[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE LABORATORY FOR NUCLEAR SCIENCE, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Mechanism of Decomposition of Benzoyl Peroxide in Cyclohexane Solution[1-3]

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A detailed mechanism for the decomposition of benzoyl peroxide at 91° in cyclohexane solution containing styrene as an inhibitor of chain decomposition is suggested by the variations in product composition with experimental conditions. Styrene is an effective inhibitor of induced decomposition: The half-life with 0.003 M peroxide increases 65% from 0.000 to 0.015 M styrene, but is constant from 0.015 to 0.12 M styrene. The yields of benzoic acid, phenyl benzoate and biphenyl were determined as a function of peroxide concentration (0.003 to 0.015 M), styrene concentration (0.000 to 0.12 M) and % reaction, using tritium-labeled benzoyl peroxide and the methods of isotope dilution. Benzene yields were measured by ultraviolet absorption spectroscopy, and cyclohexene by gas chromatography. One-half mole of benzoic acid was formed from each mole of peroxide under all conditions. The yields of benzene, phenyl benzoate and biphenyl rose from 0.000 to 0.015 M styrene (1.28, 0.021 and 0.0014 mole, respectively, at 0.015 M styrene) but fell from 0.015 to 0.12 M styrene; 92% of the phenyl groups of the peroxide are accounted for by these four products at 0.015 M styrene. The yield of cyclohexene was low ($\leqq 0.12$ mole). In the proposed mechanism, phenyl benzoate and biphenyl are formed only by geminate recombination of incompletely separated radicals, benzoic acid is formed from attack on cyclohexane by benzoate radicals, and benzene is formed from attack on cyclohexane by phenyl radicals, which arise from spontaneous decomposition of benzoate radicals. Styrene is not effective in capturing benzoate radicals in cyclohexane solution, but it does compete moderately effectively against cyclohexane for phenyl radicals. Induced decomposition in the absence of styrene is caused by cyclohexyl free radicals.

Previous work on the mechanism of decomposition of benzoyl peroxide is covered in several excellent reviews.[4-6] The rate has been shown to be the sum of two terms representing spontaneous and induced decompositions.[7,8] The induced decomposition can be suppressed by adding styrene or other inhibitors.[2] The initial step is known to be cleavage into two benzoate radicals because little or no carbon dioxide is set free in reactions in the presence of some of these inhibitors, *e. g.*, styrene,[9] hexaphenylethane,[10] phenols,[11] iodine and water,[12] or diphenylpicrylhydrazyl.[9]

Free phenyl radicals probably are formed by spontaneous decarboxylation of benzoate radicals in systems in which carbon dioxide is liberated, because the products from thermal decomposition of the optically active peroxide of 2-methyl-6-nitro-2′-biphenylcarboxylic acid in benzene, carbon tetrachloride or bromotrichloromethane are partially racemic, whereas the peroxide and products are stable toward racemization under the reaction conditions.[13] Therefore at least some of the loss of carbon dioxide occurs before the benzoate radicals attack the solvent, and it is possible that all of the loss of carbon dioxide occurs before and none during reaction of benzoate radicals with solvent or other molecules. The racemization is also inconsistent with a cyclic rearrangement not involving free radicals.

Unsolved problems are (1) to what extent the products are formed by cage (geminate) recombination of incompletely separated radicals, (2) how the reactivity of free phenyl radicals compares with that of benzoate radicals, and (3) whether induced decomposition in a solvent like cyclohexane is due primarily to peroxide radicals or solvent radicals. Answers to these questions are provided by the present study.

The "cage effect" (geminate recombination) has been predicted to be difficult to inhibit.[14] In other words, inhibitors are expected to have relatively little effect on the yield of products formed by cage (geminate) recombination, compared to products formed from separated free radicals. The yield of ethane from acetyl peroxide in isoöctane solution at 85° and the rate of peroxide decomposition are in fact almost unchanged by addition of 0.2 mole % iodine, although this lowers the yield of methane by a factor of 800.[15] The yield of ethane is independent of initial peroxide concentration, but is almost twice as large at a 20° lower temperature. Cage recombination is only likely in solution, where the solvent "cage" retards separation of newly formed radicals. In the gas-phase

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[1] This work was supported in part by the research program of the Atomic Energy Commission under Contract No. AT(30-1)-905. Reproduction is permitted for any purpose of the United States Government.

[2] *Cf.* previous paper on benzoyl peroxide by C. G. Swain, W. H. Stockmayer and J. T. Clarke, THIS JOURNAL, **72**, 5426 (1950).

[3] For further experimental details, *cf.* Lawrence J. Schaad, Ph.D. Thesis in Organic Chemistry, M.I.T., January, 1957. Cyclohexene was determined subsequently by A. J. K.

[4] A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954, pp. 72–88.

[5] J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, pp. 412–419.

[6] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 474–491.

[7] P. D. Bartlett and K. Nozaki, THIS JOURNAL, **68**, 1686 (1946); **69**, 2299 (1947).

[8] B. Barnett and W. E. Vaughan, *J. Phys. Colloid Chem.*, **51**, 926, 942 (1947).

[9] P. D. Bartlett and S. G. Cohen, THIS JOURNAL, **65**, 543 (1943); C. A. Barson and J. C. Bevington, *J. Polymer Sci.*, **20**, 133 (1956); J. C. Bevington and C. S. Brooks, *ibid.*, **22**, 257 (1956).

[10] H. Wieland, T. Ploetz and H. Indest, *Ann.*, **532**, 179 (1937); H. Wieland and A. Meyer, *ibid.*, **551**, 249 (1942); G. S. Hammond, J. T. Rudesill and F. J. Modic, THIS JOURNAL, **73**, 3929 (1951).

[11] S. L. Cosgrove and W. A. Waters, *J. Chem. Soc.*, 3189 (1949); J. J. Batten and M. F. R. Mulcahy, *ibid.*, 2948 (1956); C. Walling and R. B. Hodgdon, Jr., THIS JOURNAL, **80**, 228 (1958).

[12] G. S. Hammond and L. M. Soffer, *ibid.*, **72**, 3737, 4711 (1950).

