[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Intramolecular Radical Reactions. Decomposition of *o*-Methyl-, *o*-Benzyl-, and *o*-Phenylbenzoyl Peroxide

FREDERICK D. GREENE, GILMAN R. VAN NORMAN, JAMES C. CANTRILL, AND RICHARD D. GILLIOM

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Decompositions of *o*-methyl-, *o*-benzyl-, and *o*-phenylbenzoyl peroxides have been studied in carbon tetrachloride in the presence and absence of iodine and iodine plus water (Tables I–IV). In carbon tetrachloride alone, for the *o*-methyl compound the ratio of decarboxylation to intramolecular hydrogen transfer is 2.5 to 1. The radical derived from hydrogen transfer undergoes cross-termination with the trichloromethyl radical and like-termination. In the *o*-benzyl compound intramolecular hydrogen transfer occurs to the exclusion of decarboxylation or attack on the adjacent ring. In the *o*-phenyl compound decarboxylation occurs to the extent of 26% and, in confirmation of previous reports,[3,4] intramolecular aromatic substitution is an important process (38% yield of 3,4-benzcoumarin, IX). Decompositions of the peroxides in carbon tetrachloride in the presence of iodine and water result in substantial increases in yields of the corresponding acids, suggestive of the ability of the scavenger to compete with the intramolecular reactions.

Of the many detailed investigations of diacyl peroxides[1] little attention has been directed toward the *ortho*-substituted benzoyl peroxides.[2–4] The possibilities of intramolecular reaction that members of this class offer and the information that might be obtained thereby with respect to competition between intra- and intermolecular processes has prompted the present study of the decomposition of *o*-methyl-, *o*-benzyl-, and *o*-phenylbenzoyl peroxide.

RESULTS

The *o*-substituted benzoyl peroxides employed in this study were subjected to thermal decomposition principally under three sets of conditions: a) in carbon tetrachloride; b) in carbon tetrachloride containing iodine; c) in carbon tetrachloride, iodine and water. The data are summarized in Tables I–III. The assignment of structure to *o*-(β,β,β-trichloroethyl)benzoic acid (Table I) is based on conversion to homophthalic acid by hydrolysis under strongly acidic conditions and dehydrochlorination with base to give a compound of the expected analysis and ultraviolet absorption spectrum for *o*-(β,β-dichlorovinyl)benzoic acid. The characterization of the high melting acid frac-

TABLE I

PRODUCTS OF DECOMPOSITION OF *o*-TOLUOYL PEROXIDE AT 80°

	Yield in Moles per Mole of Peroxide		
Products	Carbon tetrachloride[a]	Carbon tetrachloride,[a] iodine[b]	Carbon tetrachloride,[a] iodine and water
Carbon dioxide	1.2[c]		
Hexachloroethane	.67		
o-Chlorotoluene	1.1		
o-Iodotoluene		.98	.07
o-Cresyl *o*-toluate	.04	.02	.02
Phthalide	.1	.2	.08
o-Toluic acid		.48	1.7
o-(β,β,β-Trichloroethyl)-benzoic acid	.44		
1,2-Di-*o*-carboxyphenylethane	.04		

[a] Initial peroxide concn., 0.055*M*. [b] Initial iodine concn., 0.25*M*. [c] Average of three determinations: 1.14, 1.19, 1.38.

TABLE II

PRODUCTS OF DECOMPOSITION OF *o*-BENZYLBENZOYL PEROXIDE AT 80°

	Yield in Moles per Mole of Peroxide			
Product	Benzene[a]	Carbon tetrachloride[a]	Carbon tetrachloride[a] and iodine[b]	Carbon tetrachloride,[a] iodine[b] and water
o-Benzylbenzoic acid	0.66	0.64	0.99	1.2
3-Phenylphthalide	.62	.66	.89	.75
1,2-Di-*o*-carboxyphenyl-1,2-diphenylethane[c]	.35	.34		

[a] Initial peroxide concn., 0.036*M*. [b] Initial iodine concn., 0.35*M*. [c] Mixture of *meso* and *dl* material.

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[1] (a) C. Walling, *Free Radicals in Solution*, John Wiley and Sons, Inc., New York, N. Y., 1957, Ch. 10. (b) E. L. Eliel, S. Meyerson, Z. Welvart, and S. H. Wilen, *J. Am. Chem. Soc.*, **82**, 2936 (1960), and references cited therein.

[2] (a) W. Cooper, *J. Chem. Soc.*, 3106 (1951); 2408 (1952). (b) A. T. Blomquist and A. J. Buselli, *J. Am. Chem. Soc.*, **73**, 3883 (1951). (c) D. F. DeTar and A. Hlynsky, *J. Am. Chem. Soc.*, **77**, 4411 (1955). (d) J. E. Leffler, R. D. Faulkner, and C. C. Petropoulas, *J. Am. Chem. Soc.*, **80**, 5435 (1958).

[3] G. W. Kenner, M. A. Murray, and C. M. B. Tylor, *Tetrahedron*, **1**, 259 (1957).

[4] D. B. Denney and P. P. Klemchuk, *J. Am. Chem. Soc.*, **80**, 3289 (1958).

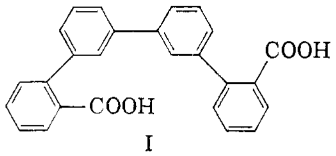
TABLE III

PRODUCTS OF DECOMPOSITION OF *o*-PHENYLBENZOYL PEROXIDE AT 80°[a]

	Yield in Moles per Mole of Peroxide	
Products	Carbon tetrachloride	Carbon tetrachloride, iodine, and water
Carbon dioxide	0.53	
o-Chlorobiphenyl	0.39	
3,4-Benzcoumarin	0.77 (0.49[b])	0.88
o-Phenylbenzoic acid	0.18 (0.31[b])	0.84
"Dimeric acid"	0.05	
Fractions A, B, and C	(0.2)	

[a] Initial peroxide concn., 0.017*M*. [b] Data of Kenner, Murray and Tylor, ref. 3.

