on seeding with an authentic specimen. The infrared spectra were identical. The distillation residue was treated with ethanol to give 2.6 g. (26%) of recovered 1,1-dimethyl-1,2,2,-2-tetraphenyldisilane, m.p. 81.5-83° (mixed m.p.).

Addition of Methyldiphenylsilyllithium to Hexaphenyldisilane.—To a stirred suspension of 7.9 g. (0.0152 mole) of hexaphenyldisilane in 25 ml. of tetrahydrofuran (THF) was added 80 ml. of a THF solution of methyldiphenylsilyllithium prepared by the cleavage of 6.0 g. (0.0152 mole) of 1,2-dimethyl-1,1,2,2-tetraphenyldisilane with excess lithium. One hour after the addition was complete, water was added, and filtration of the organic layer gave 1.73 g. (22%) of hexaphenyldisilane, m.p. 365-367° (mixed m.p.). The residue from the dried filtrate was dissolved in hot petroleum ether (b.p. 60-70°) and chromatographed on an alumina column. The petroleum ether fractions were collected. The first was evaporated to dryness and treated with ethanol to give 1.57 g. (26%) of 1,2-dimethyl-1,1,2,2-tetraphenyldisilane, m.p. 142-146°, identified by a mixed melting point with an authentic specimen. A mixed melting point with methylpentaphenyldisilane was depressed. The second petroleum ether fraction was treated similarly with ethanol to give 1.78 g. (*ca.* 29%) of solid, m. 121-133°. The melting point was not improved by recrystallization. The infrared spectrum indicated that this material was a mixture of 1,2-dimethyl-1,1,2,2-tetraphenyldisilane and methylpentaphenyldisilane, which are very difficult to separate.[1] The ethanol filtrates were combined and evaporated to give an oil. When chilled and seeded with triphenylsilane, the entire mass crystallized. The product weighed 4.7 g. (59.5%), m.p. 43-45°, and was shown by the infrared spectrum and mixed melting point to be triphenylsilane.

Addition of Dimethylphenylsilyllithium to 1,2-Dimethyl-1,1,2,2-tetraphenyldisilane.—To a solution of 11.7 g. (0.0296 mole) of 1,2-dimethyl-1,1,2,2-tetraphenyldisilane in 75 ml. of tetrahydrofuran (THF) was added 70 ml. of a THF solution of dimethylphenylsilyllithium prepared by the cleavage of 8.0 g. (0.0296 mole) of 1,1,2,2-tetramethyl-1,2-diphenyldisilane with excess lithium. Thirty minutes after the addition was complete, the reaction mixture was poured into cold hydrochloric acid. From the dried organic layer was obtained an oil which was distilled to give 9.06 g. (77.5 %) of methyldiphenylsilane, b.p. 79° (0.1 mm.), $n^{20}\text{D}$ 1.5694 (reported b.p. 82° (0.15 mm.), $n^{20}\text{D}$ 1.5747[11]; b.p. 137-139° (14 mm.), $n^{20}\text{D}$ 1.5724[12]). The identity of the silane was further confirmed by the infared spectrum which showed a strong Si-H absorption band at 4.7μ. A second fraction boiling at 96-98° (0.1 mm.), 3.6 g. (45%), crystallized on seeding with 1,1,2,2-tetramethyl-1,2-diphenyldisilane and was shown to be this compound by the infrared spectrum.

Lithium Cleavage of 1,1,1-Triethyl-2,2,2-triphenyldisilane.—One hundred milliliters of tetrahydrofuran was added slowly to a stirred mixture of 15.0 g. (0.040 mole) of 1,1,1-triethyl-2,2,2-triphenyldisilane and 2.5 g. (0.36 g. atom) of finely-cut lithium wire. The reaction started immediately; the deep colored solution gave a positive Color Test I.[13] During the addition, the flask was cooled in an ice-bath. The reaction mixture was stirred for 45 min. at 0° and allowed to warm to room temperature over a period of 30 min. Subsequent to hydrolysis with dilute acid, addition of some ether, extraction with water, and drying of the organic layer over sodium sulfate, the product was distilled. There was obtained 0.5 g. (11%) of triethylsilane, b.p. 30-35° (15 mm.), identified by the infrared spectrum; 0.65 g. (14%) of hexaethyldisilane, b.p. 103-108° (15 mm.), identified by the infrared spectrum; and 9.45 g. (92%) of slightly impure triphenylsilane, b.p. 142-148° (0.2 mm.). The infrared spectrum of the last compound indicated the presence of an impurity containing aliphatic C—H bonds. Attempts to isolate additional products by use of chromatography or recrystallization failed.

