ammonia. Ammonia was distilled, and the mixture was refluxed for three days, filtered and refluxed for another three days under a column to remove last traces of ammonia.

Alkylation Studies.—The apparatus and procedure for the kinetic studies have been described.[4] All reactions were carried out at 30.00 ± 0.02°. Nitrogen gas for the sampling operation was bubbled through ethereal sodium triphenylmethide solution to remove traces of oxygen and water vapor and to saturate the gas with ether vapor. At all other times the system was closed and contained a small positive pressure. Evaporation throughout an entire run amounted to less than 3%, most of which occurred during the initial addition of the enolate solution to the nitrogen-filled flask. In order to eliminate this error, as well as any error due to possible non-additivity of volumes of halide and enolate solutions, a "zero-time" aliquot was titrated soon after mixing. The results of thirty alkylations are listed in Tables I and II.

Vapor Pressure of Methyl Bromide-Enolate System.—A 55-ml. flask immersed in a constant-temperature bath at 25.30 ± 0.05° was attached to a manometer, gas buret and vacuum line. The flask was filled with anhydrous ether freshly distilled from lithium aluminum hydride. The system was evacuated intermittently until a constant vapor pressure of 545 mm. was obtained. The vapor pressure of ethyl ether at 25.3° is 544 mm.[14] The volume of liquid at this time was 52 ml. Five portions of about 100 ml. each of methyl bromide (Dow Chemical Co., purified by isothermal distillation) were accurately measured and added through a capillary at the bottom of the flask. After each addition, air pressure was applied to the open end of the manometer in order to fill the other leg with mercury and thereby force the vapor back into the flask. After circulating the mercury in this way several times, a constant value of the vapor pressure was obtained. The vapor pressures are plotted against mole fraction of methyl bromide in Fig. 3.

The procedure was repeated with a 0.42 *M* solution of sodiobutyrophenone. The five portions of methyl bromide were added over a period of one hour. The slope of the vapor pressure curve was the same as that for the system ether-methyl bromide. The amount of alkylation in this time is negligible. A titration after 17 hours indicated that the reaction was then only 48% complete.

Ebulliometric Studies.—A differential ebulliometer of the type described by Swietoslawski and Anderson[15] was employed. The exit led to a 2-ml. receiver and thence through Drierite to a T-tube over which was passed a very slow stream of nitrogen. Temperatures were measured to 0.001° with micro-Beckmann thermometers. In order to obtain constant reproducible temperature differences, it was necessary to drain the water from the condenser for several minutes and distil up to 2 ml. of ether.

The enolate solutions were freshly prepared in 2-3-liter batches and forced by nitrogen pressure directly from the sodium hydride into the boiler. The apparatus was flushed several times with the solution and filled to a 40.0-ml. calibration mark. After the boiling point determination, a 25.0-ml. aliquot was drained into a volumetric flask, weighed and titrated. The remainder of the solution was transferred to a 0.16-mm. infrared cell for estimation of ketone at 5.88μ. The results for eight separate preparations are listed in Table III. The concentrations of free ketone represent maximum amounts that could be present. They are calculated on the unlikely assumptions that the pure enolate has no absorption in the carbonyl region and that no moisture was adsorbed on the surfaces of the infrared cell. The aggregation numbers listed in Table III have been calculated without correction for free ketone. When corrections are applied, the average aggregation number is 3.35, an increase of about 8%.

The molal boiling point constant for ethyl ether in the instrument used, 2.00, was determined by measuring boiling point elevations of 0.1-0.4 molal solutions of triphenylmethane, m.p. 92-93°.

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[14] "International Critical Tables," Vol. 3, McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p. 19.

[15] A. Weissberger, "Physical Methods of Organic Chemistry," Vol. I, 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1949, p. 121.