tion from *o*-benzylbenzoyl peroxide as a mixture of *meso*- and *dl*-1,2-di-*o*-carboxyphenyl-1,2-diphenylethane (Table II) is based on the conversion of the mixture to the corresponding *meso*- and *dl*-dimethyl esters, separation of the esters into the two pure components (possessing markedly similar infrared spectra but differing in melting point), and establishment of the identity of the higher melting diester with the major product obtained from the decomposition of di-*t*-butyl peroxide in the presence of methyl *o*-benzylbenzoate by the Kharasch coupling reaction.[5] The major product of the decomposition of *o*-phenylbenzoyl peroxide, 3,4-benzcoumarin, has been reported by two groups[3,4] since the start of this work. The materials referred to in Table III as dimeric acid and Fractions A, B and C were not obtained in pure form. The principal component of the dimeric acid is considered to be 3,3′-(di-*o*-carboxyphenyl)biphenyl (I) on the basis of the marked similarity in infrared spectrum to *o*-phenylbenzoic acid, the probable mode of formation, and decarboxylation to a material exhibiting a prominent mass spectral peak at mass number 306, the expected parent peak for a quaterphenyl. Fractions A, B, and C are halogen-containing mixtures showing absorption in the infrared characteristic of acids (Fraction A) and of lactones of the 3,4-benzocoumarin type (Fractions B and C). A search for hexachloroethane in the products of decomposition of *o*-phenylbenzoyl peroxide failed to reveal any of this material. Vapor phase chromatographic control experiments showed that it would have been detected if present at a level above 0.02 mole per mole of peroxide. Vapor phase chromatography likewise failed to reveal the presence of biphenyl.



I

The negligible amount of carbon dioxide from the decomposition of *o*-benzylbenzoyl peroxide prompted the examination of the extent of decarboxylation in the decomposition of *p*-benzylbenzoyl peroxide. Decomposition in carbon tetrachloride at 80° afforded carbon dioxide (1.06 moles per mole of peroxide), hexachloroethane, *p*-chlorodiphenylmethane (0.98 mole per mole of peroxide), *p*-benzylbenzoic acid (0.2 mole per mole of peroxide), and two unidentified fractions. Vapor phase chromatographic analysis failed to reveal diphenylmethane in the *p*-chlorodiphenylmethane fraction.

The rates of decomposition of the peroxides in carbon tetrachloride were measured at concentrations approximating those of the product studies, both in the presence and absence of styrene.[6] The data are summarized in Table IV. The rates of the *ortho*-substituted peroxides are within a factor of three and all are several-fold faster than benzoyl peroxide. Of the benzoyl peroxides reported by Blomquist and Buselli substitution in the *ortho*-position (*o*-methoxy, *o*-nitro, *o*-phenoxy, *o*-chloro, and *o*-methyl) resulted in an increase in rate of decomposition, measured in acetophenone solution. Substitution in the *meta*- and *para*-positions in general produces a smaller effect on rate[2b,6] (ρ of −0.38 in dioxane at 80°).[6] Comparison of the rates in the presence and absence of styrene in this study is suggestive of the absence of induced decomposition in the isolation experiments employing *o*-benzyl- and *o*-phenylbenzoyl peroxide and of 15–20% induced decomposition in the experiments with *o*-phenylbenzoyl peroxide and of 15–20% induced decomposition in the experiments with *o*-methyl- and *p*-benzylbenzoyl peroxide.

TABLE IV

DECOMPOSITION OF SUBSTITUTED BENZOYL PEROXIDES IN CARBON TETRACHLORIDE AT 80°

Substituent	Initial Concn., *M*	Styrene Concn., *M*	Carbon Dioxide Evolution, %[a]	$k_1 \times 10^4$, Sec.$^{-1}$
Hydrogen	0.017	[b]	90[c]	0.30[b]
o-Methyl	0.055	0	~60	1.15
	0.049	1.0		1.0
o-Benzyl	0.033	0	trace	1.34
	0.010	0		1.31
	0.037	1.0		1.34
p-Benzyl	0.007	0	53	2.9
	0.014	0.2		2.4
o-Phenyl	0.019			2.1
	0.017		26	2.0
	0.016	1.0		2.5
	0.015	1.0		2.6

[a] Based on two moles per mole of peroxide. [b] Ref. 6, rate measured in the presence of 3,4-dichlorostyrene. [c] Ref. 8.

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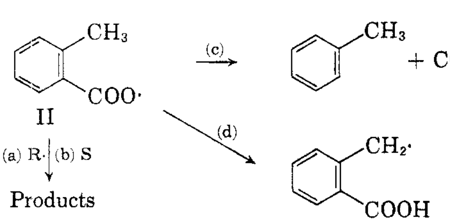
[5] M. S. Kharasch, H. C. McBay, and W. H. Urry, *J. Org. Chem.*, 10, 401 (1945).

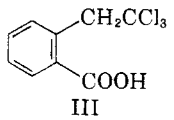
[6] C. G. Swain, W. H. Stockmayer, and J. T. Clarke, *J. Am. Chem. Soc.*, 72, 5426 (1950).

DISCUSSION

The rate-determining step in the thermal decomposition of benzoyl peroxide has been shown to be homolytic fission of the oxygen-oxygen bond[7] since decomposition in carbon tetrachloride in the presence of iodine and water (proceeding at the same rate as in carbon tetrachloride alone) afforded a high yield of benzoic acid, *i.e.*, capture of carboxylate radical by iodine followed by hydrolysis of the acyl hypoiodite to acid. DeTar and Lamb recently have confirmed this result[8] and have extended the technique to the problem of determination of multiple bond cleavage in the rate-determining step of decomposition of δ-phenylvaleroyl peroxide. The high yields of acid obtained by subjection of the *ortho*-substituted peroxides of this study to the conditions of Hammond and Soffer may be interpreted in the same way, *viz.* oxygen-oxygen fission in the rate-determining step, assuming that here also the rates of decomposition are independent of the iodine and water.

