mated to be within 10% with better accuracy for the relative values. Mass spectra were obtained using a CEC 21-103 mass spectrometer with an ionizing voltage of 70 V.

Reagents.—Hydrogen bromide (from The Matheson Co., Inc., Research Grade) was used directly; the minimum purity was 99.8%. *n*-Pentane (Phillips Pure Grade) was used directly. 1-Hexene (Phillips Pure Grade) was used directly with no purification. Analysis by glpc showed that this material was 99.6% pure, the impurity being *cis*- and *trans*-2-hexene (0.38). Cyclopentene (Phillips Research Grade) was used directly and has a minimum purity of 99.95%. *cis,cis*-1,5-Cyclooctadiene (Phillips Pure Grade), cycloheptene (Columbia Organic Chemicals), and cyclooctene (Cities Services Research and Development Co.) were purified by shaking successively with 10% aqueous sodium hydroxide, ferrous sulfate solution, and water. The olefins were dried with 3A molecular sieve and distilled through an 8-in. Vigreux column. The boiling points and glpc purities of these olefins were 1,5-cyclooctadiene, 48–50° (15 mm), 99.0%; cyclohexene, 82.8–83.5°, 99.0%; cycloheptene, 114–116°, 93.5%, and cyclooctene, 44–45° (20 mm), 99.0%. The cycloheptene was further purified by preparative glpc on a Ucon P/firebrick column (9.5-mm o.d. × 6 m long) yielding material with a purity of 98.1%.

Addition of Hydrogen Bromide to 1,5-Cyclooctadiene.—The apparatus consisted of a 150-ml cylindrical glass reactor fitted with a gas inlet tube (coarse fritted glass tip) and a thermocouple well. Hydrogen bromide was introduced through a calibrated glass rotometer and Teflon tubing. Unreacted hydrogen bromide exited from the reactor through another glass rotometer. The contents of the reactor were stirred by a magnetically driven Teflon-covered stirring bar. The reactor was surrounded with a copper coil containing recirculating isopropyl alcohol coolant. The entire reactor was placed in the irradiation zone of a 7500-Ci Co^{60} facility. The dose rate was determined for the geometry of this experimental configuration using ferrous dosimetry.

In a typical experiment, 1,5-cyclooctadiene (13.2 g, 0.12 mol) and *n*-pentane (45 ml) were placed in the reactor and cooled to the desired temperature while purging with nitrogen. Hydrogen bromide was then introduced and the irradiation was started. At the completion of the experiment (1.5 hr) the contents of the reactor were purged with nitrogen. The product was washed with water, dried (3A molecular sieve), concentrated, and distilled, giving 15.1 g (67%) of 5-bromocyclooctene: bp 84–85° (10 mm); ir (neat) 1660 (C=C) and 720 cm^{-1} (*cis*-HC=CH–); nmr (neat) δ 5.65 (m, 2, $-CH{=}CH-$), 4.25 (m, 1, $-CHBr-$), 2.2 (m, 8, $-CH_2-CHBr-$ and $-CH_2-CH{=}CH-$), and 1.6 ppm (m, 2, $-CH_2-$).

Anal. Calcd for $C_8H_{13}Br$: C, 50.8; H, 6.9; Br, 42.3. Found: C, 50.9; H, 6.9; Br, 41.8.

Further distillation yielded 7.3 g (22%) of dibromocyclooctanes: bp 96–98 (1 mm); ir complex, no bands at 1660 and 720 cm^{-1}; nmr (neat) δ 4.4 (m, 2, $-CHBr-$), 2.2 (m, 8, $-CH_2-CHBr-$), and 1.7 ppm (m, 4, $-CH_2-$).

Anal. Calcd for $C_8H_{14}Br_2$: C, 35.6; H, 5.2; Br, 59.2. Found: C, 35.9; H, 5.3; Br, 59.3.