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

Studies of the Mechanisms of the Reactions of Benzoyl Peroxide with Secondary Amines and Phenols

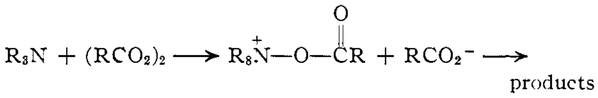
BY DONALD B. DENNEY AND DOROTHY Z. DENNEY

RECEIVED JULY 23, 1959

The reactions of dibenzylamine, diphenylamine and *p*-cresol with benzoyl peroxide, labeled with oxygen-18 in the carbonyl positions, have been studied. Dibenzylamine reacts by nucleophilic displacement on an oxygen of the peroxide link to give ultimately benzoic acid and O-benzoyl-N,N-dibenzylhydroxylamine which contains all of the excess oxygen-18 in the carbonyl oxygen. Diphenylamine reacts by the same process to give O-benzoyl-N,N-diphenylhydroxylamine which is unstable under these conditions and rearranges to give N-phenyl-N-*o*-hydroxyphenylbenzamide. The amide contains 55% of the excess oxygen-18 in the carbonyl group and 45% in the phenolic hydroxyl group. Similarly *p*-cresol reacts to give 2-hydroxy-4-methylphenyl benzoate which contains 87% of the excess oxygen-18 in the carbonyl group and 13% in the phenolic hydroxyl group. Mechanisms for these reactions are proposed and discussed.

Amine Reactions.—The reactions of amines with peroxides, in particular benzoyl peroxide, have been studied by a large number of investigators.[1]

The reaction of tertiary amines with diacyl peroxides is thought to proceed by an initial polar displacement, as shown below, to give I which then decomposes by a radical path into products.[2]



$$R_3N + (RCO_2)_2 \longrightarrow R_3\overset{+}{N}-O-\overset{\overset{\displaystyle O}{\|}}{C}R + RCO_2^- \longrightarrow \text{products}$$

I

Secondary aliphatic amines react quite simply with benzoyl peroxide to give N,N-dialkyl-O-benzoylhydroxylamines and benzoic acid. There has

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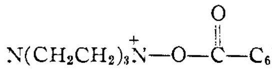
[1] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 590-595.

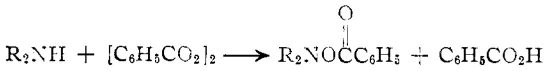
[2] W. B. Geiger, *J. Org. Chem.*, **23**, 298 (1958), has prepared N-acetoxytrimethylammonium bromide by treatment of trimethylamine with acetyl peroxide and then with concentrated hydrobromic acid. Thus it has been demonstrated that I is formed by the initial reaction of a tertiary amine with an acyl peroxide. D. Buckley, S. Dunstan and H. B. Henbest, *J. Chem. Soc.*, 4901 (1957), also have suggested this mechanism for these reactions and have spectral evidence for the



$$N(CH_2CH_2)_3\overset{+}{N}-O-\overset{\overset{\displaystyle O}{\|}}{C}-C_6H_5$$

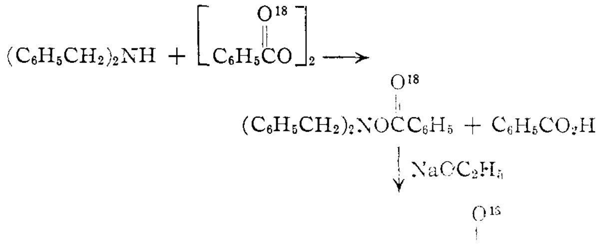
ion obtained from the reaction of triethylenediamine with benzoyl peroxide.

been some speculation concerning the mechanism of these reactions.[1] The most likely mechanism



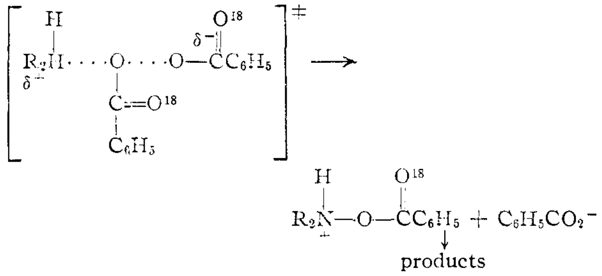
$$R_2NH + [C_6H_5CO_2]_2 \longrightarrow R_2NO\overset{\overset{\large O}{\|}}{C}C_6H_5 + C_6H_5CO_2H$$