Following rate-determining fission of the oxygen-oxygen bond in *o*-toluoyl peroxide, four possibilities are open to the radical II: a) termination reactions, b) reactions with scavengers, c) decarboxylation, and d) hydrogen transfer to afford the *o*-carboxybenzyl radical. From the decomposition in carbon tetrachloride in the presence of iodine and water *o*-toluic acid was obtained in 85% yield. The capture of II by iodine of initial concentration 0.25*M* indicates that this process is occurring at a time later than that required for primary[9] (cage) reaction, and thus indicates that the decarboxylation and hydrogen transfer observed in the absence of scavengers must occur principally after separation of the original radical partners. The phthalide isolated from the iodine-water experiments sets an upper limit of 4% on the extent of hydrogen transfer within the solvent cage. In the absence of added scavengers, decarboxylation and hydrogen transfer account for 90% of radical II, with the former process proceeding approximately two and one-half times faster than the latter. In comparison, decomposition of benzoyl peroxide in *toluene* at 84° results in 74–77% decarboxylation and in benzene at 80° in 80–86% decarboxylation.[8] If one attributes the 8% decrease in decarboxylation in toluene *vs.* benzene to abstraction of benzyl hydrogen by benzoate, one obtains a ratio of rate of decarboxylation to hydrogen transfer (intermolecular analog of path d) of ten to one, suggestive of a small (several-fold) advantage for the intramolecular reaction over the intermolecular counterpart. That the advantage is not larger may be associated with the geometry of the transition state for the intramolecular hydrogen transfer which would appear to be unfavorable for stabilization by the ring π electrons of the developing benzyl radical, a restriction that obviously does not apply to the intermolecular case. The principal fate of the *o*-methylphenyl radical, formed by loss of carbon dioxide from II, is chain transfer with the solvent to give *o*-chlorotoluene and the trichloromethyl radical. The correspondence in yield of *o*-chlorotoluene with yield of carbon dioxide indicates that intramolecular hydrogen transfer within the *o*-methylphenyl radical to give the benzyl radical, if operative at all, is unimportant. The *o*-carboxybenzyl radical derived from hydrogen transfer in II appears to be of sufficient stability to achieve statistical distribution and is ultimately consumed by cross-termination with the trichloromethyl radical giving *o*-(β,β,β-trichloroethyl)benzoic acid(III) and like-termination giving 1,2-di-*o*-carboxyphenylethane (IV). In the presence of iodine the *o*-chlorotoluene is replaced by a comparable amount of *o*-iodotoluene, and some *o*-toluic acid is formed. The latter may be attributed to hydrolysis of acyl hypoiodite by adventitious moisture. Under all of the conditions of Table I a constant, small amount (2–4%) of *o*-cresyl *o*-toluate is obtained, attributed to cyclic ester formation or cage reaction.





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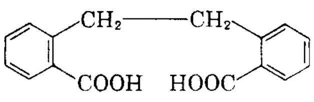
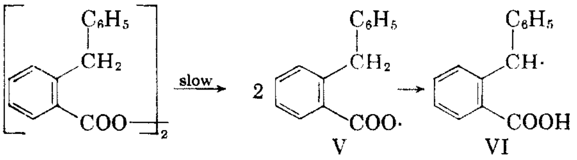


IV

The principal feature of the decomposition of *o*-benzylbenzoyl peroxide (Table II) is the cleanness of the reaction. The increased lability of the benzhydryl hydrogen (over benzyl hydrogen, compare Tables I and II) results in hydrogen transfer to the exclusion of decarboxylation. The four products obtained in this decomposition, accounting for over 95% of the peroxide, are easily derivable from termination reactions of radical VI: disproportionation to give equal amounts of 3-phenylphthalide and *o*-benzylbenzoic acid; recombination to give *meso*- and *dl*-1,2-di-*o*-carboxy-



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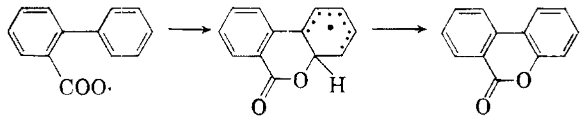
[7] G. S. Hammond and L. M. Soffer, *J. Am. Chem. Soc.*, **72**, 4711 (1950).

[8] D. F. DeTar and R. C. Lamb, *J. Am. Chem. Soc.*, **81**, 122 (1959).

[9] R. M. Noyes, *J. Am. Chem. Soc.*, **77**, 2042 (1955).

phenyl-1,2-diphenylethane.[10] The increase in yield of *o*-benzylbenzoic acid from decomposition of the peroxide in carbon tetrachloride in the presence of iodine and water indicates that efficient scavengers can compete with the hydrogen transfer reaction and points to capture of a minimum of 60% of V by iodine. (The 37% of 3-phenylphthalide from this experiment probably is derived from capture of VI by iodine followed by conversion to the lactone although conceivably some of the lactone might arise from the acyl hypoiodite of V.) The increase in yield of acid under these conditions may be interpreted in terms of hydrogen transfer occurring later than the time required for a cage reaction and indicates that the hydrogen transfer is intramolecular rather than intermolecular. Further evidence in favor of intramolecular hydrogen transfer within radical V, the inherently more attractive path, is found in the greatly reduced importance of hydrogen transfer in the decomposition of *p*-benzylbenzoyl peroxide in which substantial amounts of carbon dioxide are evolved in spite of the availability to intermolecular abstraction processes of benzhydryl hydrogen.

The product data for *o*-benzylbenzoyl peroxide indicate abstraction of hydrogen in preference to attack on the neighboring aromatic ring. *o*-Phenylbenzoyl peroxide[3,4] represents a case in which the principal choices available to the carboxylate radical are attacked on the adjacent aromatic ring or decarboxylation. The importance of the former path is reflected in the isolation of 3,4-benzcoumarin (IX) in 36% yield, in confirmation of the results of Kenner, Murray, and Tylor,[3] and of Denney and Klemchuk,[4] and in the decreased extent of decarboxylation in this system. The observation of 80–86% decarboxylation of benzoyl peroxide in *benzene*[8] *vs.* 26% decarboxylation of *o*-phenylbenzoyl peroxide in carbon tetrachloride indicates an advantage for the intramolecular process over the intermolecular counterpart. The absence of hexachloroethane from the product mixture and the complexity of this mixture are suggestive that radical VIII or, alternatively, the *pi* complex related to VIII is formed to an important extent and is of moderate stability, ultimately disappearing by disproportionation (formation of 3,4-benzcoumarin), by cross-termination reactions with trichloromethyl radical (Fractions A, B, C) generated in the formation of the *o*-chlorobiphenyl and by like termination reactions leading to a large number of possible products (including dimeric acid I). Of the 2-biphenylyl radicals derived from decarboxylation of *o*-phenylbenzoate radicals, two-thirds are converted to *o*-chlorobiphenyl by chain transfer with the solvent, leaving a maximum of one third that may be consumed *via* an intramolecularly complexed species. Decomposition of the peroxide in carbon tetrachloride in the presence of iodine and water affords a small increase in yield of 3,4-benzcoumarin (44% *vs.* 36%) and a large increase in yield of *o*-phenylbenzoic acid (42% *vs.* 9% in carbon tetrachloride alone) indicative of the occurrence in the absence of added scavengers of decarboxylation after separation of the original radical partners, in agreement with the other *o*-substituted cases of this study.



VIII IX

The possible formation of VIII to the extent of 74% (based on the observation of 26% decarboxylation) and destruction by paths in addition to the one leading to formation of lactone IX (36%) further complicates interpretation of the isotope effect, k_H/k_D, of 1.32 observed in the conversion of 2-(2-deuterophenyl)benzoyl peroxide[4] to the (partially) deuterium-labeled 3,4-benzcoumarin and consideration of the related question of reversibility in the formation of VIII from the carboxylate radical.