[13] D. F. DeTar and J. C. Howard, *ibid.*, **77**, 4393 (1955). For comparable results on aliphatic acid peroxides, *cf.* M. S. Kharasch, J. Kuderna and W. Nudenberg, *J. Org. Chem.*, **19**, 1283 (1954); F. D. Greene, THIS JOURNAL, **77**, 4869 (1955); D. F. DeTar and C. Weis, *ibid.*, **79**, 3045 (1957).

[14] J. Franck and E. Rabinowitch, *Trans. Faraday Soc.*, **30**, 120 (1934); E. Rabinowitch and W. C. Wood, *ibid.*, **32**, 1381 (1936); R. M. Noyes, *J. Chem. Phys.*, **22**, 1349 (1954); THIS JOURNAL, **77**, 2042 (1955).

[15] M. Levy, M. Steinberg and M. Szwarc, *ibid.*, **76**, 5978 (1954); M. Levy and M. Szwarc, *ibid.*, **76**, 5981 (1954); A. Rembaum and M. Szwarc, *ibid.*, **77**, 3486 (1955); J. Smid, A. Rembaum and M. Szwarc, *ibid.*, **78**, 3315 (1956); J. R. Nash, W. H. Hamill and R. B. Williams, Jr., *J. Phys. Chem.*, **60**, 823 (1956).

reaction, iodine still does not affect the rate of disappearance of the peroxide, but it suppresses ethane formation entirely.[15] The persistence of cage recombination in the presence of inhibitors is also evident with azobisisobutyronitrile (*i.e.*, 2,2′-azobis [2-methylpropionitrile]) from the following observations: the low efficiency of azobisisobutyronitrile in polymerizing liquid methyl methacrylate (52–63% at 50–77°)[16]; the nearly constant (38 ± 6%) yield of tetramethylsuccinonitrile in benzene at 60° independent of the concentration of styrene from 1 to 6 M[17]; the constant yield of tetramethylsuccinonitrile in carbon tetrachloride at 80°, independent of the concentration of *n*-butyl mercaptan from 0.18 to 0.54 M[18]; and the efficiencies of free radical production in various solvents at 63° measured by reaction with either iodine or air (45% in carbon tetrachloride, 62% in benzene, 75% in nitrobenzene).[18]

Cage recombination also has been demonstrated by the preponderance of symmetric coupling products formed from original partners relative to the statistically expected cross-coupling products when two or more kinds of radicals are formed. For example, decomposition of 0.001 M 5-phenylpentanoyl peroxide (bis-δ-phenylvaleryl peroxide) in carbon tetrachloride solution at 77° gave 26% 1,8-diphenyloctane and 28% of hexachloroethane, but less than 2% of the cross-product, 4-phenylbutyltrichloromethane.[19] Evidently at least two of the products, 1,8-diphenyloctane (26%) and 4-phenylbutyl 5-phenylpentanoate (19%), result from cage recombination, and the escaping 4-phenylbutyl radicals react so rapidly with the solvent to form 4-phenylbutyl chloride (43%) and trichloromethyl radicals that the concentration of free 4-phenylbutyl radicals is negligible.

In the present study we used the inhibitor method rather than the cross-coupling method to determine the importance of cage recombination reactions of benzoyl peroxide.

Results and Discussion

Cyclohexane was chosen as solvent instead of the more conventional solvent, benzene, to avoid any confusion between product phenyl groups derived from peroxide and those derived from solvent. Like benzene it has the simplifying feature that all hydrogens are equivalent. It is simpler than benzene in the sense that hydrogen abstraction can occur in only one way; the addition–elimination mechanism of benzene is excluded. Products previously isolated from reaction in cyclohexane were benzene, benzoic acid, phenylcyclohexane, phenyl benzoate, *p*-phenylbenzoic acid, *o*- and *p*-cyclohexylbenzoic acid and carbon dioxide.[20]

Styrene again proved to be an excellent inhibitor. As little as 0.01 M increased the half-life for decomposition of 0.003 M benzoyl peroxide at 91° from 65 to 107 minutes (Fig. 1). Further increases up to 0.15 M had no further effect on the rate. In the presence of at least 0.01 M styrene the kinetics was accurately first order throughout a given run.[3] No precipitate formed in any of the reacting solutions.[21]

From Fig. 1 it might be concluded that 0.002 to 0.005 M styrene is sufficient to eliminate all induced decomposition. However the times for 80% (instead of 50%) reaction plotted in Fig. 2 show that 0.01 M is really required. At 0.015 M, where the products were isolated, only about one molecule in 620 is styrene; at 0.12 M, one molecule in 77 is styrene. Within experimental error, there is no change in rate from 0.015 to 0.12 M styrene.

The percentage peroxide lost by induced decomposition can be calculated from the effect of styrene on half-life. Since styrene increases half-life from 65 to 107.5 min. with 0.003 M peroxide, 20% of the original peroxide is lost this way by the time it is half decomposed in the absence of styrene. The corresponding figure with 0.03 M peroxide is 32%. Hence the induced reaction is greater than first order in peroxide, in agreement with the observed falling off of rate with time on first-order plots in the absence of styrene.

Table I gives the yields of products obtained. Benzene yields were measured by ultraviolet absorption spectroscopy. Benzoic acid, phenyl benzoate and biphenyl were determined using benzoyl-*p-t* peroxide and the methods of isotope dilution. Any isotope effect should be negligible in this system.

TABLE I

MOLES OF PRODUCT FROM ONE MOLE OF BENZOYL PEROXIDE IN CYCLOHEXANE AT 91.1°

Peroxide, M	Styrene, M	PhH,[a] moles	HOBz,[b] mole	PhOBz,[c] mole	PhPh,[d] mole
0.003	0.000	1.11	0.523	0.0138	0.00096
.003	.015	1.28	.528	.0209	.00144
.003	.120	1.07	.524	.0193	.00128
.015	.075	. .	.513	.0203	.00160
.015	.075	. .	.523	.0207	.00150
.015[e]	.075	. .	.244[e]	.0105[e]	.00076[e]

[a] Benzene. [b] Benzoic acid. [c] Phenyl benzoate. [d] Biphenyl. [e] Reaction stopped and products isolated at 50% reaction.

