

was refluxed, under nitrogen, for 11 hours. The solution was brought to pH 8 by the addition of dilute hydrochloric acid; after standing for one hour 1.72 g. (92%) of crude *o*-hydroxydiphenylamine, m.p. 60–68°, was obtained. A portion of this product was purified by sublimation, followed by recrystallization from hexane to yield pure material, m.p. 70–71° (lit.⁹ 69–70°). The *o*-hydroxydiphenylamine was analyzed and found to contain 0.56 atom % excess oxygen-18. The infrared spectrum was commensurate with the assigned structure.

Nitrosobenzene.—The procedure of Coleman, McCloskey and Stewart²¹ was followed exactly. The yield was 48%, m.p. 67–68° (lit.²¹ 67°).

Diphenylhydroxylamine.—The method described by Wieland and Roth²² was followed; the yield of crude material was 1.5 g. (9.8%), m.p. 56–60°, which after crystallization from benzene–pentane gave product, m.p. 60–61° (lit.²² 60°).

Reaction of Diphenylhydroxylamine with Benzoyl Chloride.—To a cooled mixture of 1.0 g. (0.0054 mole) of diphenylhydroxylamine and 1.28 g. (0.0054 mole) of pyridine in 12 ml. of chloroform was added 0.76 g. (0.0054 mole) of benzoyl chloride in 5 ml. of chloroform. The reaction mixture was allowed to stand for 22 hours. The chloroform was removed in a stream of nitrogen on a steam-bath and the residue was dissolved in boiling acetone. Upon cooling there was deposited 0.3 g. (20%) of crude II, m.p. 207–212°.

(21) G. H. Coleman, C. McCloskey and F. Stewart, *Org. Syntheses*, **25**, 80 (1945).

(22) H. Wieland and K. Roth, *Ber.*, **53**, 210 (1920).

Recrystallization from acetone afforded product, m.p. 219–220°. A mixed melting point with labeled II showed no depression, also their infrared spectra were identical.

Labeled 2-Hydroxy-4-methylphenyl Benzoate (VII).—A mixture of 24.2 g. (0.10 mole) of benzoyl peroxide-carbonyl-O¹⁸ and 10.8 g. (0.10 mole) of *p*-cresol in 125 ml. of benzene was refluxed in a nitrogen atmosphere for one hour. After washing with 10% potassium carbonate solution and water, the benzene layer was dried over magnesium sulfate. The benzene solution was chromatographed on silica gel, the major fraction was collected using benzene–ether, 90:10, as eluent. The crude product, 14.5 g. (62%), was recrystallized three times from benzene–hexane to yield product, m.p. 163–164° (lit.¹⁵ 163°). Oxygen-18 analysis showed 1.30 atom % excess oxygen-18. The infrared spectrum was commensurate with the assigned structure.

Hydrolysis of Labeled VII.—To 3.0 g. (0.013 mole) of labeled VII was added 1.14 g. (0.02 mole) of potassium hydroxide in 12 ml. of water, the mixture was allowed to stand at room temperature, in a nitrogen atmosphere, for 30 minutes. It was then brought to pH 8 by the addition of dilute hydrochloric acid. The solution was extracted with ether which was dried with magnesium sulfate. Removal of the ether afforded 1.3 g. (81%) of a red oil which was sublimed at 42° (0.025 mm.). A portion of the sublimate was recrystallized from benzene–pentane to give pure 2-hydroxy-4-methylphenol, m.p. 65–66° (lit.¹⁵ 65°). Analysis showed it to contain 0.17 atom % excess oxygen-18. The infrared spectrum was commensurate with the assigned structure.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS, THE STATE UNIVERSITY]

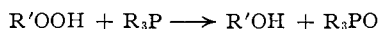
Concerning the Mechanism of the Reduction of Hydroperoxides by Trisubstituted Phosphines and Trisubstituted Phosphites¹