Cleavage of Triphenylmethyltriphenylsilane by Triphenylsilyllithium (Attempted).—To a stirred suspension of 3.0 g. (0.00597 mole) of triphenylmethyltriphenylsilane in 20 ml. of tetrahydrofuran (THF) was added 25 ml. of a THF solution of triphenylsilyllithium prepared by cleavage of 2.08 g. (0.004 mole) of hexaphenyldisilane. After one hour, the reaction mixture was carbonated by pouring jet-wise into a slurry of Dry Ice and ether. The carbonated mixture was allowed to stand for two hours to ensure complete decomposition of lithium triphenylsilanecarboxylate to the lithium salt of triphenylsilanol and carbon monoxide.[14] The mixture was then shaken with 10% sodium hydroxide. Acidification of the aqueous layer gave no acid. From the organic layer was filtered 2.71 g. (90%) of recovered triphenylmethyltriphenylsilane, m.p. 317-325° dec. A mixed melting point with an authentic specimen was not depressed.

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(11) R. A. Benkeser and D. J. Foster, THIS JOURNAL, **74**, 5314 (1952).

(12) R. D. Gorsich, Doctoral Dissertation, Iowa State College, 1957.

(13) H. Gilman and F. Schulze, THIS JOURNAL, **47**, 2002 (1925).

(14) R. A. Benkeser and R. G. Severson, *ibid.*, **73**, 1424 (1951).

AMES, IOWA

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

A Study of the Induced Decomposition of Benzoyl Peroxide in Diethyl Ether

BY DONALD B. DENNEY AND GERALD FEIG

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Benzoyl peroxide, labeled with oxygen-18 in the carbonyl oxygens, has been allowed to decompose in a mixture of diethyl ether and sodium hydride. The α-ethoxyethyl benzoate obtained from this reaction was reduced with lithium aluminum hydride to give benzyl alcohol which contained 80% of the excess oxygen-18 originally incorporated in a carbonyl oxygen of the benzoyl peroxide. These results indicate that in the induced decomposition of benzoyl peroxide in ether the α-ethoxyethyl radical attacks predominantly, if not exclusively, on one of the oxygens of the peroxide link.

The reactions of organic peroxides have received much attention in recent years.[1] The products of these reactions are often numerous and vary widely with changes in reaction conditions. These reactions are oftentimes further complicated by induced decompositions in which radicals derived from the solvent or reaction intermediates attack on the peroxide.

A peroxide decomposition that has been studied in some detail is that of benzoyl peroxide (I) in diethyl ether. Cass[2] has found that this reaction yields 1-ethoxyethyl benzoate (II) and benzoic acid (III)

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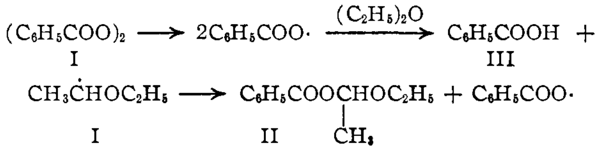
(1) (a) A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954; (b) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957.

(2) W. E. Cass, THIS JOURNAL, **69**, 500 (1947).