Benzoic acid was formed to the extent of one-half mole from each mole of peroxide under all conditions. The yields of benzene, phenyl benzoate and biphenyl increased with an increase in styrene concentration from 0.000 to 0.015 M, but fell with a further increase to 0.12 M, with the benzene falling more than the others (16%). The absolute yields per mole of peroxide consumed were not affected by a fivefold increase in the concentration of both peroxide and styrene (from 0.003 and 0.015 to 0.015 and 0.075, respectively) nor by the fraction of the peroxide which reacted. Although benzene was not measured at the higher peroxide concentrations, the fact that the absolute yields of the minor products per mole of peroxide, as well as

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(16) L. M. Arnett, THIS JOURNAL, **74**, 2027 (1952); L. M. Arnett and J. H. Peterson, *ibid.*, **74**, 2031 (1952).

(17) J. C. Bevington, *Trans. Faraday Soc.*, **51**, 1392 (1955).

(18) G. S. Hammond, J. N. Sen and C. E. Boozer, THIS JOURNAL, **77**, 3244 (1955).

(19) D. F. DeTar and C. Weis, *ibid.*, **78**, 4296 (1956); **79**, 3041 (1957).

(20) H. Gelissen and P. H. Hermans, *Ber.*, **59B**, 662 (1926); *C. A.*, **20**, 2673 (1926); P. H. Hermans and J. Van Eyk, *J. Polymer Sci.*, **1**, 407 (1946); P. F. Hartman, H. G. Sellers and D. Turnbull, THIS JOURNAL, **69**, 2416 (1947).

(21) In one comparison with 0.20 M methyl methacrylate as inhibitor for 0.03 M peroxide at 89.5°, the half life was the same as that with 0.10 M styrene (125 min.). However, a white precipitate formed when methyl methacrylate was used as inhibitor.

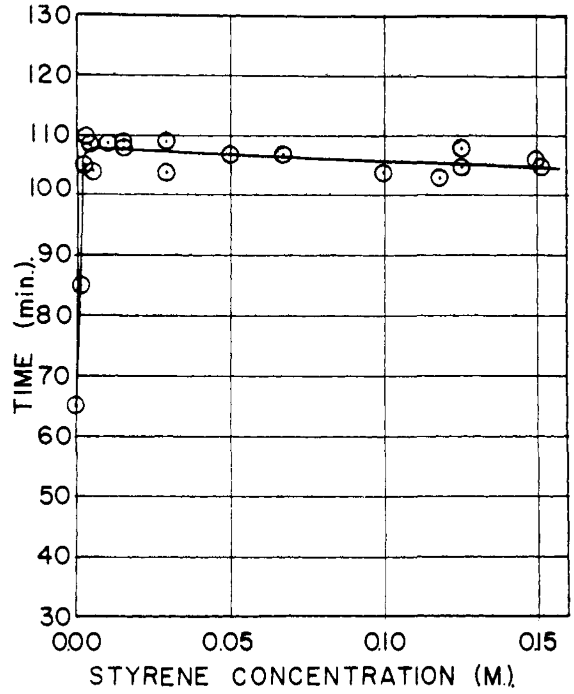

Fig. 1.—Time of 50% decomposition of 0.003 *M* benzoyl peroxide in cyclohexane at 91.1°.

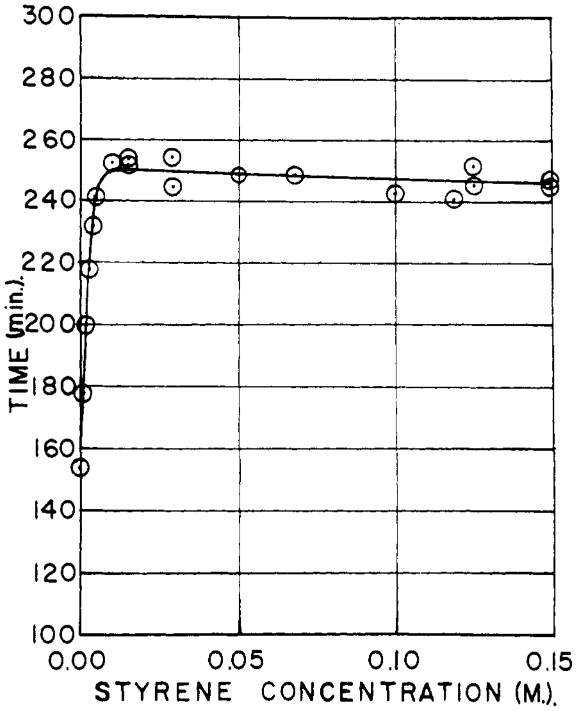

Fig. 2.—Time of 80% decomposition of 0.003 *M* benzoyl peroxide in cyclohexane at 91.1°.

their relative yields, are unchanged suggests also a constant yield for the major product, benzene. At 0.015 *M* styrene over 92% of the phenyl groups in the peroxide are accounted for in these four measured products. Evidently very few peroxide radicals end up in polymer. The yield of cyclohexene also was measured under several of these conditions, by gas chromatography, and found to be very low, *viz.*, 0.12 mole or less (see Experimental part).

The accuracy of the data on benzene, benzoic acid and phenyl benzoate is estimated to be certainly better than ±5%.[3] The data for 0.015 *M* peroxide and 0.075 *M* styrene show the range of values observed in entirely independent runs. The biphenyl determinations were less accurate (about ±10%) because the radioactivity of the biphenyl isolated was smaller than that of any of the other labeled compounds isolated, only ten times background activity.

Mechanism in the Absence of Induced Decomposition.—Let us consider the data from 0.015 *M* to 0.12 *M* styrene, *i.e.*, under conditions where the rate is constant and induced decomposition has been essentially eliminated. The yield of benzoic acid remains constant with increasing concentration of styrene in this region, yet the yield of benzene falls. Evidently styrene does not capture benzoate radicals, which therefore either react with cyclohexane (to give benzoic acid) or decarboxylate to phenyl radicals; but styrene does compete against cyclohexane for the phenyl radicals, thereby lowering the yield of benzene when the concentration of styrene is high.