Competitive Addition of Hydrogen Bromide.—The apparatus and procedure were the same as described earlier with the exception that a limited quantity of hydrogen bromide reacted. The products from the competitive additions of hydrogen bromide to 1-hexene and cyclopentene, cyclohexene, cycloheptene, cyclooctene, and all four cyclic olefins together were analyzed by glpc on a Ucon 50 HB 2000/Chromosorb W column (6-mm o.d. × 3.0 m long) programmed from 40 to 150° (180° for samples with cyclooctene) at 6°/min with a helium flow rate of 75 cc/min. The products from the competitive addition of hydrogen bromide to 1-hexene and 1,5-cyclooctadiene were analyzed by glpc on a QF-1/firebrick column (6-mm o.d. × 1.5 m long) programmed from 40 to 180° at 6°/min with a helium flow rate of 75 cc/min. All glpc analyses were performed in duplicate or triplicate. *n*-Hexyl bromide, cyclopentyl bromide, and cyclohexyl bromide were identified by comparison of the ir spectra of glpc trapped samples with those of authentic materials (Eastman Organic Chemicals, Columbia Organic Chemicals, and Eastman Organic Chemicals, respectively). Cycloheptyl bromide was identified similarly by comparison with the authentic spectrum in the Sadtler Catalog of infrared spectra.[7] Cyclooctyl bromide was identified by mass spectrometry and exhibited the following ir spectrum (CCl_4, CS_2): 2850 s, 1470 s, 1445 s, 1345 w, 1320 vw, 1285 w, 1255 w, 1225 m, 1175 m, 1170 m, 1110 w, 1085 w, 1042 m, 955 w, 930 vw, 907 w, 852 w, 805 w, 785 w, 765 w, and 713 m cm^{-1}.

Registry No.—Hydrogen bromide, 10035-10-6; *cis,-cis*-1,5-cyclooctadiene, 111-78-4; I, 17223-82-4; 1,4-dibromocyclooctane, 17255-72-0; 1,5-dibromocyclooctane, 17255-73-1.

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[7] Sadtler Catalog, Sadtler Research Laboratories, Philadelphia, Pa., 1959.

Peroxide-Induced Reductions of 4-Methyl-4-trichloromethyl-2,5-cyclohexadienone with Secondary Alcohols[1]

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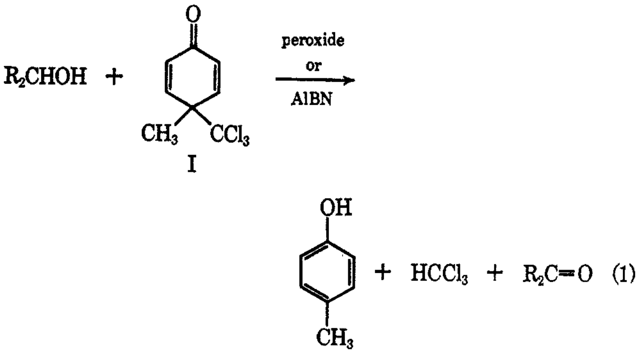
We have found that 4-methyl-4-trichloromethyl-2,5-cyclohexadienone (I) is reduced by secondary alcohols



(1)

to *p*-cresol and chloroform with concurrent oxidation of the alcohol in a free-radical chain reaction. Table I lists the products obtained from some *t*-butyl peroxide induced reactions of I with 2-butanol.

TABLE I

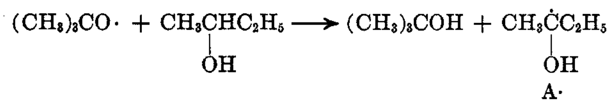
REACTIONS OF I WITH 2-BUTANOL AND *t*-BUTYL PEROXIDE[a]

Reactants, mmol				Products, mmol		
I	2-Butanol	*t*-Butyl peroxide	Recovered I	*p*-Cresol	2-Butanone	$HCCl_3$
2.37	6.80	1.16	0	2.11	2.87	1.46
2.32	67.4	.16	0.73	1.40	1.63	1.07
0.72	21.8	.076	0.32	0.34	0.43	0.29

[a] For 9 hr at 125°.

A mechanism that would account for these products and their distribution includes the chain sequence in

$$(CH_3)_3COOC(CH_3)_3 \longrightarrow 2(CH_3)_3CO\cdot \qquad (2)$$



$$(CH_3)_3CO\cdot + \underset{\displaystyle OH}{CH_3CHC_2H_5} \longrightarrow (CH_3)_3COH + \underset{\displaystyle \underset{\displaystyle A\cdot}{OH}}{CH_3\dot{C}C_2H_5} \qquad (3)$$

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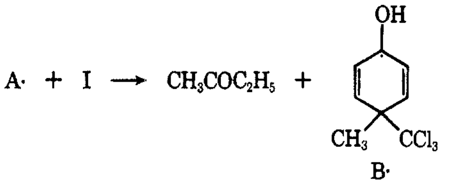
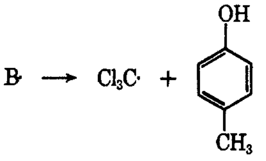
[1] This work was supported by a grant from the National Institutes of Health (AM-08517-02).

[2] Taken from the thesis submitted by K. L. J. in partial fulfillment of the requirements for the Ph.D. degree from the University of Kansas, 1968.