involves nucleophilic attack by the amine on the peroxide to give a pair of ions which undergo proton transfer to give the products. Effective proof of the correctness of this view now has been obtained by allowing dibenzylamine to react with benzoyl peroxide, labeled with oxygen-18 in the carbonyl oxygens. The procedure was that of Gambarjan and Cialtician.[3] The O-benzoylhydroxylamine obtained contained all of the excess oxygen-18



$$(C_6H_5CH_2)_2NH + \left[C_6H_5\overset{\overset{O^{18}}{\|}}{C}O\right]_2 \longrightarrow (C_6H_5CH_2)_2NO\overset{\overset{O^{18}}{\|}}{C}C_6H_5 + C_6H_5CO_2H \xrightarrow{NaOC_2H_5} (C_6H_5CH_2)_2NOH + C_6H_5\overset{\overset{O^{18}}{\|}}{C}—O—C_2H_5$$

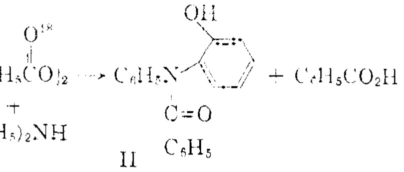
originally incorporated in one carbonyl group of the benzoyl peroxide. Ethanolysis of the O-benzoylhydroxylamine afforded dibenzylhydroxylamine which contained no excess oxygen-18 and ethyl benzoate which contained all of the excess oxygen-18 present in the O-benzoylhydroxylamine. Since it is well established that transesterification proceeds by addition of an alkoxide ion to the carbonyl carbon atom of an ester and then expulsion of the appropriate anion, then it is established here that the carbonyl oxygen in the ethyl benzoate was a carbonyl oxygen in the hydroxylamine benzoate. This being the case the only reasonable mechanism for this reaction involves a transition state



products

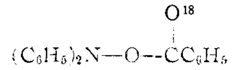
in which the amine displaces on one of the oxygens of the peroxidic link to give a pair of ions which rapidly react to give products. It is interesting to note that the initial displacement reaction is the same as was found for the reaction of trisubstituted phosphines with benzoyl peroxide.[4] It seems only reasonable to assume that tertiary amines react by the same initial displacement reaction.

The reactions of secondary aryl and secondary aralkyl amines with benzoyl peroxide do not yield O-benzoylhydroxylamines but rather hydroxybenzanilides. Several mechanisms for these reactions have been proposed,[5-8] but experimental verification for any one of them has been lacking. In order to further study these reactions diphenylamine was allowed to react with benzoyl peroxide labeled with oxygen-18 in the carbonyl positions.[9] The hydroxybenzanilide (II) obtained contained 95% of the excess oxygen-18 originally present in one of the carbonyl groups of the benzoyl peroxide. Evidently some loss of oxygen-18 occurred during the isolation and purification of the amide. Basic hydrolysis of II yielded *o*-hydroxydiphenylamine



II

which contained 45% of the excess oxygen-18 present in II. Since it has been demonstrated that monophenols do not undergo oxygen-18 exchange under basic conditions,[10] one can then assign the following distribution of oxygen-18 to II, carbonyl oxygen 55% of the excess and the phenol oxygen 45% of the excess. The results show that practically complete equilibration of the label has occurred. These data coupled with those obtained from the dibenzylamine reaction reported above allow the formulation of a mechanism for these reactions. It seems only reasonable to assume that the initial reaction proceeds to give O-benzoyl-N,N-diphenylhydroxylamine (III) in which the oxygen-18 label is localized in the carbonyl oxygen.



$$(C_6H_5)_2N—O—\overset{\overset{O^{18}}{\|}}{C}C_6H_5$$

III

This postulation follows naturally from the dialkylamine reaction. That III is an intermediate in this reaction and can isomerize to II has been demonstrated by allowing diphenylhydroxylamine to react with benzoyl chloride; from this reaction II was obtained.