Since benzoate radicals do add to styrene in benzene solution,[9] it appears that their failure to add to styrene in cyclohexane may be due to their relatively high reactivity toward cyclohexane as a result of stabilization of the transition state by polar resonance of the type $[\mathrm{BzO^{-}H{\cdot}C_6H_{11}^{+}}]$. Such polar resonance would be less important in the abstraction of hydrogen from benzene or in the reaction of phenyl radicals with cyclohexane (because of the lesser stability of phenyl ions). Naturally if the reaction of benzoate radicals with cyclohexane is sufficiently rapid, the probability of their reacting with the solute styrene becomes statistically small. Another oxygen radical, *t*-butoxy radical, is known to abstract hydrogen 1200 times as rapidly from cyclohexane as from benzene, from the *t*-butyl alcohol/acetone ratio in the decomposition products of di-*t*-butyl peroxide in the two solvents.[22] Another factor favoring reaction of benzoate radicals with styrene in benzene solution may be their stabilization by either π-complex formation with the benzene[23] or reversible covalent addition to the benzene (σ-complex or aromatic radical formation).[24] It is known that aromatic solvents can act as chain transfer agents in the polymerization of styrene without becoming incorporated in the polymer chain.[25] Furthermore, aromatic solvents increase selectivity in aliphatic chlorination reactions, again presumably by stabilizing the radicals (here chlorine atoms) by complex formation.[26] In any case, it is a prediction of our work that, unlike the results in benzene solution,[9] the end groups of polystyrene formed in cyclo-

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[22] A. L. Williams, E. A. Oberright and J. W. Brooks, THIS JOURNAL, **78**, 1190 (1956).

[23] C. E. Boozer and G. S. Hammond, *ibid.*, **76**, 3861 (1954); C. E. Boozer, C. E. Hamilton and J. N. Sen, *ibid.*, **77**, 3238 (1955).

[24] R. S. Mulliken, *J. Phys. Chem.*, **56**, 801 (1952); H. C. Brown and J. D. Brady, THIS JOURNAL, **74**, 3570 (1952).

[25] F. R. Mayo, *ibid.*, **75**, 6133 (1953).

[26] G. A. Russell, *ibid.*, **79**, 2977 (1957).

hexane solution should be predominantly cyclohexyl or phenyl rather than benzoate groups.

Phenyl benzoate and biphenyl evidently are formed by cage recombination reactions, because the independence of their yields on peroxide concentration and % reaction at a 5:1 styrene/peroxide ratio shows that their rates of formation must be of the same kinetic order in peroxide as the rates of formation of all other products, and therefore almost certainly first order. The relatively minor decreases (~8%) in these two products with increasing concentration of styrene, if significant, may be due to competition for phenyl radicals by styrene molecules included in the walls of the original cages. It is not possible from these results to tell what fraction of the benzene or benzoic acid results from competition by solvent molecules in the walls of the cages before the radicals separate. However, at least part of the benzene probably is formed by free (separated) phenyl radicals because 0.12 M styrene decreases the yield of benzene twice as much as it decreases the yield of phenyl benzoate.

Thus a mechanism consistent with all of the observations in the presence of 0.015–0.012 M styrene is

$$\mathrm{BzOOBz} \longrightarrow 2\mathrm{BzO}\cdot \tag{1}$$

$$\mathrm{BzO}\cdot \longrightarrow \mathrm{Ph}\cdot + \mathrm{CO_2} \tag{2}$$

$$\mathrm{Ph}\cdot + \mathrm{BzO}\cdot \longrightarrow \mathrm{PhOBz}\ \text{(cage recomb.)} \tag{3}$$

$$2\mathrm{Ph}\cdot\ (\text{or } \mathrm{Ph}\cdot + \mathrm{BzO}\cdot) \longrightarrow \mathrm{PhPh}\ \text{(cage recomb.)} \tag{4}$$

$$\mathrm{BzO}\cdot + \mathrm{RH} \longrightarrow \mathrm{R}\cdot + \mathrm{HOBz} \tag{5}$$

$$\mathrm{Ph}\cdot + \mathrm{RH} \longrightarrow \mathrm{R}\cdot + \mathrm{PhH} \tag{6}$$

$$\mathrm{Ph}\cdot + \text{styrene} \longrightarrow \text{products not isolated} \tag{7}$$

$$\mathrm{R}\cdot + \text{styrene} \longrightarrow \text{products not isolated} \tag{8}$$

where BzO· is the benzoyloxy radical, Ph· is the phenyl radical and R· is the cyclohexyl radical.

Several other explanations for the constancy in the yield of benzoic acid were considered and eliminated. The benzoic acid cannot be formed by a polar hydrolysis by a constant amount of water present as an impurity, because if there had been excess water the yield of benzoic acid should have been 1.0 (not 0.5) mole and if there had been insufficient water the kinetics should have deviated from accurately first order (which it did not do). Benzoic acid cannot be formed in a simple non-radical cyclic attack of peroxide on cyclohexane to give cyclohexene because the amount of cyclohexene formed was negligible compared to the benzoic acid. It cannot be formed in a reaction which produces an equivalent yield (0.5 mole) of cyclohexyl benzoate because with 0.015 M styrene only 0.15 mole of phenyl or benzoate groups is unaccounted for and therefore assignable as cyclohexyl benzoate or other products. Benzoic acid cannot arise from hydrolysis of polymer end groups or phenyl benzoate during the procedure for extracting benzoic acid because quite vigorous conditions are required for end-group hydrolysis,[9] and the cold aqueous sodium bicarbonate extraction used was shown not to hydrolyze benzyl benzoate or phenyl benzoate (see Experimental part). The unique constancy of benzoic acid above 0.015 M styrene is probably not the result of a medium effect by styrene which lowers the rate of formation of all products except benzoic acid, because a fivefold increase in the concentrations of *both* peroxide and styrene did not change any of the measured yields significantly.

Mechanism of Induced Decomposition.—Since benzoate radicals are not captured by styrene and phenyl radicals are captured to only a small and variable extent (see previous section), the effective elimination of induced decomposition over the whole range from 0.015 to 0.12 M styrene must be the result of the capture of cyclohexyl radicals by styrene. Therefore induced decomposition in the absence of styrene is caused by cyclohexyl radicals and not by phenyl radicals. Since induced decomposition of this kind should not form phenyl benzoate or biphenyl, the yield of these two should increase when induced decomposition is eliminated by adding 0.015 M styrene. The % increase should be the same for each, and within experimental error it is: 51% for phenyl benzoate and 50% for biphenyl.