(4)



(5)

$$Cl_3C\cdot + CH_3CHOHC_2H_5 \longrightarrow HCCl_3 + A\cdot \quad (6)$$

$$2Cl_3C\cdot \longrightarrow C_2Cl_6 \quad (7)$$

eq 4–6. Reaction 4 is a hydrogen atom transfer reaction from the α-hydroxyalkyl radical A· to the carbonyl function of I yielding the intermediate radical B· and 2-butanone. This reaction is similar to reductions of carbonyl functions by α-hydroxyalkyl radicals reported previously.[3] Although β elimination of trichloromethyl radicals in radical fragmentation reactions generally do not occur at moderate temperatures,[4] the fragmentation reaction of B· yielding *p*-cresol and a trichloromethyl radical (eq 5) most likely finds its driving force in the energy derived from the formation of the aromatic ring. Hydrogen abstraction by the eliminated trichloromethyl radical yielding chloroform and the chain-carrying α-hydroxyalkyl radical has been reported to occur in the oxidation of alcohols by carbon tetrachloride.[5]

Equivalent amounts of *p*-cresol, 2-butanone, and chloroform should be formed if the chain sequence in eq 4–6 is the only source of these products. The somewhat larger than stoichiometric amounts of 2-butanone probably resulted from interaction of the α-hydroxyalkyl radical A· with peroxide, a reaction known to yield the ketone[6] along with *t*-butyl alcohol and a *t*-butoxy radical (eq 8). Formation of 2-butanone by the chain sequence in eq 2 and 8 could account for part of the ketone formed in excess of the *p*-cresol.[7] The fact that chloroform is found in quantities somewhat less than the *p*-cresol supports the suggestion that eq 7, the coupling of two trichloromethyl radicals, is the termination reaction. This course of reaction would produce *p*-cresol but eq 7 would be a route of reaction of some of the trichloromethyl radicals rather than the chain-propagating reaction (eq 4) which would yield chloroform.

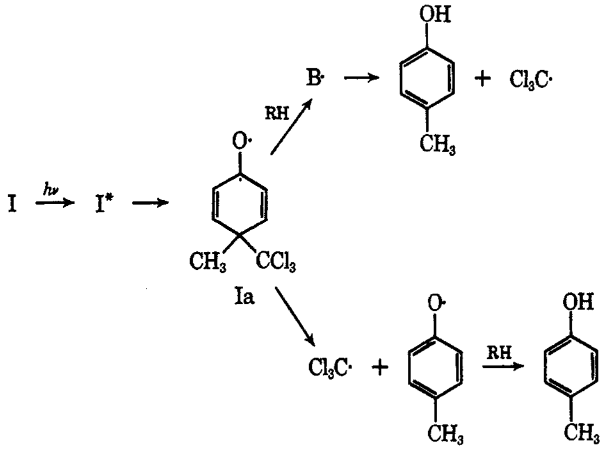
$$A\cdot + (CH_3)_3COOC(CH_3)_3 \longrightarrow CH_3COC_2H_5 + (CH_3)_3COH + (CH_3)_3CO\cdot \quad (8)$$

The accuracy of the analytical method for determining the amounts of these products (see Experimental Section) precludes much value in further speculation concerning the quantitative relationships. It is interesting to note, however, that, as the initial peroxide content is decreased, the kinetic chain length of the sequence in eq 4–6 appears to increase and the deviations from the predicted stoichiometry are smaller.

Reaction of I with 1-butanol and *t*-butyl peroxide at 125° also produced *p*-cresol as did reaction of 2-butanol and I induced with azobisisobutyrylnitrile at 80°. Heating I with *t*-butyl alcohol and *t*-butyl peroxide at 125°, however, did not result in formation of detectable amounts of *p*-cresol. In this case, a source of α-hydroxyalkyl radical necessary to transfer a hydrogen to I is not available.

Although photochemical reactions of I have been reported to yield a variety of products in different solvents,[8] Schüster and Patel found that *p*-cresol and chloroform are formed in photochemical reactions of I in ethyl ether, dioxane, cyclohexane, and 2-propanol.[8c] The suggestion was made that radical B·, which would fragment (eq 5) could result from abstraction of a hydrogen from the solvents by the triplet species Ia resulting from photoexcitation of I[8c] (Scheme I). The alternative path, namely fragmentation of the triplet species yielding the trichloromethyl radical and the *p*-methylphenoxy radical which could react with the solvent producing chloroform, was also suggested.[9] Although such routes seem probable for photochemical reactions in solvents that cannot yield a radical capable of hydrogen atom transfer to I, the *p*-cresol and chloroform formed in the photochemical reactions of I in 2-propanol could result, at least in part, by the chain sequence in eq 4–6 outlined for the peroxide-induced reactions.