It has been stated that in general there is no evidence for free radical formation in secondary amine–peroxide systems.[1] The evidence is indeed confused but some of the products obtained can be explained most easily by the use of radical mechanisms. For several reasons it is felt that the rearrangement of III, which ultimately leads to II, is an ionic process. One is the fact that the rearrangement of arylhydroxylamines to aminophenols by an ionic mechanism is well known.[11] Another important point stems from the report[9] that diphenylamine and acetyl peroxide react to form N-*o*-hydroxyphenylacetanilide, which is analogous to II. The initial product of this reaction is undoubtedly O-acetyl-N,N-diphenylhydroxylamine. Rearrangement of this material by a homolytic

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(3) S. Gambarjan and O. Cialtician, *Ber.*, **60A**, 390 (1927).

(4) M. A. Greenbaum, D. B. Denney and A. K. Hoffmann, THIS JOURNAL, **78**, 2563 (1956).

(5) J. T. Edward, *J. Chem. Soc.*, 1464 (1954).

(6) L. Horner and W. Kirmse, *Ann.*, **597**, 66 (1955).

(7) J. E. Leffler and W. B. Bond, THIS JOURNAL, **78**, 335 (1956).

(8) W. B. Bond, *J. Polymer Sci.*, **22**, 181 (1956).

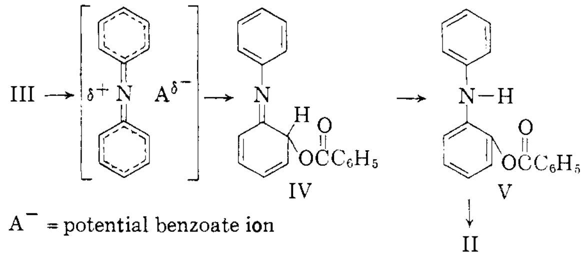
(9) The procedure followed was that of S. Gambarjan, *Ber.*, **42**, 4003 (1909).

(10) I. A. Makalkin, *Acta Physicochim. U.R.S.S.*, **16**, 88 (1942); *C. A.*, **37**, 2355 (1943).

(11) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 621–624.

process would involve the formation of acetoxy radicals which are known to decarboxylate spontaneously[12]; thus the acetanilide cannot be formed by this radical process. It should not be construed from the statements above that O-acetyl-N,N-diphenylhydroxylamine cannot undergo homolysis to an acetoxy radical, since this may well occur, but it will not lead to the acetanilide. Finally the oxygen-18 results are not compatible with a homolytic process for the rearrangement of III, since rearrangement *via* a benzoyloxy radical would give complete equilibration of the label. The oxygen-18 data do indicate practically complete equilibration so they cannot be used to eliminate unequivocally the formation of a benzoyloxy radical.

An ionic mechanism quite adequately explains the results obtained. It is represented by the equations



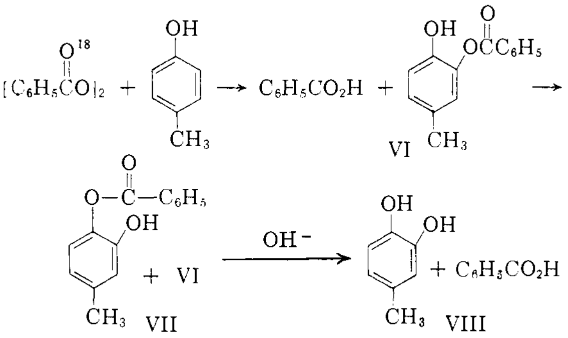
A^- = potential benzoate ion

The partial equilibration of the label must occur during the conversion of III to IV since the isomerization of V to II is a simple intramolecular addition of the amine nitrogen of V to the carbonyl carbon atom followed by ring opening and proton transfer. These transformations cannot account for oxygen-18 equilibration. The partial equilibration observed is reminiscent of several ion pair reactions studied earlier,[13] and this isomerization undoubtedly falls into this class of reactions. Discrete structures involving partial bonding to the oxygens of the potential benzoate ion in the ion pair or pairs can be written.[13] This has not been done in this case since it is impossible to know what their relative contributions are.

