm{R_cH}]^2 k_3/k_4\}\mathrm{R_i}^{1/2}/\delta_t}{\{[\mathrm{R_tH}]^2(k_1/k_2)^2 + 2\phi[\mathrm{R_tH}][\mathrm{R_cH}]k_1k_3\delta_c/\delta_t k_2 k_4 + ([\mathrm{R_cH}]k_3\delta_c/\delta_t k_4)^2\}^{1/2}}$$

where $\phi = k_7/(k_5k_6)^{1/2}$, $\delta_t = k_5^{1/2}/k_1$ and $\delta_c = k_6^{1/2}/k_3$. Using the value of $R_i^{1/2}/\delta_t$ calculated from the rate of oxidation of tetralin, the value of δ_c/δ_t calculated from the relative rates of oxidation of tetralin and cumene, and the values of k_1/k_2 and k_3/k_4 obtained by equation 1, the above expression can be solved for ϕ from a knowledge of the hydrocarbon concentrations and the rates of oxidation. Treatment of the data of Table II in this manner gives ϕ values of 8.3, 6.5, 6.2 and 5.3 for the oxidations of solutions containing 32, 68, 91.5 and 97 mole % of cumene, respectively. Since at low cumene concentrations a small error in the rate of oxidation produces a considerable error in ϕ, a weighted average of 6 was taken as the value of ϕ. Using this value of ϕ, k_7 is calculated to be 6×10^6 mole^{-1} l. sec.$^{-1}$ at 90°. Thus, a cumylperoxy radi-

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[26] L. Bateman and G. Gee, *Trans. Faraday Soc.*, **47**, 155 (1951); L. Bateman, J. L. Bolland and G. Gee, *ibid.*, **47**, 274 (1951); L. Bateman, G. Gee, A. L. Morris and W. F. Watson, *Disc. Faraday Soc.*, **10**, 250 (1951).

[27] The rate constant for the interaction of a cumylperoxy radical and a tetralylperoxy radical has been written $2k_7$ to make k_5, k_6 and k_7 comparable. At equal concentrations of two species a and b, collisions between a and b are twice as likely to occur as collisions between a and a or b and b.

cal and a tetralylperoxy radical terminate about 150 times as readily as two cumylperoxy radicals and one-fourth as readily as two tetralylperoxy radicals. Because of this the cross-termination reaction must play a significant part in lowering the rate of oxidation when tetralin is added to cumene, particularly in view of the statistical factor of 2 favoring the cross-termination reaction.[27]

From equations 4 and 5 it is possible to calculate the concentration of peroxy radicals and hence the rate of termination in a given mixture of cumene and tetralin if the rate of oxidation and the values of $k_1 - k_7$ are known. Data obtained in this way using values of 51, 3.2, 1.3 and 30 moles^{-1} l. sec.$^{-1}$ for k_1, k_2, k_3 and k_4, respectively, are presented in Fig. 1 where the percentage of termination occurring by each of the three possible termination reactions is expressed as a function of the hydrocarbon concentration.

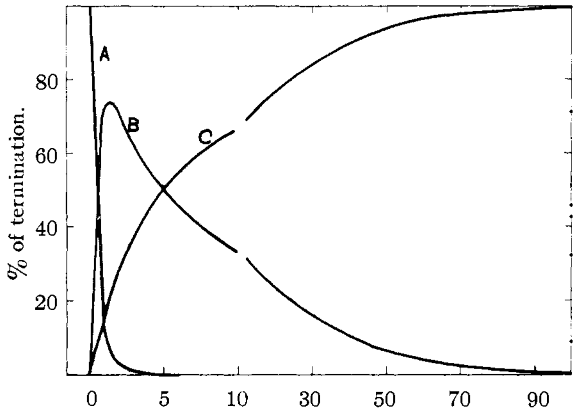


Fig. 1.—Relative importance of the termination reactions in the oxidation of mixtures of cumene and tetralin at 90°: curve A, $2R_cO_2\cdot \rightarrow$; curve B, $R_cO_2\cdot + R_tO_2\cdot \rightarrow$; curve C, $2R_tO_2\cdot \rightarrow$.