The low yield of cyclohexene even in the absence of styrene is reasonable because cyclohexyl radicals, formed by di-*t*-butyl peroxide in cyclohexane solution, have been shown to couple rather than to disproportionate.[27]

The yield of benzoic acid in the absence of styrene is still one-half mole. This means that induced decomposition gives the same yield of benzoic acid from the peroxide as spontaneous decomposition in spite of the fact that it can give at most only one-half as many benzoate radicals as the spontaneous decomposition. This suggests that either (1) part of the induced decomposition gives benzoic acid directly without the intermediacy of free benzoate radicals

$$\mathrm{R}\cdot + \mathrm{BzOOBz} \longrightarrow \mathrm{BzOH}$$

or (2) the benzoate radicals which are produced by induced decomposition are more efficient sources of benzoic acid because of the proximity of the other products of induced decomposition. Under explanation 1, the most likely other products would be cyclohexene and benzoate radical. The observed yield of cyclohexene was indeed higher (0.12 mole) in the absence of styrene than with 0.015 M styrene (0.02 mole). Using this difference and the fact that only about one-third of the decomposition is induced, the calculated yield of benzoic acid in the absence of styrene is $(^2/_3)(0.52) + 0.10 + (^1/_3)(0.52/2) = 0.53$ mole, in good agreement with the observed 0.52. Under explanation 2, it would be necessary to assume that about one-third of the benzoate radicals formed by induced decomposition react immediately after their formation with the cyclohexyl benzoate or phenylcyclohexane formed simultaneously so that this part of the induced decomposition gives a quantitative yield of benzoic acid. The radicals from cyclohexyl benzoate or phenylcyclohexane may then be trapped by styrene. The rest of the benzoate radicals react like the bulk of the benzoate radicals from spontaneous decomposition: more than half of them decarboxylate to phenyl radicals, which mostly react with cyclohexane to give benzene, but about one-quarter of them react with

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[27] E. H. Farmer and C. G. Moore, *J. Chem. Soc.*, 131 (1951).

cyclohexane to give benzoic acid before they have time to decarboxylate.

By explanation 1 (which is preferred) the yield of benzene for induced decomposition should be one-half of that for spontaneous decomposition. Since the yield of benzene from spontaneous decomposition of one mole of peroxide in the absence of competition for phenyl radicals by styrene should be somewhat larger than 1.28 moles and since only about one-third of the total decomposition is induced, the 13% lower yield of benzene (1.11 moles) in the absence of styrene is consistent with the other observations. Explanation 2 predicts a yield of benzene slightly too low.

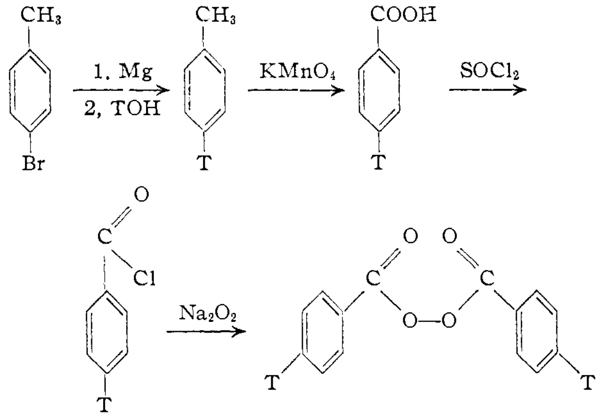
Experimental

Materials.—Benzene and ethyl ether were Mallinckrodt anhydrous analytical reagents. Chloroform, methanol and petroleum ether (30–60°) were Fisher "Certified" reagents. Ethanol was U. S. Industrial Chemicals U. S. P. absolute grade. Cyclohexane is described below. Benzoyl peroxide was recrystallized from chloroform–methanol, m.p. 106–107°, 100% pure by iodometric titration. Styrene was redistilled just before use, b.p. 66° (50 mm.). Phenyl benzoate was recrystallized twice from ethanol, m.p. 68.5–70.5°. Benzoic acid melted at 123.0–123.5°. Cyclohexene was redistilled from calcium hydride through a 65-cm. Fenske (glass helices) column[28] at atmospheric pressure. The middle third, b.p. 82.5–83°, n^{25}_{D} 1.4436, was stored over sodium wire. Portions of this were redistilled rapidly through a 30-cm. Holzman column[29] just before use.

Purification of Cyclohexane.—Phillips "pure grade" of cyclohexane was found to contain an impurity which destroys 7–10% of the benzoyl peroxide in a 0.03 *M* solution during eight hours at 25°, but no more during the next 24 hours. The impurity is not water because cyclohexane dried over sodium reacts the same as cyclohexane saturated with water. It is not cyclohexene nor anything formed readily from cyclohexene by passing air through it and exposing it to ultraviolet light, because peroxide in purified cyclohexane was not decomposed significantly in three days at 25° after addition of 0.03 *M* irradiated oxygen-containing cyclohexene. This unknown impurity was removed by distilling the cyclohexane through a 110-cm. Fenske column, collecting the middle half of the distillate, b.p. 80.5°, n^{25}_{D} 1.419–1.423, and passing it over a 1-meter column of Davison Chemical Co. 28–200 mesh silica gel. It was stored over sodium wire. Cyclohexane purified in this way did not react with benzoyl peroxide. Dow 95% cyclohexane destroyed 40% of the peroxide in a 0.03 *M* solution at 25°, but when purified in the same way it gave the same decomposition rates as the purified Phillips product.

Kinetic Procedure.—Each of the 15-ml. Pyrex reaction tubes was filled with approximately 12 ml. of solution, then frozen in a solid carbon dioxide–acetone-bath, evacuated and filled with nitrogen three times, then sealed under atmospheric pressure of nitrogen. The tubes were then heated in a constant-temperature oil-bath regulated to ±0.1°. After the desired time in the oil-bath, tubes were removed, quenched in cold water, and an aliquot removed and titrated for peroxide by the method previously described.[2] For accuracy at low peroxide concentrations (0.003 *M*) the method was modified slightly. One ml. of half-saturated sodium iodide in acetone was pipetted into the aliquot and 1 g. of solid carbon dioxide added. After about one minute, 15 ml. of water saturated with carbon dioxide and 1 ml. of starch indicator was added. This mixture was titrated with 0.1 *M* sodium thiosulfate.