The decomposition of *o*-phenoxybenzoyl peroxide to yield phenyl salicylate[2c] may represent a case exhibiting the further possibility of association of carboxylate radical with the aryl carbon attached to the oxygen, resulting in over-all phenyl migration, a process that also appears to be operative in the conversion of silver 3,3,3-triphenylpropionate to phenyl 2,2-diphenylacrylate by the action of bromine in carbon tetrachloride.[11]

It is of interest to compare the data of the diaroyl peroxides of this study with the diacyl peroxides, δ-phenylvaleroyl peroxide,[12,8] and ε-phenylcaproyl peroxide.[13] In these cases a substantial percentage of the products appears to arise from cage (and/or cyclic) reactions. The carboxylate radicals that escape cage reaction undergo decarboxylation.[14] Although intramolecular hy-

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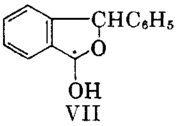
[10] Conversion of VI to VII is a further possibility but such a formulation is neither required by the data nor able to account as satisfactorily for the formation of the coupling product of VI.



VII

A comparison at equal radical concentrations of the efficiency toward polymerization of styrene of *o*-benzylbenzoyl peroxide *vs.* benzoyl peroxide indicates that the former is about half as efficient as the latter.

[11] J. W. Wilt and D. D. Outhoudt, *J. Org. Chem.*, **23**, 218 (1958).

[12] D. F. DeTar and C. Weis, *J. Am. Chem. Soc.*, **78**, 4296 (1956).

[13] C. A. Grob and H. Kammüller, *Helv. Chim. Acta*, **40**, 2139 (1957).

[14] For thermochemical evidence on the greater exothermicity of carbon dioxide loss from alkylcarboxylate than from arylcarboxylate, see L. Jaffe, E. J. Prosen, and M. Szwarc, *J. Chem. Phys.*, **27**, 416 (1957).

drogen transfer apparently cannot compete with decarboxylation in these cases, intramolecular reactions may occur within the resulting primary carbon radicals, as seen in the isolation of tetralin in 30% yield from the decomposition of δ-phenylvaleroyl peroxide in benzene[12] and of 5,6-diphenyldecane in 14% yield from the decomposition of ε-phenylcaproyl peroxide.[13,15]

EXPERIMENTAL

o-Toluic acid was prepared by carbonation of the Grignard reagent derived from *o*-bromotoluene (Eastman white label). Recrystallization from benzene-hexane afforded material, m.p. 104–105° (lit. m.p. 104–105°).

o-Toluoyl peroxide was prepared by the general method[16] of Price and Krebs utilizing ether instead of toluene as solvent for the *o*-toluoyl chloride (prepared from the acid and thionyl chloride and distilled before use). Recrystallization of the crude product from ethanol afforded *o*-toluoyl peroxide as colorless needles, m.p. 54.5–55° (lit.,[2b] m.p. 52.5–53.5°) in a yield of 78%.

o-Cresyl o-toluate was prepared by reaction of *o*-toluoyl chloride and *o*-cresol in ethyl ether containing an equivalent of pyridine. After 16 hr. at 25° the mixture was filtered, the ether was washed three times with dilute hydrochloric acid, three times with dilute sodium hydroxide solution, with water and dried over magnesium sulfate. Filtration, removal of the ether, and distillation of the residue afforded the ester, b.p. 135–136° at 1 mm., n_D^{27} 1.5651.

Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.80; H, 6.40.

Decomposition of o-toluoyl peroxide (*See* Table I). A. *In carbon tetrachloride.* A 6.0-g. sample (22 mmoles) of the peroxide in 400 ml. of carbon tetrachloride was placed in a flask equipped with a gas inlet tube and condenser. The top of the condenser was connected to a trap and this in turn to a gas washing bottle, protected from the atmosphere by an Ascarite-filled tube, containing a standardized barium hydroxide solution. The peroxide solution was swept with nitrogen for 1 hr. with the barium hydroxide bottle disconnected. The bottle then was connected, the nitrogen flow was decreased, and the peroxide solution was heated at reflux for 20 hr. Carbon dioxide yield, determined by titration of the excess hydroxide in the barium hydroxide solution by standard perchloric acid, was 26.1, 25.1, 30.4 mmoles in three decompositions.

One half of the carbon tetrachloride solution was reduced to dryness through a 20-inch Vigreux column. The residue was treated with pentane, filtered from a small amount of 1,2-di-*o*-carboxyphenylethane (see below), and chromatographed on a silica gel column in pentane. The first compound eluted by pentane was hexachloroethane, 1.05 g. Recrystallization from ligroin afforded material, m.p. 188–189° (sealed tube); mixed melting point showed no depression. The second component eluted by pentane was *o*-chlorotoluene, 0.64 g., n_D^{20} 1.5247 (lit. n_D^{20} 1.5247) of identical infrared spectrum with an authentic sample. From a control experiment with hexachloroethane and *o*-chlorotoluene, 60% of the former and 33% of the latter were reisolated in pure form by the above procedure. Elution with pentane-ether (10:1) afforded 0.11 g. of *o*-cresyl *o*-toluate, identical in infrared spectrum with that of the authentic sample. Elution with pentane-ether (5:1) yielded 1.2 g. of an acid, *o*-(β,β,β,-trichloroethyl)benzoic acid contaminated with a small amount of phthalide. Recrystallization from ligroin afforded the pure acid, m.p. 113–114°.

Anal. Calcd. $C_9H_7O_2Cl_3$: C, 42.64; H, 2.78; Cl, 41.97; neut. equiv. 254. Found: C, 42.44, 42.70; H, 2.80, 3.19; Cl, 41.42, 41.93; neut. equiv., 251.

A 350-mg. sample of this acid was added to 1 ml. of concd. sulfuric acid and heated on a steam bath for 1 hr. Six milliliters of water was added and heating was continued for 1 hr. The solution was cooled to room temperature and extracted with benzene. Upon cooling the aqueous solution to 0°, crystals separated. One recrystallization from water afforded 200 mg. of homophthalic acid, m.p. 175° (lit.,[17] m.p. 175°). The infrared spectrum was identical in all respects with an authentic sample of homophthalic acid prepared from indene.

Elution of the silica gel column with pentane-ether (1:1) afforded 0.12 g. of 1,2-di-*o*-carboxyphenylethane. Recrystallization from 95% ethanol gave material, m.p. 228–230° (lit.,[18] m.p. 231°). The diacid was esterified with diazomethane and the dimethyl ester was recrystallized from methanol yielding material, m.p. 99–100° (lit.,[18] m.p. 100°).