BY DONALD B. DENNEY, WILLIAM F. GOODYEAR² AND BERNARD GOLDSTEIN

RECEIVED SEPTEMBER 14, 1959

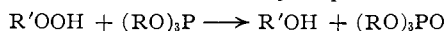
Reduction of *trans*-9-decalyl hydroperoxide by trisubstituted phosphines yielded *trans*-9-decalol. Cumene hydroperoxide was reduced with triphenylphosphine in ethanol–H₂O¹⁸ to give cumyl alcohol and triphenylphosphine oxide, neither of which contained excess oxygen-18. Similar results were obtained when *trans*-9-decalyl hydroperoxide was reduced with tri-*n*-butylphosphine in the presence of H₂O¹⁸. A mechanism is proposed for these reactions and the analogous reactions of hydroperoxides with trisubstituted phosphites. The fundamental step of the mechanism involves displacement by the nucleophile on the hydroxyl group of the hydroperoxide.

The reaction of hydroperoxides with trisubstituted phosphines was first reported by Horner and Jurgeleit.³ The reaction was found to be a simple



one which proceeds to give the phosphine oxide and the alcohol derived from the hydroperoxide. These authors suggested a general mechanism for this and similar reactions, but did not attempt to elaborate any detailed mechanisms.

More recently Walling and Rabinowitz⁴ have found that trialkyl phosphites also react with hydroperoxides to give trialkyl phosphates and the alcohol derived from the hydroperoxide. They



studied the reaction of *t*-butyl hydroperoxide with triethyl phosphite, which gave *t*-butyl alcohol and triethyl phosphate. Work in this Laboratory has confirmed the generality of their findings.⁵

(1) Support of part of this work by Research Corporation is gratefully acknowledged.

(2) National Science Foundation Predoctoral Fellow, 1957–1959.

(3) L. Horner and W. Jurgeleit, *Ann.*, **591**, 138 (1955).

(4) C. Walling and R. Rabinowitz, *THIS JOURNAL*, **81**, 1243 (1959).

(5) Unpublished work of R. Ellsworth.

Apparently no studies of the mechanism of these reactions have been made, although Walling and Rabinowitz have suggested a mechanism.⁴ One piece of evidence which is pertinent to any discussion of mechanism is the finding by Davies and Feld⁶ that optically active α -phenylethyl hydroperoxide is reduced by triphenylphosphine with complete retention of configuration to α -phenylethyl alcohol.

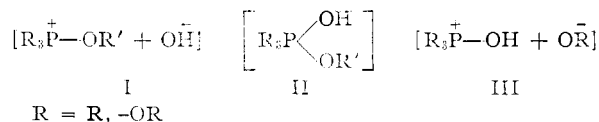
It was the purpose of the work presented in this report to study the mechanism of these reactions. It has been found that *trans*-9-decalyl hydroperoxide is reduced by triphenylphosphine to *trans*-9-decalol, thus indicating, in agreement with Davies and Feld,⁶ that these reactions proceed with retention of configuration. The fact that *trans*-9-decalol was the only product isolated is not conclusive proof that the reaction proceeds exclusively with retention of configuration, since small amounts of the *cis* isomer could have been lost during the isolation. A mixture of *cis*- and *trans*-9-decalols would probably have formed if during the reaction a 9-decalyl carbonium ion was an intermediate.

(6) A. Davies and R. Feld, *J. Chem. Soc.*, 4637 (1958).

The experiment does show that inversion does not take place and in conjunction with the experiment of Davies and Feld one concludes that these reactions proceed with retention of configuration.

On an *a priori* basis, several mechanisms were considered for these reactions. It appeared that they could be distinguished by a tracer study using H_2O^{18} . Cumene hydroperoxide was allowed to react with triphenylphosphine in a mixture of ethanol- H_2O^{18} ; similarly *trans*-9-decalyl hydroperoxide was reduced in ethanol- H_2O^{18} with tri-*n*-butylphosphine. In both cases the alcohol contained no excess oxygen-18 and in the case of the cumene hydroperoxide reduction the triphenylphosphine oxide was also shown to contain no excess oxygen-18. In a somewhat similar experiment cumene hydroperoxide was reduced with tri-*n*-butylphosphine in methanol. The product obtained was cumyl alcohol and no cumyl methyl ether could be detected. These results indicate that the two oxygens of the hydroperoxide ultimately find their way into the alcohol and phosphine oxide or phosphate.