The total steady-state concentration of peroxy radicals in cumene–tetralin mixtures in the presence of 0.02 *M* *t*-butyl perbenzoate at 90° is shown as a function of the concentration in Fig. 2. The sharp decrease in the total radical concentration that occurs when tetralin is added to cumene parallels the diminished rate of oxidation observed. As the concentration of tetralin is increased the rate of oxidation rises after passing through a minimum even though the steady-state concentration of peroxy radicals slowly diminishes. Here the increase in the concentration of the more reactive tetralin offsets the small decrease in the peroxy radical concentration. Presumably the same situation is duplicated when indan, dibenzyl ether, styrene or cyclohexene is added to cumene. α-Methylstyrene, which produces a tertiary peroxy radical, does not retard the oxidation of cumene undoubtedly because the tertiary peroxy radical derived from α-methylstyrene has a termination rate constant very nearly equal to that of a cumylperoxy radical and no decrease in radical concentration occurs when α-methylstyrene is added to cumene.

The ratio of δ_c/δ_t at 90° as calculated from the absolute rate constants of Bamford and Dewar[12] and Melville and Richards[11] is 1.7 whereas the value calculated from the rates of oxidation of cumene and tetralin in the presence of 0.02 *M* *t*-butyl perbenzoate is 3.1. The discrepancy between these values may indicate that the efficiency of initiation by radicals from *t*-butyl perbenzoate is considerably greater in the more reactive tetralin. Alternately, errors in the reported absolute rate constants or the energies of activations used to correct them to 90° may be involved.

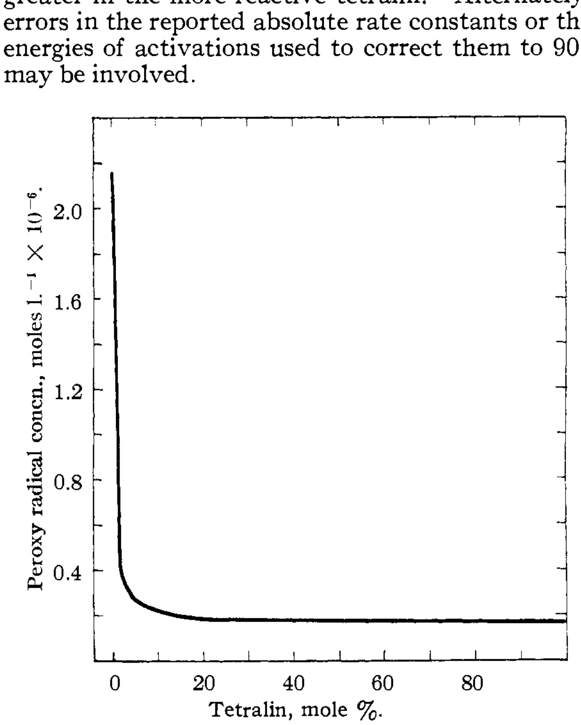
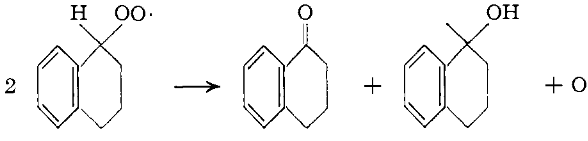
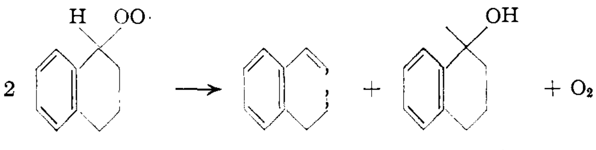


Fig. 2.—Total peroxy radical concentration in the oxidation of cumene–tetralin mixtures at 90° in the presence of 0.02 *M* *t*-butyl perbenzoate.

The 500-fold variation in the values of the termination rate constants for cumylperoxy and tetralylperoxy radicals may occur because secondary peroxy radicals can undergo a termination reaction[28] that is not possible for tertiary peroxy radicals.



Furthermore, if termination occurs by the mechanism[12]



the possibility exists that a hydrogen atom is transferred more readily from a tetralylperoxy radical than from a cumylperoxy radical.

The termination reaction of secondary peroxy radicals involving the formation of alcohols and ketones is preferred to the termination reaction leading to the formation of alcohols and unsatu-

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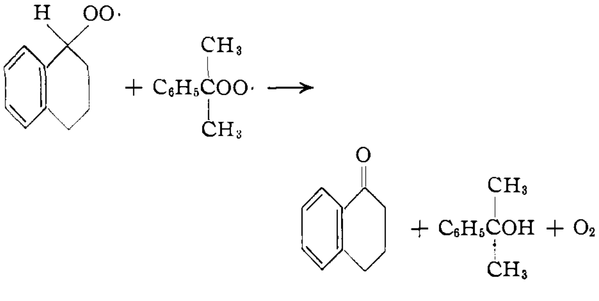
[28] A. E. Woodward and R. B. Mesrobian, This Journal, **75**, 6189 (1953).

rated materials. Thus, dibenzyl ether has an effect on the oxidation of cumene similar to that produced by tetralin or indan. However, the peroxy radicals derived from dibenzyl ether do not contain an adjacent methylene group and can terminate by disproportionation in only one manner. Moreover, small amounts of fluorene and diphenylmethane, compounds containing only one methylene group, also have been observed to cause a considerable decrease in the rate of oxidation of cumene.