The second half of the original carbon tetrachloride solution of the peroxide decomposition was heated under reduced pressure to remove solvent and the bulk of the hexachloroethane and *o*-chlorotoluene. Treatment of the residue with petroleum ether (b.p. 30–60°) afforded 0.11 g. of a colorless solid, crude 1,2-di-*o*-carboxyphenylethane, m.p. 180–220°, raised to m.p. 225–229° by recrystallization from ethanol. The petroleum ether filtrate was chromatographed on alumina. Elution with benzene-ether (7:1) afforded 0.16 g. of phthalide, m.p. 73–74° after recrystallization from ligroin (b.p. 90–100°); mixture melting point with an authentic sample gave no depression and infrared spectra were identical.

B. *In benzene.* Analysis was made only for 1,2-di-*o*-carboxyphenylethane. A 2.2-g. sample of *o*-toluoyl peroxide in 40 ml. of benzene was heated at reflux for 24 hr. during which time a small amount of precipitate appeared. The mixture was cooled, filtered, giving a residue of 109 mg. of 1,2-di-*o*-carboxyphenylethane, m.p. 231–232°.

C. *In carbon tetrachloride containing iodine.* A solution of 6 g. of *o*-toluoyl peroxide and 25 g. of iodine in 400 ml. of carbon tetrachloride was heated at reflux for 17 hr. The solution was cooled and the supernatant liquid was decanted from the precipitated iodine. Excess iodine was destroyed by extraction of the cooled solution with sodium bisulfite solution. The dried carbon tetrachloride layer was reduced to a small volume, diluted with petroleum ether (b.p. 30–60°) and chromatographed on silica gel. Elution with petroleum ether afforded 3.59 g. of *o*-iodotoluene, n_D^{20} 1.6030 (lit. n_D^{20} 1.6085), identical in infrared spectrum with authentic material. A control experiment identical in procedure to the actual product isolation indicated 80% recovery of *o*-iodotoluene. Elution with petroleum ether–ether (100:1) afforded 0.1 g. of *o*-cresyl *o*-toluate. Elution with petroleum-ether–ether (10:1) afforded 1.3 g. of *o*-toluic acid, m.p. 104–105°, mixed m.p. 104–105°. Elution with pet. ether–ether (5:1) afforded 0.28 g. of a compound, m.p. 122–128°, that was not identified. (Sublimation afforded material, m.p. 135–136°.) Elution with petroleum ether–ether (4:1) afforded 0.62 g. of phthalide, m.p. 72–73°; mixed melting point showed no depression.

D. *In carbon tetrachloride containing iodine and water.* A mixture of 3 g. of *o*-toluoyl peroxide, 27 g. of iodine, 75 ml. of water, and 200 ml. of carbon tetrachloride was heated at reflux for 20 hr. Excess iodine was destroyed by extraction with bisulfite solution. The bisulfite solution was extracted with ether and the combined ether–carbon tetrachloride

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(15) For examples of related intramolecular aromatic substitution reactions, see S. Winstein, R. Heck, S. Lapporte, and R. Baird, *Experientia*, **12**, 138 (1956); see also D. B. Denney and P. P. Klemchuk (ref. 4).

(16) C. C. Price and E. Krebs, *Org. Syntheses*, Coll. Vol. III, 649 (1955).

(17) O. Grummitt, R. Egan, and A. Buck, *Org. Syntheses*, Coll. Vol. III, 449 (1955).

(18) C. Fischer and R. Wolffenstein, *Chem. Ber.*, **37**, 3219 (1904).

phases were extracted with sodium hydroxide solution. Acidification with hydrochloric acid, extraction of the aqueous phase with ether, drying of the ether phase over magnesium sulfate, filtration, and removal of the ether afforded 2.6 g. of *o*-toluic acid, m.p. 103–104°; mixture melting point showed no depression.

o-(β,β-Dichlorovinyl)benzoic acid. A 400-mg. sample of *o*-(β,β,β-trichloroethyl)benzoic acid, 1 g. of potassium hydroxide, and 30 ml. of 95% ethanol was heated on a steam bath for 0.5 hr. Dilution with water and acidification with hydrochloric acid gave a solid. Recrystallization from isooctane afforded 200 mg., m.p. 117–118°, λ^{250}_{max} in ethanol ($\epsilon = 8{,}040$), λ^{290} ($\epsilon = 2{,}250$).

Anal. Calcd. for $C_9H_6O_2Cl_2$: C, 49.81; H, 2.78; Cl, 32.66. Found: C, 50.03; H, 2.63; Cl, 32.95.

o-Benzylbenzoic acid was prepared by the reduction of *o*-benzoylbenzoic acid according to the procedure of Barnett, Cook, and Nixon,[19] m.p. 115–117° (lit.,[19] m.p. 118°).

o-Benzylbenzoyl peroxide. To a solution of 30 g. of *o*-benzylbenzoic acid in 100 ml. of anhydrous ethyl ether was added 6 ml. of pyridine followed by the slow addition of 15 ml. of thionyl chloride with stirring (magnetically). The mixture was stirred for 3 hr. at room temperature and filtered to remove the pyridine hydrochloride. Removal of the ether under reduced pressure afforded a light yellow oil, *o*-benzylbenzoyl chloride. This liquid was dissolved in 150 ml. of petroleum ether, (b.p. 30–60°). After standing at room temperature for 30 min. the solution was filtered to remove a small amount of insoluble matter and cooled to −80°, resulting in the separation of the acid chloride as a semi-solid mass. When the acid chloride was needed, the petroleum ether layer was decanted and the acid chloride was dissolved in 120 ml. of ether. To this ether solution was added 6 g. of sodium peroxide and 10 drops of water. The mixture was stirred for 6 hr. at 0° during which time 1 ml. of water was added. The mixture was filtered and the filtrate was evaporated to dryness under reduced pressure. The colorless residue was dissolved in 50 ml. of chloroform and poured into 250 ml. of methanol with stirring, resulting in the slow precipitation of needles, 18 g. The 18-g. sample was dissolved in 20 ml. of chloroform, added to 100 ml. of methanol and cooled, yielding 16 g. (53% yield based on acid), m.p. 72.5–73°.

Anal. Calcd. for $C_{28}H_{22}O_4$: C, 79.60; H, 5.25. Found: C, 79.41; H, 5.07. Iodometric analysis indicated a purity of 99 ± 1%.

Decomposition of o-benzylbenzoyl peroxide (see Table II). Description of decomposition in carbon tetrachloride is reported in detail. Data on decomposition in benzene, in carbon tetrachloride and iodine, in carbon tetrachloride in the presence of iodine and water are summarized in Table II. Product isolations were made by the procedure described below and those described under *o*-toluoyl peroxide.