Synthesis of Benzoyl-*p*-*t* Peroxide.—This was made by the sequence shown.



Under an atmosphere of nitrogen, 173 g. of *p*-bromotoluene (redistilled, b.p. 182.5–183°) in 200 ml. of ethyl ether was added over a period of 55 min. to 22 g. of magnesium turnings in 100 ml. of ethyl ether. After addition the mixture was refluxed for 20 minutes. To the resulting brown reaction mixture, 65 ml. of tritiated water (from Atomic Energy Research Establishment, Isotope Division, Harwell, Berks., England) was added and refluxing was continued for four hours. Then 360 ml. of 6 *M* hydrochloric acid was added. The yellow ether layer was separated, washed with water, dried with anhydrous sodium sulfate, and distilled. The fraction boiling at 110–113° was collected (49.8 g.). The low-boiling fractions were redistilled to give 11.7 g. more of the 110–113° fraction. The total yield was 61.5 g. (67%, based on bromotoluene).

Toluene-*p*-*t* (61.5 g.) and water (1000 ml.) were heated to 85° and 213 g. of potassium permanganate added slowly (35 min.) with stirring. Heating at 85° was continued overnight. Then the hot mixture was filtered. The red-brown precipitate was extracted twice with 500 ml. of hot water. These extracts were combined with the original filtrate, and benzoic acid precipitated by addition of concd. hydrochloric acid. Recrystallization of the precipitate from water gave 55.7 g. (68%) of benzoic-*p*-*t* acid, m.p. 122–123.5°.

Thionyl chloride (149 g.) was added to 55.7 g. of benzoic-*p*-*t* acid. The orange-brown mixture was refluxed two hours, then distilled, giving 57.8 g. (90.1%) of benzoyl-*p*-*t* chloride, b.p. 83–86° (14–17 mm.). To 500 ml. of water cooled to 6° in an ice–salt-bath, 20.6 g. of sodium peroxide was added. Benzoyl-*p*-*t* chloride (57.8 g.) in 150 ml. of cyclohexane was added with stirring. Stirring and cooling were continued for 30 min. after addition was completed. The mixture was filtered, giving a white precipitate, which was dissolved in chloroform and dried over sodium sulfate. Methanol added to the dry chloroform solution precipitated long needles of benzoyl-*p*-*t* peroxide. The peroxide was collected and again precipitated from a chloroform solution with methanol. This gave 39.5 g. (68.9% or 28.3% overall yield based on *p*-bromotoluene) of benzoyl-*p*-*t* peroxide which melted with decomposition at 103–105°. The peroxide had a specific activity of 19.25 ± 0.87 millicuries per mole on Feb. 1, 1956, and a purity of 98.9 ± 0.4% by iodometric titration.

Measurement of Product Yields.—Yields of biphenyl, phenyl benzoate and benzoic acid were determined by isotope dilution. Details of a typical decomposition will be given.

A cyclohexane solution 0.003 *M* in benzoyl-*p*-*t* peroxide and 0.12 *M* in styrene was made by dissolving 0.7268 g. of peroxide and 12.477 g. of freshly distilled styrene in sufficient pure, dry cyclohexane to make 1000 ml. of solution. This solution was put into 9 Pyrex tubes, each holding about 125 ml., frozen, evacuated, and sealed under nitrogen. These tubes were heated at 91.1° for 21 hours, then opened and 987 ml. of the mixture removed. Non-radioactive benzoic acid (1.0152 g.), phenyl benzoate (1.0128 g.) and biphenyl (1.0122 g.) were dissolved in this solution and mixed thoroughly.

Benzoic acid was re-extracted with aqueous sodium bicarbonate. The water layer was separated, acidified with concentrated hydrochloric acid, and extracted with three 50-ml. portions of chloroform. Solvent was evaporated from the chloroform extracts. The residue of benzoic acid was dissolved in ethyl ether, and purified by repeating the above process. The residue of benzoic acid obtained this second time was crystallized from hot water giving white crystals of benzoic acid. These were analyzed for tritium, repuri-

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[28] M. R. Fenske, C. O. Tongberg and D. Quiggle, *Ind. Eng. Chem.*, **26**, 1169 (1934).

[29] C. W. Gould, Jr., G. Holzman and C. Niemann, *Anal. Chem.*, **20**, 361 (1948).

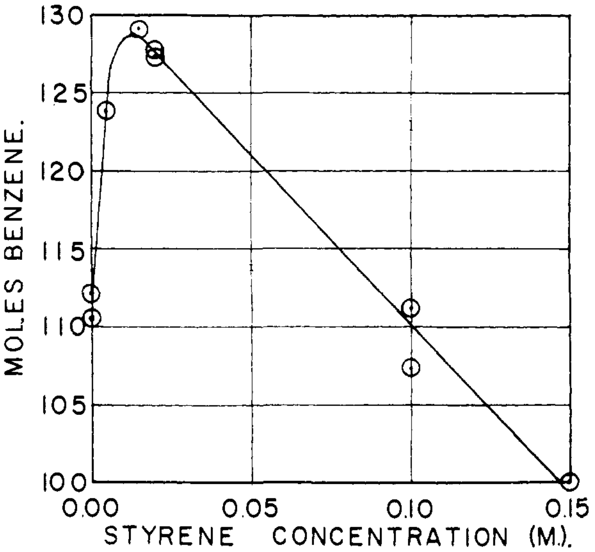

Fig. 3.—Moles of benzene obtained from one mole of 0.003 *M* benzoyl peroxide in cyclohexane at 91.1°.

fied, by ether–bicarbonate extraction and recrystallization, and again analyzed for tritium, until activity no longer changed on one or more repetitions of this cycle. The recrystallized benzoic acid melted at 123.0–123.5°, mixed m.p. with pure benzoic acid 123.0–123.5°.