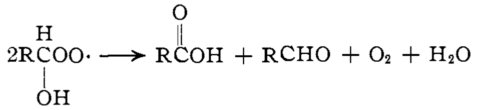
Similar arguments can be used to explain the variation between the rate constants for the cross-termination of a cumylperoxy with a tetralylperoxy radical and the termination of two cumylperoxy radicals. In particular, the reaction



readily explains why the cross-termination reaction occurs nearly 150 times as readily as the reaction between two cumylperoxy radicals.

It seems reasonable that some other systems, besides those of cumene and reactive hydrocarbons that produce a secondary peroxy radical, should display a concentration–rate relationship similar to that observed for the oxidation of mixtures of cumene and tetralin. The addition of quite a variety of olefins and hydrocarbons, that are not usually considered to be oxidation inhibitors, causes a drastic reduction in the rate of oxidation of benzaldehyde. For example, styrene, a substance quite easily oxidized itself,[14] retards the oxidation of benzaldehyde at 25°,[29] while small amounts of benzaldehyde do not appreciably affect the rate of the catalyzed copolymerization of styrene and oxygen at 50°.[30] The effect of $\Delta^{9,9'}$-bifluorene on the rate of oxidation of benzaldehyde is very similar to the effect of tetralin on the oxidation of cumene; small amounts of $\Delta^{9,9'}$-bifluorene retard the rate of oxidation when added to benzaldehyde and a minimum in the rate is observed at an olefin concentration 0.01 M.[31] However, the termination rate constant reported for perbenzoate radicals is unusually high, 2.1×10^8 mole^{-1} l. sec.$^{-1}$ at 5°,[32] and if this value is correct it seems unlikely that the retardation noted when styrene or $\Delta^{9,9'}$-bifluorene is added to benzaldehyde can result from an increase in the rate of termination. The alternate explanation must be that these hydrocarbons lead to the formation of peroxy radicals which propagate much slower than perbenzoate radicals, an effect similar to that observed in the copolymerization of styrene with vinyl acetate or methyl methacrylate.[33]

Primary and secondary alcohols retard the oxidation of many hydrocarbons, olefins and aldehydes.[34] Here it has been suggested that the peroxy radicals formed from the alcohol do not propagate as readily as the peroxy radicals derived from the hydrocarbon.[34b] Alcohols also may influence the rate of oxidation of hydrocarbons by increasing the rate of termination since for the peroxy radical derived from a primary alcohol the following attractive termination reaction can be written.



$$2R\underset{\substack{|\\ OH}}{\overset{H}{C}}OO\cdot \longrightarrow R\overset{\overset{O}{\|}}{C}OH + RCHO + O_2 + H_2O$$

Experimental

Materials.—Technical grade tetralin was shaken with sulfuric acid, washed, dried, and rectified in a Podbielniak column (>50 plates) under nitrogen. Phillips 99 mole % minimum cumene was fractionated in a similar manner. Center fractions whose boiling point and refractive index were constant and which checked the best literature values[35] were passed through a column packed with 60–200 mesh activated silica gel. The densities of cumene, tetralin and their mixtures were determined at 90° and found to follow the equation

$$d_4^{90} = 0.913 - 0.00110X$$

where X is the percentage by weight of cumene in the mixture.

α-Tetralol and 2-phenyl-2-propanol were prepared by the reduction of the corresponding hydroperoxides with lithium aluminum hydride.[9] The samples used for infrared standards were distilled, b.p. 67–68° (0.8 mm.) and 93–95° (13 mm.), respectively. Lucidol brand t-butyl perbenzoate was distilled, b.p. 70–72° at 0.3–0.4 mm., n^{20}_{D} 1.5004.