In carbon tetrachloride. A 12-g. sample of *o*-benzylbenzoyl peroxide in 800 ml. of carbon tetrachloride was decomposed at reflux temperature under slow nitrogen flow for 20 hr. as described above for *o*-toluoyl peroxide. A white precipitate appeared in the carbon tetrachloride solution as the reaction progressed. The yield of carbon dioxide was negligible. The carbon tetrachloride reaction mixture was cooled and filtered affording a residue of 4.2 g. This material was dissolved in sodium carbonate solution and reprecipitated by hydrochloric acid, 4.1 g. dec. p. 270–290°, insoluble in methanol or benzene, fairly soluble in acetone. The acid gave analyses corresponding to 1,2-di(*o*-carboxyphenyl)-1,2-diphenylethane, a mixture of the *meso* and *dl* modifications.

Anal. Calcd. for $C_{28}H_{22}O_4$: C, 79.60; H, 5.25; neut. eq., 211. Found: C, 79.32; H, 5.29; neut. eq., 222.

A 2.0-g. sample of the acid was esterified with diazomethane. Repeated recrystallizations from methanol-benzene gave a dimethyl ester, m.p. 207–207.5°.

Anal. Calcd. for $C_{30}H_{26}O_4$: C, 79.98; H, 5.82. Found: C, 80.01; H, 5.96.

The infrared spectrum of this material was identical with the material prepared by use of the Kharasch coupling reaction[5] on methyl *o*-benzylbenzoate (see below). From the mother liquors a second isomer was obtained, m.p. 143–145°, markedly similar in infrared spectrum to the 207° compound.

Anal. Calcd. for $C_{30}H_{26}O_4$: C, 79.98; H, 5.82. Found: C, 79.77; H, 6.00.

One half of the original carbon tetrachloride filtrate from the peroxide decomposition was reduced to dryness under reduced pressure, dissolved in ether, and extracted with aqueous sodium hydroxide solution. Acidification afforded 2.0 g. of crude *o*-benzylbenzoic acid, identical in infrared spectrum to authentic material. Reprecipitation and recrystallization from acetic acid gave material, m.p. 114–117°, mixed melting point with authentic sample 115–117°. The ether solution from which the *o*-benzylbenzoic acid had been extracted was dried over magnesium sulfate, filtered, and evaporated leaving 1.95 g., m.p. 110–115°, of crude 3-phenylphthalide of identical infrared spectrum with authentic material. Recrystallization from 95% ethanol gave material, m.p. 114–115°; mixture melting point with an authentic sample of 3-phenylphthalide[20] gave no depression.

Subjection of a portion of the original decomposition solution (after removal of the dimeric acid by filtration) to chromatography on silica gel afforded only the same two products reported above, *o*-benzylbenzoic acid and 3-phenylphthalide.

1,2-Di(o-carbomethoxyphenyl)-1,2-diphenylethane. A solution of 8.6 g. of methyl *o*-benzylbenzoate (b.p. 167–170° at 10 mm., lit.,[19] b.p. 320° at 760 mm., prepared by Fischer esterification of the corresponding acid) and 6.0 g. of di-*t*-butyl peroxide was heated at 125° for 52 hr. Repeated recrystallizations of the residue from acetone afforded 3.5 g. (40% yield) of material, m.p. 204–205°, identical in infrared spectrum with the diester derived from the diacid isolated from the peroxide decomposition above, mixture m.p. 204–206°.

Reaction of silver o-benzylbenzoate with iodine. A 175-ml. portion of carbon tetrachloride was distilled from phosphorus pentoxide into a flask containing 10 g. of silver *o*-benzylbenzoate (prepared by the usual procedure—addition of aqueous silver nitrate solution to an aqueous solution of the acid at *p*H of 9, followed by filtration, washing, and rigorous drying of the silver salt). An 8-g. sample of iodine was added and the mixture was heated at reflux for 17 hr. The mixture was filtered and excess iodine was destroyed by extraction of the filtrate by sodium bisulfite solution. From the filtrate was isolated 1.0 g. of 3-phenylphthalide and 3.3 g. of *o*-benzylbenzoic acid by the procedure described above.

Effectiveness of o-benzylbenzoyl peroxide in polymerization of styrene. A 0.044-g. sample of the peroxide was dissolved in 25 ml. of freshly distilled styrene. To a second 25-ml. portion of styrene was added 0.145 g. of benzoyl peroxide. To a third flask was added 25 ml. of styrene alone. The solutions were heated for 1 hr. at 80°, cooled, and poured into 200 ml. of methanol. The polystyrene (softening point 125–165°) obtained from the sample of pure styrene, the benzoyl peroxide–initiated sample and the *o*-benzylbenzoyl peroxide–initiated sample amounted to 0.1 g., 4.6 g., and 2.1 g., respectively. In conjunction with the first order rate constants for decomposition of these two peroxides (see Table IV), the polystyrene yields indicate that *o*-benzylbenzoyl peroxide is approximately half as effective as benzoyl peroxide in initiating the polymerization of styrene.

o-Phenylbenzoic acid was prepared from fluorenone by

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[19] E. de B. Barnett, J. W. Cook, and I. G. Nixon, *J. Chem. Soc.*, 508 (1927).

[20] F. Ullmann, *Ann.*, 291, 23 (1896).

the procedure of Gutsche and Johnson,[21] m.p. 112–113° (lit.[21] m.p. 110–113°).

o-Phenylbenzoyl chloride was prepared by the action of thionyl chloride on the acid. Distillation afforded material, b.p. 99.5–101° at 0.3 mm. (lit.,[22] b.p. 169° at 16 mm.). Some closure to fluorenone occurs during distillation (weak carbonyl absorption in the infrared at 1728 cm.$^{-1}$).

o-Phenylbenzoyl peroxide was prepared by the general procedure of Price and Krebs.[16] The toluene solution of product was taken to a residual oil under reduced pressure. The oil solidified on treatment with pentane. Recrystallization from benzene–petroleum ether (b.p. 30–60°) afforded material of dec. p. 101.5–102.5° (lit.,[3,4] dec. p. 107–108°).

Anal. Calcd. for $C_{26}H_{18}O_4$: C, 79.17; H, 4.60. Found: C, 79.27; H, 4.65.