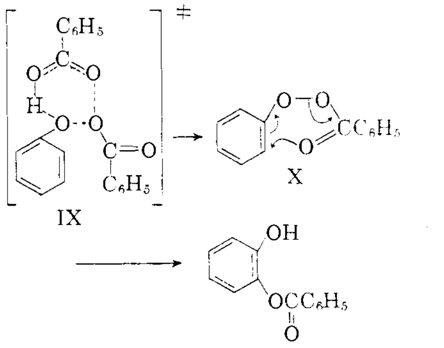
It should be emphasized that the amount of oxygen-18 equilibration observed in a transformation such as III to IV should be controlled to some degree by the reaction conditions; for example one would expect that a better ionizing solvent would lead to even more equilibration than was found in the present experiment. It is therefore important to realize that the percentage equilibration probably cannot be generalized to any system; however, the over-all mechanism is undoubtedly the same for all secondary aryl and aralkyl amines.

Phenol Reactions.—It has been known for many years that phenols react quite rapidly with benzoyl peroxide. Until quite recently there was considerable confusion concerning the mechanism of these reactions. Walling and Hodgdon[14] have reported a series of experiments which enabled them to suggest that the reactions were almost certainly ionic reactions.

As a part of the study of the reactions of nucleophiles with peroxides, work in this Laboratory has been in progress concerning the reactions of phenols with benzoyl peroxide. The reaction studied was that of *p*-cresol with benzoyl peroxide,[15] labeled with oxygen-18 in the carbonyl groups. The reaction proceeds to give initially 2-hydroxy-5-methylphenyl benzoate (VI) which rapidly isomerizes to a mixture of VI and 2-hydroxy-4-methylphenyl benzoate (VII) which was the compound isolated. Oxygen-18 analysis of VII showed that it contained essentially all of the excess oxygen-18 originally present in one carbonyl group of the benzoyl peroxide. Hydrolysis of VII to 2-hydroxy-4-methylphenol was effected by solution in aqueous potassium hydroxide at room temperature. Acidification after 30 minutes afforded VIII. Oxygen-18 analysis of VIII showed it contained 13% of the excess oxygen-18 present in VII. It seems inconceivable that exchange of oxygen-18 took place under these conditions and therefore one can assign the following distribution of oxygen-18 to VII, 87% of the excess oxygen-18 in the carbonyl group and 13% of the excess in the phenolic hydroxyl group.



From a mechanistic point of view these results completely eliminate the formation of a benzoyloxy radical during the reaction, since this would have led to VII in which half of the oxygen-18 was in the ester carbonyl and the other half was in the phenolic hydroxyl group. These results do support the mechanism proposed by Walling and Hodgdon,[14] with one minor change. Their mechanism is outlined below, where IX represents the transition state for the displacement reaction and X is an unstable perester. It was suggested that X forms product by an intramolecular rearrangement similar to the Claisen rearrangement.



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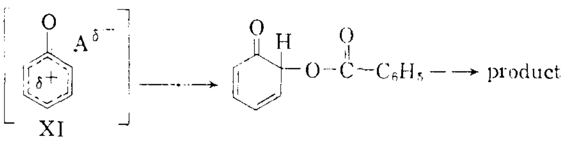
[12] Reference 1, p. 493.

[13] D. B. Denney and D. G. Denney, THIS JOURNAL, **79**, 4806 (1957); D. B. Denney and B. Goldstein, *ibid.*, **79**, 4948 (1957).

[14] C. Walling and R. B. Hodgdon, Jr., *ibid.*, **80**, 228 (1958).

[15] S. L. Cosgrove and W. A. Waters, *J. Chem. Soc.*, 3189 (1949).

Since it has been demonstrated that displacement by amines and phosphines takes place on the oxygens of the peroxide link it seems reasonable to assume that the same is true in the phenol reactions. Formation of X proceeds then as suggested.[14] The tracer experiment shows that rearrangement of X leads to some equilibration but that the carbonyl oxygen retains 87% of the excess oxygen-18. These results can be explained in terms of an ion pair or ion pairs, XI, which allow



XI

$A^{\delta-}$ = potential benzoate ion

some equilibration.[16] It is interesting to note that much less equilibration occurred in this rearrangement than in the diphenylamine–benzoyl peroxide system. This probably is due, at least in part, to the greater instability of the potential cation of XI relative to that derived from III. This is due to the fact that in XI the positive charge can only be dispersed over one ring and it also involves a partial positive charge on oxygen rather than the less electronegative nitrogen. Other factors such as solvent and reaction temperature also can affect the extent of equilibration.