Oxidation Procedure.—The catalyst was added to the oxidation flask as a 0.1 M solution in benzene. The benzene was removed by evacuating at 20 mm. and the hydrocarbon weighed in the flask. The oxidation flask, which consisted of a heavy-walled erlenmeyer flask attached to a 30-cm. length of 16 mm. tubing, was connected to a gas manometer and evacuated and filled with oxygen a number of times. The flask then was attached to a reciprocating rack contained in a thermostated oil-bath and the rate of oxygen absorption measured by manual control of the mercury level in the gas manometer.

Analytical Procedures.—The products of the competitive oxidations were analyzed for total hydroperoxide by the method of Kokatnur and Jelling[36] or for total peroxide by the method of Blomquist and Ferris.[25]

The ratios of cumyl and tetralyl hydroperoxides in the oxidation products were determined by removing most of the cumene and tetralin by distillation at 1 mm. with a pot temperature below 60°. The hydroperoxide concentrates then were reduced in ethyl ether by a 100 mole % excess of lithium aluminum hydride[9] and the alcohols liberated from the reduction products by treatment with methanol and a saturated solution of ammonium chloride. The hydrolyzed mixtures were evaporated to room temperature and pressures not below 5 mm. to a solid residue which was extracted with four 100-ml. portions of ethyl ether. The ethereal extracts were dried over anhydrous sodium sulfate,

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[29] E. Raymond, *J. chim. phys.*, **28**, 480 (1931).

[30] Dr. A. A. Miller, private communication.

[31] G. Wittig and W. Lange, *Ann.*, **536**, 266 (1938); G. Wittig and G. Pieper, *ibid.*, **546**, 142, 172 (1941); **558**, 207, 218 (1947); G. Wittig, *ibid.*, **558**, 201 (1947).

[32] T. A. Ingles and H. W. Melville, *Proc. Royal Soc.* (*London*), **218A**, 175 (1953).

[33] C. Walling, THIS JOURNAL, **71**, 1930 (1949).

[34] (a) C. F. Frye, C. B. Kretschmer and R. Wiebe, *Ind. Eng. Chem.*, **46**, 1517 (1954); (b) J. L. Bolland and H. R. Cooper, *Proc. Royal Soc.* (*London*), **225A**, 405 (1954).

[35] U. S. National Bureau of Standards Circular 461, "Selected Values of Properties of Hydrocarbons," Washington, D. C., 1947; G. Egloff, "Physical Constants of Hydrocarbons," Vol. IV, Reinhold Publ. Corp., New York, N. Y., 1947.

[36] V. R. Kokatnur and M. Jelling, THIS JOURNAL, **63**, 1432 (1942).

evaporated to constant weight at 5 mm. and diluted with about 5 ml. of cumene. Infrared spectra were obtained for the standards and the unknowns in a single cell especially reserved for this purpose.

A prepared mixture of 0.1206 g. of α-tetralol, 0.0896 g. of 2-phenyl-2-propanol and 0.134 g. of tetralin in 2 ml. of cumene was analyzed by the absorption at 8.52 and 10.00 μ. The analysis indicated the presence of the alcohols in a weight ratio of 1.35 to 1 whereas the solution was prepared to contain the alcohols in the ratio of 1.40 to 1.

The rate of decomposition of *t*-butyl perbenzoate in cumene and tetralin solutions was determined by sealing evacuated samples of a standard solution of *t*-butyl perbenzoate in ampoules. At appropriate times ampoules were removed from an oil-bath, opened and analyzed for peroxide content.[25] The following data were obtained for solutions of *t*-butyl perbenzoate originally 0.02 *M*.

TABLE IV

DECOMPOSITION OF *t*-BUTYL PERBENZOATE IN CUMENE AND TETRALIN SOLUTIONS AT 90°

Time, hr.	% of peroxide decomposed Cumene	Tetralin
6	7.0	7.0
12	13.1	13.2
18	17.3	18.5
24	24.0	25.1
30	29.2	31.0
36	34.0	36.9
42	38.1	42.2
48	41.5	47.0

SCHENECTADY, NEW YORK

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF WAYNE UNIVERSITY]

Reactions of α-Halotetralone and Certain Alkyl Derivatives with Base[1]

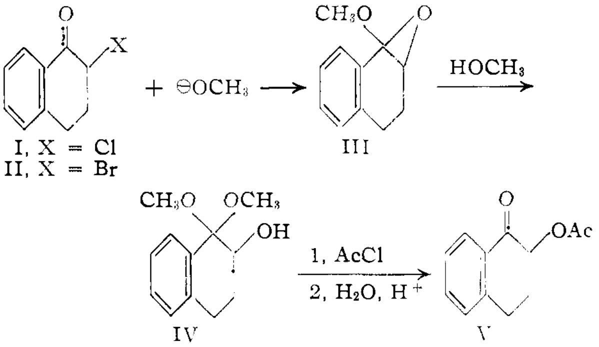
BY CALVIN L. STEVENS, JOHN J. BEEREBOOM, JR., AND KENNETH G. RUTHERFORD[2]