Decomposition of o-phenylbenzoyl peroxide in carbon tetrachloride (Table III). A 1-g. sample of the peroxide in 150 ml. of carbon tetrachloride was decomposed under slow nitrogen flow for 21 hr. at reflux temperature as described above for *o*-toluoyl peroxide. Carbon dioxide yield amounted to 0.53 mole per mole of peroxide. (A duplicate run gave the same value: 0.53 mole.) Concentration of the carbon tetrachloride solution through a 20-inch Vigreux column to a small volume and cooling afforded 0.05 g. of base-soluble material, referred to below as dimeric acid, dec. p. 282–286°. Extraction of the carbon tetrachloride solution with sodium bicarbonate and acidification with hydrochloric acid afforded 0.09 g. of crude *o*-phenylbenzoic acid. Two reprecipitations from an alkaline solution by acid yielded material, m.p. 110–113°, mixed m.p. 110–113°. The carbon tetrachloride solution of the remaining products of decomposition of the peroxide was chromatographed on 25 g. of acid-washed alumina eluting with carbon tetrachloride. The first fraction solidified on standing, 0.15 g. *o*-chlorobiphenyl. Recrystallization from petroleum ether (b.p. 30–60°) gave material, m.p. 33–34°, mixed melting point with authentic material 33–34° (lit., m.p. 32°). Vapor phase chromatography of a portion of the crude material gave a small peak (carbon tetrachloride) and a large peak (*o*-chlorobiphenyl). No bands ascribable to hexachloroethane or to biphenyl were present. The second fraction, eluted with carbon tetrachloride–ether (50 to 1), was 0.29 g. of crude 3,4-benzcoumarin. Three recrystallizations from petroleum ether afforded material (prepared by the procedure of Graebe and Schestakow, lit.,[23] m.p. 92.5°), m.p. 92–94°.

From a parallel experiment employing 10 g. of peroxide were obtained three additional fractions (A, B and C) corresponding to 17% of the peroxide by weight. Extraction of the carbon tetrachloride solution with bicarbonate afforded a third layer at the interface which was separated, dissolved in methanol-water, and acidified affording 0.9 g. of precipitate, Fraction A. Repeated recrystallizations failed to give a pure material: broad decomposition range, 143–147°; poorly defined infrared spectrum with broad absorption at 1710 cm.$^{-1}$.

Anal. Found: C, 67.05; H, 4.01; Cl, 14.82. Chromatography of the dried carbon tetrachloride solution afforded, in addition to the fractions described above, Fraction B, 0.57 g., eluted with ether and Fraction C, 0.3 g. eluted with ether-methanol (10:1). Repeated recrystallizations of Fractions B and C afforded samples of dec. p. 140–144° and 161–164° respectively, poorly defined infrared spectra with broad absorption at 1725 cm.$^{-1}$ (Fraction B) and 1730 cm.$^{-1}$ (Fraction C).

Anal. of Fraction C. Found: C, 60.65; H, 3.62; Cl, 21.71.

Control experiments. A solution of 30.8 mg. of hexachloroethane in 150 ml. of carbon tetrachloride was treated exactly like the solution of peroxide decomposition products. The yield from the chromatogram was 19.1 mg. (62% recovery), m.p. 183–186° (sealed tube). Mixtures of hexachloroethane and *o*-chlorobiphenyl were easily separated and distinguished by vapor phase chromatography on a silicone-firebrick column.

Chromatography on alumina of a synthetic mixture of 0.106 g. of *o*-chlorobiphenyl and 0.045 g. of 3,4-benzcoumarin afforded 0.087 g. of the former, m.p. 31–33° (82% recovery) and 0.035 g. of the latter, m.p. 91–93° (78% recovery).

Decarboxylation of "dimeric acid" from o-phenylbenzoyl peroxide. A mixture of 0.039 g. of the material, dec. p. 282–286°, 0.064 g. of copper chromite and 5.5 ml. of quinoline was heated at reflux for 2 hr. After cooling, 20 ml. of ether was added and the mixture was poured into 50 ml. of 10% hydrochloric acid. The mixture was filtered and the filtrate was extracted with ether. The ether layer was washed with 10% hydrochloric acid, with water, dried over magnesium sulfate, and the solvent removed. The residue was dissolved in benzene and chromatographed on a column consisting of an upper layer of 1 g. of alumina and a lower layer of 3 g. of silica gel. Elution with benzene afforded 8 mg. of tan solid. Sublimation at 155° and 0.3 mm. gave slightly tan material, m.p. 79–93° (lit.,[24] m.p. of 1,3-(diphenyl)biphenyl 84.5–85°). Mass spectral analysis showed a major peak at mass 306 (calcd. mol. wt., 306).

Decomposition of o-phenylbenzoyl peroxide in the presence of iodine and water (Table III). A mixture of 1.31 g. of the peroxide, 4.55 g. of iodine, 3.64 ml. of water, and 100 ml. of carbon tetrachloride was heated at reflux for 10 hr. and worked up by the above procedure and that described in the corresponding experiment with *o*-toluoyl peroxide.

p-Benzylbenzoic acid was prepared by the reaction of oxalyl chloride and diphenylmethane according to the procedure of Liebermann.[25] Recrystallization from benzene afforded material, m.p. 161–162° (lit., m.p. 155–156°).

p-Benzylbenzoyl peroxide was prepared by the method described above for *o*-benzylbenzoyl peroxide. Recrystallization from carbon tetrachloride-methanol afforded the peroxide, m.p. 87–88°. Iodometric analysis indicated a purity of 99 ± 1%.

Anal. Calcd. for $C_{28}H_{22}O_4$: C, 79.60; H, 5.25. Found: C, 79.49; H, 5.30.

p-Chlorodiphenylmethane was prepared by Wolff-Kishner reduction of *p*-chlorobenzophenone, affording material, b.p. 118° (1 mm.), n^{27}_{D} 1.5840 (lit.,[26] b.p. 298° at 743 mm.).

p-Benzylphenyl p-benzylbenzoate was prepared by the reaction of *p*-benzylbenzoyl chloride (crude, from 2 g. of acid by the action of thionyl chloride) and 2 g. of *p*-benzylphenol in 20 ml. of pyridine. After 15 hr. at 25° the mixture was poured into water and the precipitate was recrystallized from hexane, 1.4 g., m.p. 70–71°.

Anal. Calcd. for $C_{29}H_{22}O_2$: C, 85.68; H, 5.86. Found: C, 85.87; H, 6.06.