It is quite clear that reactions of benzoyl peroxide with nucleophilic substances can be quite rapid and can supersede the normal homolytic cleavage. It is therefore important to consider such reactions when working with these systems. For example Barson and Bevington[17] recently have shown that benzoyl peroxide decomposes in the presence of thiophenol to give benzoic acid in essentially quantitative yield. They have interpreted their results in terms of a mechanism involving homolytic cleavage of benzoyl peroxide followed by reaction with thiophenol. It seems more likely that this is a process similar to the amine and phenol reactions and it probably should be reinvestigated before their interpretation is accepted.

Acknowledgments.—It is a pleasure to acknowledge the generous financial assistance of the Alfred P. Sloan Foundation. Some of the mass-spectral analyses were performed by Dr. Paul Schleyer and also the Colgate-Palmolive Co. whose assistance we gratefully acknowledge.

Experimental[18]

Benzoic Acid-$CO^{18}O^{18}H$.—The procedure of Denney and Denney[13] was followed exactly. The yield was 96% of material, m.p. 121–122°, (lit.[13] 123–124°) containing 1.31 atom % excess oxygen-18 in each oxygen. The anilide was prepared by standard methods, m.p. 159–160° (lit.[19] 161°), and was found to contain 1.28 atom % excess oxygen-18.

Benzoyl Chloride-$CO^{18}Cl$.—The procedure of Denney and Denney[13] was followed. The yield was 90.4%, b.p. 93–94° (27 mm.).

Benzoyl Peroxide-*carbonyl*-O^{18}.—To a stirred mixture of 51.7 g. (0.455 mole) of 30% hydrogen peroxide, 96.5 g. (0.91 mole) of sodium carbonate and 135.0 g. (1.61 moles) of sodium bicarbonate in 2.2 l. of water was added at 0°, 128 g. (0.91 mole) of benzoyl chloride-*carbonyl*-O^{18}. This mixture was stirred for 10 hours; the solid which formed was separated by filtration. It was then washed thoroughly with water to afford 106 g. (96.2%) of crude product, m.p. 108–110°. This was recrystallized from chloroform-methanol to yield 67 g. (60.5%) of benzoyl peroxide-*carbonyl*-O^{18}, m.p. 109.5–110.5° (lit.[20] 108°). Analysis showed it contained 1.32 atom % excess oxygen-18 in each carbonyl oxygen. This benzoyl peroxide was used in the reaction with diphenylamine.

Another sample of benzoyl peroxide was prepared from benzoic acid containing 1.31 atom % excess oxygen-18 in each position. This sample analyzed for 1.31 atom % excess oxygen-18 in each carbonyl position and was used in the dibenzylamine reaction and the reaction with *p*-cresol.

O-Benzoyl-N,N-dibenzylhydroxylamine-*carbonyl*-O^{18}.—A solution of 14.52 g. (0.06 mole) of benzoyl peroxide-*carbonyl*-O^{18} in 240 ml. of ether was added to 23.64 g. (0.12 mole) of dibenzylamine dissolved in 100 ml. of ether. The reaction mixture was allowed to reflux for 7 hours and was then washed with a solution of 20 g. of sodium carbonate in 200 ml. of water. After washing with water and drying with magnesium sulfate, the ether was evaporated in a stream of nitrogen. There was obtained 18.0 g. (94%) of crude material, m.p. 81–90°, which was recrystallized from methanol to yield 11.0 g. (57%) of product, m.p. 94–95° (lit.[3] 95.5–96.5°). Analysis showed that this material contained 1.32 atom % excess oxygen-18.