SCHEME I



Experimental Section

Materials.—4-Methyl-4-trichloromethyl-2,5-cyclohexadienone, mp 103–104.2° (lit.[10] 103.8–104.2°), was prepared by the method previously described. All other reagents were commercial materials and redistilled before using.

***t*-Butyl Peroxide Induced Reactions of I with 2-Butanol.**—2-Butanol, *t*-butyl peroxide, and I, in the amounts shown in Table I, were weighed into Pyrex reaction tubes. The tubes were sealed and heated in a constant-temperature bath at 125° for 9 hr. Each of the reaction mixtures, which became brown to

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[3] E. S. Huyser and D. C. Neckers, *J. Amer. Chem. Soc.*, **85**, 3641 (1963).

[4] P. Skell and R. C. Woodworth, *ibid.*, **77**, 4638 (1955).

[5] G. A. Razuvaev, B. N. Moryganov, and A. G. Kronman, *J. Gen. Chem. USSR*, **26**, 2485 (1956).

[6] E. S. Huyser and C. J. Bredeweg, *J. Amer. Chem. Soc.*, **86**, 2401 (1964).

[7] Some 2-butanone may also be formed by the reactions of I that do not yield *p*-cresol as the product. The nature of these reactions, which account for about 10% of the amount of I that has reacted, were not investigated; their products appeared as dark, intractable tars.

[8] (a) E. E. van Tamelen, K. Kirk, and G. Brieger, *Tetrahedron Lett.*, 939 (1962); (b) J. King and D. Leaver, *ibid.*, 539 (1965); (c) D. I. Schüster and D. J. Patel, *J. Amer. Chem. Soc.*, **88**, 1825 (1966); (d) D. I. Schüster and D. J. Patel, *ibid.*, **89**, 184 (1967).

[9] D. I. Schüster and D. J. Patel, *ibid.*, **87**, 2515 (1965).

[10] M. S. Newman and A. G. Pinkus, *J. Org. Chem.*, **19**, 3978 (1954).

black in color, was divided into two parts for gas chromatographic analysis. The lower boiling compounds (2-butanone and chloroform) were determined on an F & M Model 5750 gas chromatograph equipped with a Mosley recorder and disk integrator using a 15 ft by 0.25 in. column packed with 17% E-600 on Chromosorb W. Ethyl acetate was used as the internal standard for these analyses. The higher boiling components of the reaction mixture (unreacted I and *p*-cresol) were determined on the same chromatograph using a 5 ft by 0.125 in. column packed with 10% W-98 on Chromosorb W. Diphenyl ether was used as an internal standard for these analyses. The results for three different runs are given in Table I.

The presence of 2-butanone and *p*-cresol as reaction products was demonstrated by isolation of these materials from another reaction mixture. 2-Butanone was distilled from the reaction mixture at 80°: 2,4-dinitrophenylhydrazone mp 114–115.5° (lit.[11] mp 117°); semicarbazone mp 143–144° (lit.[11] mp 146°). After removal of the lower boiling components, *p*-cresol was extracted from the reaction mixture with a 20% sodium hydroxide solution. The 2,6-dibromo-*p*-cresol prepared from the extracted material melted at 47.5–48° (lit.[11] mp 49°). The aryloxyacetic acid derivative melted at 136.5–137° (lit.[11] mp 136°).

Other Reactions of I.—Sealed tubes containing I, 1-butanol, and *t*-butyl peroxide in one case and I, *t*-butyl alcohol, and *t*-butyl peroxide in another (initial ratios of components 7:1:0.01) were heated for 24 hr at 125°. The 1-butanol reaction mixture turned dark during this period and gas chromatographic analysis showed the presence of *p*-cresol as a reaction product. No detectable amounts of *p*-cresol were found in the tube containing *t*-butyl alcohol nor did the contents of the tube become highly colored during the heating period but assumed only a pale yellow color.

In another reaction a mixture of I, 2-butanol, and azobisisobutyrylnitrile was heated at 80° for several hours. Gas chromatographic analysis indicated formation of *p*-cresol, chloroform, and 2-butanone.

Registry No.—I, 3274-12-2; 2-butanol, 78-92-2; *t*-butyl peroxide, 110-05-4.

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[11] R. L. Shriner, R. C. Fuson, and D. Y. Curtin," The Systematic Identification of Organic Compounds," 4th ed, John Wiley and Sons, Inc., New York, N. Y., 1956.