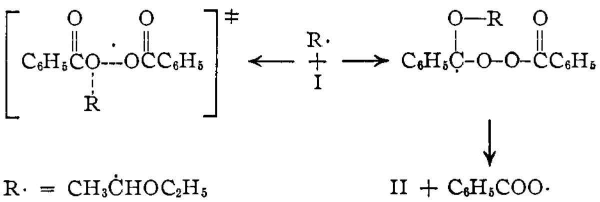
as the major products. The kinetics of this reaction have been elucidated by Cass[3] and also Nozaki and Bartlett.[4] The kinetic studies indicate that two modes of decomposition are operating: spontaneous unimolecular decomposition and an induced chain decomposition. Other evidence for the induced decomposition is afforded by the finding that the decomposition is retarded by known inhibitors and, in a similar system,[4] accelerated by the addition of free radicals. Both Cass and Nozaki and Bartlett agree that a chain reaction is involved. Walling[5] has estimated, based on calculations made from the data of Nozaki and Bartlett, that the chain length is approximately fifty. The most plausible reaction scheme may be represented by the series of equations



$$\underset{\text{I}}{(C_6H_5COO)_2} \longrightarrow 2C_6H_5COO\cdot \xrightarrow{(C_2H_5)_2O} \underset{\text{III}}{C_6H_5COOH} +$$

$$\underset{\text{I}}{CH_3\dot{C}HOC_2H_5} \longrightarrow \underset{\text{II}}{C_6H_5COO\underset{\substack{|\\CH_3}}{C}HOC_2H_5} + C_6H_5COO\cdot$$

Two possibilities have been discussed[5] for the mechanism of the reaction of the α-ethoxyethyl radical with benzoyl peroxide. The α-ethoxyethyl radical may displace on an ether oxygen atom of the benzoyl peroxide to give 1-ethoxyethyl benzoate and a benzoyloxy radical or it could add to one of the carbonyl oxygens to give a radical which would then decompose into II and a benzoyloxy radical. The two possibilities can be illustrated in the manner shown

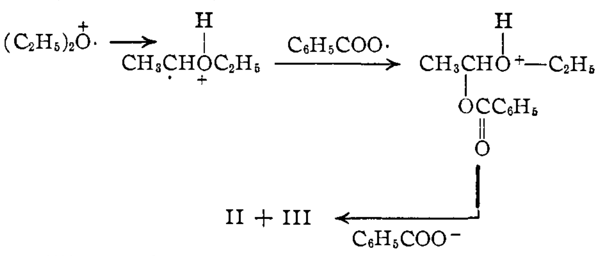


$R\cdot = CH_3\dot{C}HOC_2H_5$

Walling[5] has suggested that addition followed by dissociation is perhaps more reasonable since displacement on oxygen is not observed during the decomposition of dialkyl peroxides.[6]

Another, rather unique, mechanism for the decomposition of benzoyl peroxide in diethyl ether has been proposed by Kenner.[7] This mechanism is outlined below. It should be noted that Kenner's mechanism makes no provision for an induced decomposition and is therefore not in agreement with the kinetic studies.[3,4]

It was the purpose of this research to study the mechanism of the induced decomposition of benzoyl peroxide in diethyl ether. Benzoyl peroxide, labeled with oxygen-18 in both carbonyl positions, was allowed to decompose in refluxing diethyl ether for seven days. After removal of the benzoic acid, the ether solution of II was reduced with lithium aluminum hydride to give benzyl alcohol. Oxygen-18 analysis showed that the benzyl alcohol had 56% of the excess oxygen-18 originally incorporated in a carbonyl oxygen of the benzoyl peroxide. These results indicate that the oxygen atoms of the benzoyloxy group in II are almost completely equilibrated.[8] The equilibration could have arisen in several ways. Partial equilibration of the label would be found if the α-ethoxyethyl radical attacks on both the ether oxygens and the carbonyl oxygens of the benzoyl peroxide. It is not safe to conclude that this is the only mechanism for equilibration since II should be considerably more reactive toward ionization and displacement than a conventional ester.[9] Indeed it was observed that II decomposed to benzoic acid on standing. Since benzoic acid is produced along with II during the reaction, it could catalyze ionization of II or displace on it; both of these reactions would cause equilibration of the label. It also seemed possible that some equilibration or loss of oxygen-18 could occur during the lithium aluminum hydride reduction of II. It should be noted however that the lithium aluminum hydride reduction of 1-benzoyloxy-1,6-epoxycyclodecane-*carbonyl*-O^{18}, a relatively similar system, produced benzyl alcohol which contained essentially all of the oxygen-18.[10]



$$\text{I} + (C_2H_5)_3O \longrightarrow (C_2H_5)_2\overset{+}{O}\cdot + C_6H_5COO\cdot + C_6H_5COO^-$$

$$(C_2H_5)_2\overset{+}{O}\cdot \longrightarrow CH_3\underset{\cdot}{C}H\overset{\overset{H}{|}}{\underset{+}{O}}C_2H_5 \xrightarrow{C_6H_5COO\cdot} CH_3\underset{\substack{|\\ OCC_6H_5 \\ \| \\ O}}{C}H\overset{\overset{H}{|}}{O}{}^{+}\!-\!C_2H_5 \xrightarrow{C_6H_5COO^-} \text{II} + \text{III}$$