The remainder of the mixture was concentrated to 20 ml. and chromatographed over 25 g. of Davison Chemical Co. 28–200 mesh silica gel. The column was eluted with 200 ml. of petroleum ether, 100 ml. of 1:4 benzene–petroleum ether, 160 ml. of 1:3 benzene–petroleum ether and finally 200 ml. of benzene. Fractions of about 25 ml. were collected, and the solvent evaporated. Biphenyl fractions 4–12 (0.9 g. of soft solid) were extracted with hot ethanol. Addition of water to the ethanol extract gave white crystals of biphenyl. These were recrystallized from water–ethanol, sublimed, and recrystallized twice more to constant specific activity and melting point (69–70°). Phenyl benzoate fractions 23 and 24 (0.6 g. of white needles, m.p. 64–68.5°) were crystallized from water–ethanol four times to constant specific activity and melting point (68.5–70°). From the molar activities of the products their yields were calculated.[3]

In the run which was stopped at 50% reaction, it was also necessary to remove unreacted benzoyl peroxide from the reaction mixture. To do this, benzoic acid was first extracted with aqueous sodium bicarbonate. The acid-free reaction mixture was evaporated at room temperature, the residue dissolved in acetone and treated with sodium iodide. Unreacted benzoyl peroxide oxidized the iodide to give iodine and benzoic acid. Chloroform was added, and the iodine extracted with aqueous sodium thiosulfate. Then the chloroform solution was extracted with aqueous sodium bicarbonate, dried with Drierite and concentrated to 10 ml. Biphenyl and phenyl benzoate were separated from the concentrate by chromatographing over silica gel as before.

To measure the benzene by ultraviolet absorption spectroscopy, it was necessary to separate it by distillation from styrene. A 0.00307 *M* solution of benzene (b.p. 80.1°) in cyclohexane (b.p. 80.6°) had an optical density of 0.72 at 255 mμ corresponding to a molar extinction coefficient of 235. A 50-ml. sample of this solution was distilled slowly through a 65-cm. Fenske column (about 9 theoretical plates).[28] The first 25 ml. of distillate had an optical density at 255 mμ of 1.37; that of the next 10 ml. was 0.01. Instead of there being no separation as expected, apparently all the benzene distilled over in the first 25 ml. A search of literature showed that indeed these two compounds do form an azeotrope. A mixture of 51.8 weight % benzene in cyclohexane boils at 77.7°.[30] Accordingly benzene yields were determined by decomposing 100.0-ml. aliquots at 91.1°, removing 50.0 ml. and distilling it slowly. The first 25 ml. was collected and its ultraviolet absorption measured. As a check, the next 10 ml. of distillate also was collected and analyzed, but usually showed little absorption. Only the optical density at 255 mμ was needed to determine benzene yields, but in all cases the entire absorption spectrum from 220 to 320 mμ was determined. Identity of these spectra with those of pure benzene ensured absence of contamination by styrene. The data obtained are plotted in Fig. 3.

To measure the cyclohexene formed, tubes were heated at 91° for 21 hours, cooled, opened and the contents distilled through a 30-cm. Holzman column[29] at atmospheric pressure. No attempt at fractionation was made, and everything boiling below 100° was forced over by flaming the column head during the final stages of the distillation. Residues were solid when cooled to room temperature and comprised under 1% of the charge. Reference solutions were prepared in 10-ml. volumetric flasks by breaking, under the surface of the cyclohexane, sealed ampoules made from melting-point tubing containing quantities of cyclohexene and benzene weighed accurately on a microbalance. Corrections for the volume of glass were negligible. Portions (0.50 ml.) of either unknown or reference solutions were measured out with a 0.50-ml. hypodermic syringe and injected into gas–liquid chromatography column containing a solution of silver nitrate in triethylene glycol adsorbed on firebrick at 45°. Preheater temperature was set at 150°. Retention times were characteristic and increased in the order cyclohexane < benzene < cyclohexene. Base lines were drawn in beneath benzene and cyclohexene peaks as smooth extensions of the tailing-off cyclohexane peak. Peak heights were measured at the maximum separation between the sketched-in base line and the curve itself in a direction normal to the true base line along the bottom of the paper. Concentrations of cyclohexene in reaction mixtures were estimated by quantitative comparison of peak heights of unknown solutions with those produced by reference solutions of known concentration. The accuracy of the results is only of the order of ±20% because of the very low concentrations of cyclohexene involved. As an over-all check on the procedure, 1.405 mg. of cyclohexene was added to a 5-ml. sample of reaction mixture before distillation and put through the procedure described. This reaction mixture contained 0.0003 *M* cyclohexene before the addition, 0.0037 after. The value found by analysis was 0.0043 *M*, which is within the estimated accuracy of the method (±20%). Table II lists benzene and cyclohexene yields found in four different runs by this method.

Table II

Yields of Benzene and Cyclohexene Determined by Gas-Liquid Chromatography

Peroxide, *M*	Styrene, *M*	Benzene, *M*	Cyclohexene, *M*
0.015	0.000	0.015	0.0018
.015	.015	.019	.0014
.015	.075	.018	.0003
.015	.600	.007	.0003

Tritium Analyses.—The compound to be analyzed was reduced by heating 10–20 mg. for 3 hours at 640° in an evacuated Pyrex 1720 tube with powdered zinc and nickelic oxide.[31] The hydrogen formed was transferred to an ionization chamber (Applied Physics Corp., Pasadena, Calif.), and the current produced measured with a vibrating reed electrometer (model 30, Applied Physics Corp.) attached to a Brown recording voltmeter.[3,32] These procedures were calibrated against tritiated water of known activity supplied by Tracerlab, Inc., Boston, Mass. Activities were corrected to Feb. 1, 1956, with the formula

$$\frac{\text{activity on } 2/1/56}{\text{activity observed}} = e^{0.6931t/t_{1/2}}$$

where t is days between 2/1/56 and the measurement (posi-

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[30] L. H. Horsley, "Azeotropic Data," American Chemical Society, Washington, D. C., 1952, p. 167.

[31] K. E. Wilzbach, L. Kaplan and W. G. Brown, *Science*, **118**, 522 (1953).

[32] W. A. Sheppard, Ph.D. Thesis in Organic Chemistry, M.I.T., November, 1954, pp. 125–156; C. G. Swain, V. P. Kreiter and W. A. Sheppard, *Anal. Chem.*, **27**, 1157 (1955).

tive if measurement made after 2/1/56; negative if before), and $t_{1/2}$ is the half-life of tritium, 12.46 × 365 days.[33]

Absence of Diphenyl and Phenyl Benzoate in Benzoyl-*p-t* Peroxide.—To show that the 2% of phenyl benzoate and 0.15% of biphenyl in the decomposition products were not present as radioactive impurities in the original peroxide, a non-radioactive sample of each of these was added to benzoyl peroxide-*p-t*, reisolated, and analyzed for tritium.