RECEIVED MARCH 9, 1955

α-Bromotetralone (II), when allowed to react with alcoholic sodium methoxide, gave the α-hydroxy ketal IV in 80% yield. The intermediate epoxyether III could not be isolated. The corresponding α-chloroketone gave the α-hydroxy ketal in 33% yield. α,α-Dichlorotetralone (VI), α-chloro-α-methyltetralone (XII) and α-chloro-α-ethyltetralone (XIII), when treated with alcoholic sodium methoxide, were dehydrohalogenated to the corresponding naphthols.

The investigation of the reactions of α-halotetralones with base was undertaken because α-chlorotetralone (I) was one of the few α-haloketones which had been reported to undergo a carbon skeleton rearrangement in the presence of alcoholic sodium methoxide, but which could not form a cyclopropanone intermediate.[3,4] Previously, α-halocyclohexyl phenyl ketone, a haloketone which similarly cannot form a cyclopropane intermediate, had given a high yield of epoxyether when treated with alcoholic sodium methoxide.[5] In the present study, no evidence of carbon skeleton rearrangement could be found. In addition to reactions proceeding *via* epoxyethers, dehydrohalogenation of certain of the α-halotetralone derivatives gave naphthols.

α-Bromotetralone (II) was converted smoothly at room temperature by alcoholic sodium methoxide into the crystalline hydroxy ketal IV in 80% yield. The hydroxy ketal was acetylated with acetyl chloride and the ketal group preferentially hydrolyzed with dilute acid to give the keto acetate V. Although the formation of α-hydroxy ketals from α-haloketones is known to proceed *via* the epoxyethers,[6] the reactive intermediate III could not be isolated from the α-bromotetralone II. In this respect the haloketone II resembled α-chlorocyclohexanone, the epoxyether of which could not be isolated in this Laboratory.[7]



The chlorotetralone I was prepared in 97% yield by direct chlorination of tetralone in methylene chloride at 0°. Since the chlorotetralone II melted sharply at 44–45°, and since Mousseron[3] reported the melting point as 72°, the position of the halogen was determined by conversion of both the bromotetralone and the chlorotetralone to the same crystalline iodoketone, using sodium iodide in acetone solution. Straus[8] has shown that the bromine in II is in the position alpha to the ketone; therefore, the chlorine atom of I must be in the same position. Furthermore, both haloketones I and II gave the same keto acetate V when treated with sodium acetate. The formation of V *via* the hydroxy ketal provides additional support for structure I.

Although the chloroketone I reacted with alcoholic sodium methoxide more slowly than the bromoketone I, the only product isolated was the hy-

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[1] Abstracted in part from the M.S. thesis of J. J. Beereboom, Jr., Wayne University, 1952, and the Ph.D. thesis of K. G. Rutherford, Wayne University, 1955.

[2] Supported in part by a Grant-in-aid from the Research Corporation of New York.

(3) M. Mousseron and A. D. Grange, *Bull. soc. chim.*, [5] **10**, 428 (1943); M. Mousseron and Nguyen-Phuoc-Du, *Compt. rend.*, **218**, 281 (1944).

(4) *Cf.* also the discussion of R. B. Loftfield (THIS JOURNAL, **73**, 4707 (1951)), and of C. L. Stevens and E. Farkas (*ibid.*, **74**, 5352 (1952)).

(5) C. L. Stevens and E. Farkas, *ibid.*, **74**, 618 (1952).

(6) C. L. Stevens, W. Malik and R. Pratt, *ibid.*, **72**, 4758 (1950); C. L. Stevens, M. L. Weiner and R. C. Freeman, *ibid.*, **75**, 3977 (1953); C. L. Stevens and J. J. DeYoung, *ibid.*, **76**, 718 (1954); C. L. Stevens, E. Farkas and B. Gillis, *ibid.*, **76**, 2695 (1954).

(7) C. L. Stevens and J. Tazuma, *ibid.*, **76**, 715 (1954).

(8) F. Straus, O. Bernoully and P. Mautner, *Ann.*, **444**, 165 (1925); F. Straus and A. Rohrbacher, *Ber.*, **54B**, 40 (1921).