Decomposition Reactions of 1-Phenyl-1-cyclohexyl Peracetate

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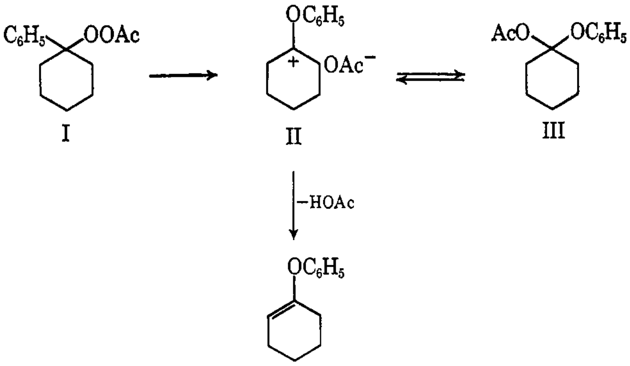
In a study of the decomposition of 1-phenyl-1-cyclohexyl peracetate (I) in several solvents, we have observed that the products obtained depend strikingly on the solvent employed.

Table I summarizes the major decomposition products determined by gas chromatographic analysis. In absolute ethanol, the major products formed were phenol and cyclohexanone. The same result was found in *n*-butyl alcohol. These products are the result of an ionic Criegee type of rearrangement,[2a] involving migration of the phenyl group to electron-deficient oxygen.[2b] Ring opening has been observed[2b] in the reaction of 1-phenylcyclohexyl hydroperoxide with acetic acid–CrO_3, and other cases are known where alkyl migration to electron-deficient oxygen is more highly favored than phenyl migration.[3] It has been shown that the decomposition of 1-methyl-1-cyclohexyl peracetate in ethanol and acetic acid gave 6-ketoheptanol and 6-ketoheptyl acetate, respectively.[4] These reactions presumably involve migration of a ring carbon atom to electron-deficient oxygen.

In the decomposition of I in glacial acetic acid, 1-phenoxycyclohexene was found to be a major product, along with phenol and cyclohexanone (Table I). The isolated 1-phenoxycyclohexene was characterized by its infrared and nuclear magnetic resonance spectra and elemental analysis.

The nature of the products formed in ethanol and acetic acid rule out a homolytic reaction path. Homolytic cleavage of the peroxide linkage would generate 1-phenylcyclohexyloxy radicals, and the expected products would be those derived from ring opening, *e.g.*, caprophenone[5] and possibly also 1-phenylcyclohexanol. The major products actually found (Table I) can be interpreted as having been formed from an intermediate phenoxycarbonium ion[6] (II). Although 1-phenoxycyclohexene was a major decomposition product in acetic acid,[7] it was not detected in ethanol. This product may be formed in acetic acid directly from the cation II, or from an acylal (III).



In ethanol, apparently II is trapped and converted into ketal; however further work is needed to establish this pathway.

Decomposition of I in heptane and in pyridine produced a mixture of mainly 1-phenoxycyclohexene and caprophenone, with virtually no phenol or cyclohexanone (Table I). Therefore, it appears that in these solvents the decomposition takes both an ionic path and a radical path. The ionic pathway did not lead to phenol or cyclohexanone, and this suggests that in the absence of a nucleophilic solvent such as ethanol the phenoxycyclohexene is formed directly from the intermediate phenoxycarbonium ion (or the phenoxy acylal III).

The peracetate I is an example of a system which decomposes by an ionic or radical pathway depending on the solvent. A similar example is the decomposition of

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[1] Address all correspondence to the author at Richmond College, Staten Island, N. Y. 10301.

[2] (a) R. Criegee, *Ann.*, **560**, 127 (1948); (b) H. Kwart and R. T. Keen, *J. Amer. Chem. Soc.*, **81**, 943 (1959).

[3] S. L. Friess and N. Farnham, *ibid.*, **72**, 5518 (1950).

[4] H. Francois, G. Bex, and R. Lalande, *Bull. Soc. Chim. Fr.*, 3702 (1965).

[5] D. H. Hey, C. J. M. Stirling, and G. H. Williams, *J. Chem. Soc.*, 1054 (1957).

[6] E. Hedaya and S. Winstein, *J. Amer. Chem. Soc.*, **89**, 1661 (1967); see also references cited in this paper.

[7] Cumyl perbenzoate rearranges to $PhOCMe_2OCOPh$ in *n*-octane–$PhNO_2$ which decomposes to $PhOCMe{=}CH_2$ and PhCOOH. See N. V. Yablokova, V. A. Yablokova, and O. F. Rachkova, *Reaktsionnaya Sposobnost Organ. Soedin., Tartusk. Gos. Univ.*, **3** (2), 223 (1966); *Chem. Abstr.*, **67**, 2670*a* (1967).