Biphenyl (1.0284 g., 6.669 millimoles) and benzoyl peroxide-*p-t* (0.5185 g. 2.141 millimoles) were dissolved in 25 ml. of acetone. Five grams of sodium iodide and 1 ml. of concd. hydrochloric acid were added. Iodine formed was reduced with aqueous sodium thiosulfate. Water and chloroform were added, the chloroform layer separated and extracted with aqueous sodium bicarbonate. Evaporation of the chloroform gave biphenyl, which was recrystallized from water–ethanol and analyzed for tritium. Activity of this biphenyl was 9.46×10^{-7} curie per mole; that of benzoyl peroxide 19.25. Therefore the amount of radioactive biphenyl in the peroxide is 0.0153%. Therefore about 10% of the biphenyl isolated from decomposition products may have been in the starting peroxide.

Phenyl benzoate (0.9574 g., 4.830 millimoles) and benzoyl peroxide-*p-t* (0.5068 g., 2.092 millimoles) were mixed and the phenyl benzoate reisolated as above. Reisolated phenyl benzoate had an activity of 3.01×10^{-6} curie per mole, corresponding to 0.0361% radioactive phenyl benzoate in the starting peroxide. Therefore only 2% of the phenyl benzoate isolated from the decomposition products could have been in the peroxide used.

These two experiments also show that the method of removing undecomposed peroxide in the run stopped at 50% reaction did not form biphenyl or phenyl benzoate.

Stability of Phenyl Benzoate to Base.—To show that phenyl benzoate is not hydrolyzed by the sodium bicarbonate used to extract benzoic acid, approximately 1 g. of phenyl benzoate was dissolved in 1000 ml. of cyclohexane and extracted with two 50-ml. portions of aqueous sodium hydroxide (1 g. of sodium hydroxide in 50 ml. of solution). The water layers were combined, acidified with hydrochloric acid, and extracted with ethyl ether. Titration of the ether layer with 0.0155 *M* sodium hydroxide showed that not more than 0.2% of the ester had been hydrolyzed.

Stability of Benzoyl Peroxide to Base.—Treatment of 0.596 g. of benzoyl peroxide in the same way with aqueous sodium bicarbonate showed that not more than 0.15% hydrolyzed. It was necessary to show this to know that the sodium bicarbonate used to extract benzoic acid in the run stopped at 50% reaction did not hydrolyze unreacted benzoyl peroxide.

Stability of Benzyl Benzoate to Base.—Approximately 1 g. of benzyl benzoate was dissolved in cyclohexane and extracted with aqueous sodium bicarbonate solution. The water layer was separated, acidified with hydrochloric acid and extracted with ether. Evaporation of the ether gave no visible precipitate of benzoic acid.

Acknowledgment.—We are indebted to Dr. Frederick D. Greene for helpful suggestions and discussion.

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[33] G. H. Jenks, F. H. Sweeton and J. A. Ghormley, *Phys. Rev.*, **80**, 990 (1950).

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SPRAGUE ELECTRIC CO.]

Nucleophilic Displacement Reactions in Aromatic Systems. III. The Rates of Reaction of 2,4-Dinitrochlorobenzene with *n*-Butylamine and with Hydroxide Ion in 50% Dioxane–50% Water

BY SIDNEY D. ROSS

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The rates of reaction of 2,4-dinitrochlorobenzene with *n*-butylamine and sodium hydroxide, both separately and together, in 50% dioxane–50% water at 24.8 ± 0.1° have been measured. The results suggest but do not prove that the reaction with the amine is subject to catalysis by both *n*-butylamine and hydroxide ion.

Bunnett and his co-workers have claimed that the reaction of piperidine with 2,4-dinitrochlorobenzene in 95% ethanol is first-order and not a higher order in piperidine[1] and that added sodium hydroxide does not accelerate this same reaction in 50% dioxane–50% water.[2] It was further argued that these observations rigorously exclude the possibility of base-catalysis in this and similar systems.

Results from this Laboratory have shown that a complete description of the reaction of 2,4-dinitrochlorobenzene with both primary and secondary amines in chloroform and in ethanol requires two kinetic terms, one first-order in amine and the other second-order in amine.[3] In a more detailed study of the reaction of 2,4-dinitrochlorobenzene with *n*-butylamine in chloroform it was further found that added triethylamine, which does not itself react with 2,4-dinitrochlorobenzene at an appreciable rate, nevertheless accelerates the rate of the reaction of the chloride with *n*-butylamine.[4] This latter result is in accord with a comparable, earlier observation made by Brady and Cropper[5] for the reaction of 2,4-dinitrochlorobenzene with methylamine in ethanol.

The pertinent measurements made by Bunnett, *et al.*, with 2,4-dinitrochlorobenzene and piperidine[1,2] were all with relatively low initial concentrations of both the amine (maximum concentration, 0.04 *M*) and sodium hydroxide (maximum concentration, 0.04 *M*). More important, neither the amine nor the hydroxide ion concentrations were varied appreciably. It has been our experience that for such experimental conditions third-order kinetic terms may very easily escape detection. This has raised doubts in our minds with respect to Bunnett's conclusions and led us to investigate the reaction of 2,4-dinitrochlorobenzene with *n*-butylamine and with hydroxide ion, both separately and together, in 50% dioxane–50% water. *n*-Butylamine was used in preference to piperidine because it reacts with the chloride at a more conveniently measurable rate.

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[1] J. F. Bunnett and H. D. Crockford, *J. Chem. Ed.*, **33**, 552 (1956).

[2] J. F. Bunnett and K. M. Pruitt, *Elisha Mitchell Sci. Soc.*, **73**, 297 (1957).

[3] S. D. Ross and M. Finkelstein, THIS JOURNAL, **79**, 6547 (1957).

[4] S. D. Ross and R. C. Petersen, *ibid.*, **80**, 2447 (1958).

[5] O. L. Brady and F. R. Cropper, *J. Chem. Soc.*, 507 (1950).