Since the reductions by the phosphines and phosphites appear to be essentially the same, it seems only reasonable to assume that they follow the same mechanism. Walling and Rabinowitz⁷ suggested that the initial step in the phosphite reduction gives the intermediate I. Such an intermediate could also arise in the phosphine reaction. Several pieces of evidence indicate that compound I



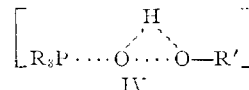
cannot be an intermediate in this reaction. For example, if compound I is formed then it must decompose to products faster than the hydroxide ion equilibrates with the H_2O^{18} . This would have to be a remarkable process indeed. In the phosphite reaction, I is composed of a tetraalkoxyphosphonium ion and a hydroxide ion. In order to account for the fact that only one alcohol is obtained on the decomposition of I, *i.e.*, the one from the hydroperoxide, one must devise a mode of decomposition of I which will give only this alcohol. This is hard to rationalize since, in the absence of any other factors, one would predict a statistical mixture of alcohols and phosphates. Certainly stereochemical and electronic factors could influence the reaction; however, it would be peculiar indeed if they always led to only one alcohol and one phosphate. All of the available data indicate that I is not an intermediate in these reactions and therefore it will not be considered further.

Another mechanistic possibility for these reactions involves the formation of a pentacovalent compound II. A similar intermediate has been postulated to explain the decomposition of tetraalkylphosphonium hydroxides to phosphine oxides and hydrocarbons.⁷ If II is to be an acceptable intermediate, it must decompose to products faster than it can ionize to I; otherwise one would find oxygen-18 in the products. Furthermore, II like I

(7) M. Zanger, C. A. Vauderwerf and W. E. McEwen, *THIS JOURNAL*, **81**, 3806 (1959).

would be required to decompose to only one alcohol, a process which seems unreasonable.

A most reasonable mechanism for these reactions involves attack by the phosphine or phosphite on the hydroxyl oxygen of the hydroperoxide to give, in a smooth displacement reaction, the intermediate III, which yields the products by a simple proton transfer. This mechanism is in agreement with all of the available data. Alternatively, one could suggest that the initial displacement reaction proceeds with simultaneous proton transfer *via* a transition state IV. The only reason



for considering such a transition state is the fact that phosphites reduce hydroperoxides essentially instantaneously in pentane at -40° .⁵ Since these are conditions which do not normally lead to the production of ions, it seems reasonable to consider IV as a possibility. Whether III or IV represents the correct path might well be established by determining the magnitude of the deuterium isotope effect, when a hydroxyl-deuterated hydroperoxide is allowed to react with a phosphine or phosphite.

It should be pointed out that the displacement on the hydroxyl oxygen of the hydroperoxide is quite reasonable since on steric grounds this oxygen is the most accessible, particularly when it is a *t*-alkyl or *t*-aralkyl hydroperoxide which is reacting. Also, the hydroxyl oxygen is probably the most electropositive oxygen and therefore reaction at this position by the nucleophile should be favored.⁵

Experimental⁹

Reduction of *trans*-9-Decalyl Hydroperoxide with Tri-*n*-butylphosphine.—To a cold solution of 1.00 g. (0.0059 mole) of *trans*-9-decalyl hydroperoxide in 10 ml. of chloroform there was added 3.58 g. (0.018 mole) of tri-*n*-butylphosphine. The reaction mixture was allowed to remain at room temperature for several hours. The solution then was washed with four 25-ml. portions of 6 *N* hydrochloric acid and one 25-ml. portion of water, and then dried over magnesium sulfate. The solvent was removed *in vacuo* and the crude product was chromatographed on silica gel (15 g.) using benzene as the eluent. In this manner 0.46 g. (59.8%) of *trans*-9-decalol, m.p. 53–54° (lit.¹⁰ 52–53°), was obtained. A mixed melting point with an authentic sample showed no depression.