Ethanolysis of O-Benzoyl-N,N-dibenzylhydroxylamine-*carbonyl*-O^{18}.—A solution of 10.0 g. (0.031 mole) of O-benzoyl-N,N-dibenzylhydroxylamine-*carbonyl*-O^{18} in 300 ml. of dry ether was added to 0.043 mole of sodium ethoxide in 90 ml. of absolute ethanol and allowed to stand at 25° for 18 hours. After washing with 200 ml. of water, the dibenzylhydroxylamine was precipitated, from the organic phase, as its oxalate by the addition of 8.0 g. (0.089 mole) of oxalic acid in 400 ml. of ether. The heavy yellow precipitate was filtered, washed with ether and stirred with aqueous sodium carbonate for 4 hours. After drying there was obtained 3.9 g. (63%) of crude dibenzylhydroxylamine, m.p. 125–126°, which was recrystallized from methanol to yield 3.5 g. (56.5%) of material, m.p. 125–126° (lit.[3] 123°). Analysis of the dibenzylhydroxylamine showed it contained 0.01 atom % excess oxygen-18.

The combined ether extracts were washed with dilute aqueous hydrochloric acid, 5% sodium carbonate solution and water. After drying over magnesium sulfate, the ether was evaporated on a steam-bath to yield 3.1 g. (67%) of a red oil. This was molecularly distilled at 20 mm.; one fraction, b.p. (block) 103–111°, was analyzed and found to contain 1.31 atom % excess oxygen-18. The infrared spectrum of this material was identical to that of an authentic sample of ethyl benzoate.

Labeled II.—A solution of 24.2 g. (0.10 mole) of benzoyl peroxide-*carbonyl*-O^{18} in 125 ml. of chloroform was added over one hour to a cooled mixture of 16.9 g. (0.10 mole) of diphenylamine in 100 ml. of chloroform. The resulting mixture was extracted with 5% aqueous sodium bicarbonate, water and then dried over magnesium sulfate. The chloroform was removed *in vacuo* and the residue was triturated with ether. In this manner there was obtained 7.83 g. (27%) of tan crystals, m.p. 212–214°. Recrystallization from acetone yielded pure II, m.p. 215–217° (lit.[9] 214°). Analysis showed it contained 1.25 atom % excess oxygen-18. The infrared spectrum was commensurate with the assigned structure.

Hydrolysis of Labeled II.—A mixture of 3.0 g. (0.014 mole) of II and 20 ml. of 10% aqueous potassium hydroxide

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[16] Reference 13 contains a much more complete discussion of the presumed structures of ion pairs of this type; see also S. Winstein and G. C. Robinson, THIS JOURNAL, **80,** 169 (1958).

[17] C. A. Barson and J. C. Bevington, *Tetrahedron*, **4**, 147 (1958).

[18] Oxygen-18 analyses were carried out using the method of W. E. Doering and E. Dorfman, THIS JOURNAL, **75,** 5595 (1953), as modified by D. B. Denney and M. A. Greenbaum, *ibid.*, **79**, 979 (1957). The atom % excess oxygen-18 reported is an average of at least two separate analyses; accuracy estimated as ±0.01 atom %. The melting points were taken on a Fisher-Johns melting point apparatus and are uncorrected.

[19] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1940, p. 191.

[20] N. A. Lange, "Handbook of Chemistry," Handbook Publishers, Sandusky, Ohio, 1946, p. 374.

was refluxed, under nitrogen, for 11 hours. The solution was brought to *p*H 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 Stewart[21] was followed exactly. The yield was 48%, m.p. 67–68° (lit.[21] 67°).

Diphenylhydroxylamine.—The method described by Wieland and Roth[22] 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°. 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*-O^{18} 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 *p*H 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 Phosphites[1]

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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-H$_2$O^{18} 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 H$_2$O^{18}. 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

$$\mathrm{R'OOH + R_3P \longrightarrow R'OH + R_3PO}$$

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 Rabinowitz[4] have found that trialkyl phosphites also react with hydroperoxides to give trialkyl phosphates and the alcohol derived from the hydroperoxide. They

$$\mathrm{R'OOH + (RO)_3P \longrightarrow R'OH + (RO)_3PO}$$

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]

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 Feld[6] 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.

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[1] Support of part of this work by Research Corporation is gratefully acknowledged.

[2] National Science Foundation Predoctoral Fellow, 1957–1959.

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