Decomposition of p-benzylbenzoyl peroxide in carbon tetrachloride. A 6.37-g. sample (15.1 mmoles) of the peroxide in 1500 ml. of carbon tetrachloride was decomposed under slow nitrogen flow for 60 hr. as described above for *o*-methylbenzoyl peroxide. Yield of carbon dioxide was 15.9 mmoles. The carbon tetrachloride was removed through a 24-inch Vigreux column. The residue was dissolved in ether and extracted fifteen times with 50-ml. portions of 5% sodium bicarbonate solution. The bicarbonate solution was acidified and extracted with ether; the ether was dried over magnesium sulfate, filtered, and evaporated giving 0.63 g. of crude *p*-benzylbenzoic acid, m.p. 118–123°. Recrystallization from petroleum ether (b.p. 70–90°) afforded material, m.p. 153–155°, mixed m.p. 154–156°. The original ether layer containing the neutral products of the peroxide decomposition was evaporated, dissolved in petroleum ether, filtered

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(21) C. D. Gutsche and W. S. Johnson, *J. Am. Chem. Soc.*, **68**, 2239 (1946).

(22) W. Schlenk and E. Bergmann, *Ann.*, **464**, 33 (1928).

(23) C. Graebe and P. Schestakow, *Ann.*, **284**, 317 (1895).

(24) G. F. Woods and F. T. Reed, *J. Am. Chem. Soc.*, **71**, 1348 (1949).

(25) C. Liebermann, *Chem. Ber.*, **45**, 1207 (1912).

(26) P. J. Montagne, *Rec. trav. chim.*, **26**, 267 (1907).

from a small amount of insoluble matter, and chromatographed on 30 g. of acid-washed alumina. The first fraction was hexachloroethane, 0.63 g.

The second fraction, 3.0 g. of a colorless liquid, n_{D}^{27} 1.5842 was identified as *p*-chlorodiphenylmethane by identity of infrared spectrum with that of authentic material and by chromic acid oxidation in acetic acid to *p*-chlorobenzophenone, m.p. 73–74° after recrystallization from ethanol, mixture m.p. 73–74°. The *p*-chlorodiphenylmethane fraction gave a single peak on gas phase chromatography on a firebrick-silicone column with no peak at the position shown by an authentic sample of diphenylmethane. The third fraction, eluted from the alumina by ether, was a semisolid which resisted attempts at purification. The infrared spectrum was similar to but not identical with that of *p*-benzylphenyl *p*-benzylbenzoate.

Kinetic determinations were made in carbon tetrachloride at 80°, following the peroxide concentration by iodometric analysis.[27] Initial concentrations closely approximated the conditions of the product studies. The data are summarized in Table IV.

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CAMBRIDGE 39, MASS.

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[27] F. D. Greene, *J. Am. Chem. Soc.*, **78**, 2254 (1956).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

Cleavage of Tetrahydrofuran during Reductions with Lithium Aluminum Hydride[1]

WILLIAM J. BAILEY AND FRITZ MARKTSCHEFFEL[2]

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A mixture of aluminum chloride and lithium aluminum hydride was shown to cleave tetrahydrofuran to *n*-butyl alcohol. There appears to be a direct relationship between the maximum amount of *n*-butyl alcohol produced under extended reflux and the theoretical amount of aluminum hydride produced. Although the reduction of most compounds with lithium aluminum hydride in tetrahydrofuran does not result in cleavage, the reduction of alkyl halides and benzylphosphonium halides under these conditions gave *n*-butyl alcohol and hydrocarbon in nearly equivalent amounts. Dioxane, diethoxyethane and di-*n*-butyl ether were cleaved with the mixed reagent, but at a much slower rate than was tetrahydrofuran.

Because of its unique solvent properties tetrahydrofuran has found extensive and successful use as a solvent for reductions with lithium aluminum hydride. However, during an investigation of the reductive cleavage of benzylphosphonium compounds[3] with lithium aluminum hydride in tetrahydrofuran, it was found that an excess of hydride was required for high yields and *n*-butyl alcohol was formed as a by-product by the reductive cleavage of the solvent. Therefore, a research program was undertaken in order to investigate this unusual reductive cleavage.

In general, the ether bond is resistant to attack by lithium aluminum hydride and other complex hydrides at temperatures to 80–100°.[4,5] When the oxygen is part of a ring possessing strain, such as ethylene oxide and thebain, or containing the N—C—O— grouping, cleavage takes place, but ordinary cyclic ethers, such as tetrahydrofuran, tetrahydropyran, and dioxane, are reported to be stable. Of course, activated ethers, such as allyl ethers and cyclohexyloxyacetic acid,[6] are known to be cleaved under vigorous conditions. It has been reported[7] that during the reduction of active carbon dioxide at 0° or active acetyl chloride at −78° in diethyl carbitol 4 to 7% of inactive ethanol was formed. In addition, Karrer *et al.*,[8] showed that lithium aluminum hydride in the presence of cobaltous chloride would cleave phenyl benzyl and phenyl allyl ethers in refluxing ethyl ether.

More recently, a mixture of lithium aluminum hydride and aluminum chloride has been suggested as a more specific reducing agent.[9] Eliel *et al.*[10] recently have applied this reagent to the reduction

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[1] This work was done in fulfillment of a contract with the Army Chemical Corps.

[2] Army Chemical Corps Postdoctoral Fellow, 1957–59.

[3] W. J. Bailey, S. A. Buckler, and F. Marktscheffel, *J. Org. Chem.*, in press.

[4] P. Karrer, *Angew. Chem.*, **62**, 334 (1950).

[5] N. G. Gaylord, *Reductions with Complex Metal Hydrides*, Interscience Publishers, Inc., New York, N.Y., 1956.

[6] M. Mousseron, M. R. Jacquier, M. Mousseron-Cavet, and R. Zagdoun, *Bull. soc. chim. France*, [5] **19**, 1042 (1952).

[7] J. D. Cox and R. J. Warne, *Nature*, **165**, 563 (1950); J. D. Cox and R. J. Warne, *J. Chem. Soc.*, 3167 (1950); and R. Ostwald, P. T. Adams, and B. M. Tolbert, *J. Am. Chem. Soc.*, **74**, 2425 (1952).

[8] P. Karrer and A. Chatterjee, *Helv. Chim. Acta*, **33**, 802 (1950); P. Karrer and O. Rütner, *Helv. Chim. Acta*, **33**, 812 (1950).

[9] B. R. Brown, *J. Chem. Soc.*, 2756 (1952); E. Wiberg and A. Jahn, *Z. Naturforsch.*, **7b**, 580 (1952); R. F. Nystrom, *J. Am. Chem. Soc.*, **77**, 2544 (1955).

[10] E. L. Eliel and M. Rerick, *J. Org. Chem.*, **23**, 1088 (1958); E. L. Eliel and V. G. Badding, *J. Am. Chem. Soc.*, **81**, 6087 (1959).