Reduction of *trans*-9-Decalyl Hydroperoxide with Tri-*n*-butylphosphine in the Presence of H_2O^{18} .—To a solution of 4.63 g. (0.027 mole) of *trans*-9-decalyl hydroperoxide in a mixture of 40 ml. of ethanol and 10 ml. of H_2O^{18} (1.5 atom % oxygen-18) was added at 0°, 8.20 g. (0.043 mole) of tri-*n*-butylphosphine in 50 ml. of ethanol. After standing at room temperature for several hours, the solvents were removed *in vacuo*. The residue was dissolved in 25 ml. of chloroform and this solution was extracted with two 25-ml. portions of 0.5 *N* hydrochloric acid and two 25-ml. portions of water. The chloroform solution was dried over magnesium sulfate. Evaporation of the solvent afforded 3.20 g. of material which was molecularly distilled, block temperature 70–95° (0.07 mm.). This material was further purified.

(8) D. B. Denney and M. A. Greenbaum, *ibid.*, **79**, 979 (1957).

(9) Oxygen-18 was determined by the method of W. E. Doering and E. Dorfman, *THIS JOURNAL*, **75**, 5595 (1953), as modified by D. B. Denney and M. S. Greenbaum, *ibid.*, **79**, 979 (1957). All melting points were determined on a Kofler hot-stage. Analyses by G. Robertson, Florham Park, N. J.

(10) R. Criegee, *Ber.*, **77B**, 22 (1944).

fied by sublimation and crystallization from pentane to give *trans*-9-decalol, m.p. 51–54°. The infrared spectrum was identical with that of an authentic sample. Oxygen-18 analysis showed 0.00, 0.03 atom % oxygen-18.

Reaction of Cumene Hydroperoxide with Triphenylphosphine in the Presence of H₂O¹⁸.—To a stirred solution of 15.72 g. (0.10 mole) of cumene hydroperoxide in 40 ml. of absolute ethanol and 30 ml. of H₂O¹⁸ (1.5 atom % oxygen-18) was added 26.23 g. (0.10 mole) of triphenylphosphine in 100 ml. of ethanol. After stirring at room temperature for two hours, the ethanol and water were removed *in vacuo*. The viscous residue was triturated with three 50-ml. portions of petroleum ether. The residue after this treatment was washed with 100 ml. of ether and then recrystallized from hexane-ether to give 10.6 g. of triphenylphosphine oxide, m.p. 154–156°, no depression on admixture with an authentic sample. Oxygen-18 analysis showed 0.00, 0.00 atom % oxygen-18.

The petroleum ether extracts were concentrated and the residue was distilled under reduced pressure. The distillation was exceedingly difficult since triphenylphosphine oxide precipitated and caused bumping. In this connection it should be pointed out that subsequent work has shown that chromatography of these reaction mixtures is the easiest way of separating them. The distillation afforded relatively pure alcohol, b.p. 74–90° (28 mm.). Some of this material

(1.7 g., 0.012 mole), was treated with 2.0 g. (0.017 mole) of phenyl isocyanate and the mixture was heated at 75° for five hours. Water was added and the solid, containing the urethan and diphenylurea, was extracted with boiling carbon tetrachloride. The carbon tetrachloride extracts were evaporated to give material m.p. 103–115°. Two recrystallizations from petroleum ether gave 0.052 g. of the phenylurethan, m.p. 113–114° (lit.¹¹ 113°). The infrared spectrum of this material was identical with an authentic sample and there was no melting point depression on admixture with an authentic sample. The oxygen-18 analysis of the phenylurethan showed 0.00, 0.00 atom % oxygen-18.

Reaction of Cumene Hydroperoxide with Tri-*n*-butylphosphine in Methanol.—Tri-*n*-butylphosphine (56.6 g., 0.280 mole) in 25 ml. of methanol was added dropwise at 10° to 43.4 g. (0.276 mole) of cumene hydroperoxide in 100 ml. of methanol. The methanol was removed *in vacuo* and the residue distilled; total weight of distillate, 35.8 g. (92%). The major fraction, 27.1 g., b.p. 69–72° (5 mm.), appeared from its infrared spectrum to be only cumyl alcohol. A Zeisel methoxyl analysis on this fraction showed no methoxyl group was present.

(11) B. Schroeter, *Ber.*, **36**, 1863 (1903).

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[CONTRIBUTION NO. 521 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND Co.]

Syntheses by Free-radical Reactions. XI. Additive Dimerizations with Bromine Atoms

By C. M. LANGKAMMERER, E. L. JENNER, D. D. COFFMAN AND B. W. HOWK

RECEIVED AUGUST 20, 1959

Bromine atoms have been obtained by the one-electron oxidation of bromide anions with either cerium(IV) ions or hydroxyl radicals. These atoms, generated in stoichiometric quantities, brought about the additive dimerization of butadiene to form unsaturated eight-carbon dibromides, BrC₄H₆–C₄H₆Br, in 46% yield.

The one-electron *reduction* of molecules containing oxygen–oxygen bonds to produce free radicals, as brought about by a variable valence metal ion, has been employed extensively in the generation of free radicals.¹ Radicals from such "oxidation–reduction systems" have been used to initiate polymerization,² effect oxidation³ and bring about additive dimerization.^{4,5} Systems in which the metal ion plays the opposite role, *i.e.*, functions as a one-electron *oxidizing* agent, have been postulated from results of kinetic studies. Thus, halide anions have been oxidized to free halogen, presumably *via* halogen atoms.⁶ However, this mode of radical generation has not been utilized in preparative chemistry.

We have now demonstrated the formation of free radicals in a one-electron oxidation by using them

(1) F. Haber and J. Weiss, *Naturwissenschaften*, **20**, 948 (1932); F. Haber and J. Weiss, *Proc. Roy. Soc. (London)*, **A147**, 332 (1934); Cheves Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 565–575.

(2) R. G. R. Bacon, *Trans. Faraday Soc.*, **42**, 140 (1946); J. H. Baxendale, M. G. Evans and G. S. Park, *ibid.*, **42**, 155 (1946); A. I. Medalia and I. M. Kolthoff, *J. Polymer Sci.*, **4**, 377 (1949).

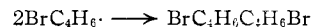
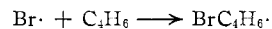
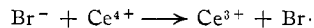
(3) H. J. H. Fenton, *J. Chem. Soc.*, **65**, 899 (1894); J. H. Merz and W. A. Waters, *ibid.*, S15 (1949); I. M. Kolthoff and A. I. Medalia, *THIS JOURNAL*, **71**, 3777 (1949).

(4) (a) D. D. Coffman and E. L. Jenner, *ibid.*, **80**, 2872 (1958); (b) D. D. Coffman and H. N. Cripps, *ibid.*, **80**, 2877, 2880 (1958).

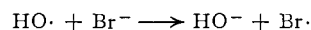
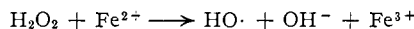
(5) M. S. Kharasch, F. S. Arimoto and W. Nudenberg, *J. Org. Chem.*, **16**, 1556 (1951); M. S. Kharasch and W. Nudenberg, *ibid.*, **19**, 1921 (1954).

(6) E. L. King and M. L. Pandow, *THIS JOURNAL*, **75**, 3063 (1953).

in the additive dimerization of butadiene. Earlier papers in this series^{4,7} described the reaction of free radicals (R·) with 1,3-dienes (M) to form additive dimers (R–M–M–R). In the current study, bromine atoms were generated by the one-electron oxidation of bromide anion by cerium(IV) ion and were captured by butadiene to give unsaturated C₈-dibromides.



Alternatively, the bromine atoms were obtained by the oxidation of bromide ions by hydroxyl radicals generated from hydrogen peroxide and ferrous ion. This approach is similar to the



previously reported finding⁷ that amino radicals, generated from hydroxylamine and titanous ion, would convert bromide ions to bromine atoms.



In the earlier work it was noted that amino radicals would not convert chloride ions to chlorine atoms. In the present work hydroxyl radicals have been

(7) C. J. Albisetti, D. D. Coffman, F. W. Hoover, E. L. Jenner and W. E. Mochei, *ibid.*, **81**, 1489 (1959).