In order to determine if II equilibrates in ether containing benzoic acid, unlabeled II was allowed to react for sixty-one hours with oxygen-18 labeled benzoic acid in refluxing diethyl ether. Analysis of recovered II showed that exchange had occurred. The recovered II had at least 11% of the excess oxygen-18 originally incorporated in the benzoic acid.[11] These results indicated that at least some of the equilibration of the label was due to reaction of II.

In order to minimize equilibration of II, it was decided to remove the benzoic acid as it was formed

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[3] W. E. Cass, THIS JOURNAL, **68**, 1976 (1946).

[4] K. Nozaki and P. D. Bartlett, *ibid.*, **68**, 1686 (1946).

[5] Reference 1b, p. 479.

[6] J. H. Raley, F. F. Rust and W. E. Vaughan, THIS JOURNAL, **70**, 1336 (1948), have found that di-*t*-butyl peroxide decomposes in the gas phase by means of a unimolecular process uncomplicated by any sort of induced chain process. On the other hand, E. R. Bell, F. F. Rust and W. E. Vaughan, *ibid.*, **72**, 337 (1950), have shown that in the liquid phase one of the products of the decomposition of di-*t*-butyl peroxide is isobutene epoxide which presumably arises by an intramolecular decomposition of the radical $(CH_3)_2\overset{\overset{\dot{C}H_2}{|}}{C}OOC(CH_3)_3$. The fact that the epoxide is formed certainly indicates that displacement on oxygen by a radical is not a prohibited process.

[7] J. Kenner, *Tetrahedron*, **3**, 78 (1958).

[8] Since II was not analyzed for oxygen-18 it is assumed that it contained all of the excess oxygen-18 present in a potential benzoyloxy group of the benzoyl peroxide; II might not contain all of the theoretical amount of oxygen-18 since a small amount could have been lost by exchange during the processing of the ether solution of II. Such exchange would lower the value found for the oxygen-18 content of the benzyl alcohol.

[9] A. Streitwieser, Jr., *Chem. Revs.*, **56**, 675 (1956).

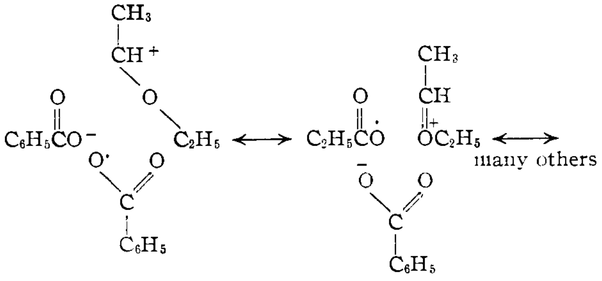
[10] D. B. Denney and D. G. Denney, THIS JOURNAL, **79**, 4806 (1957).

[11] The value of 11% is a minimum value since it was shown later that these analyses were low. They were not repeated since the exchanged sample of II had decomposed. Since exchange had been demonstrated, the experiment was not repeated.

by converting it to an insoluble salt. The base selected for this task was sodium hydride, after it was found that it reacted rapidly with benzoic acid dissolved in ether. The other substances in the reaction mixture were apparently unaffected by the sodium hydride, since there was no modification in the course of the reaction or in the yield of II.

The decomposition of labeled benzoyl peroxide in ether to which sodium hydride had been added gave II and sodium benzoate. Reduction of II with lithium aluminum hydride gave benzyl alcohol which contained 80% of the excess oxygen-18 originally incorporated in a carbonyl oxygen of the benzoyl peroxide. This finding shows that displacement by the α-ethoxyethyl radical on an ether oxygen of the benzoyl peroxide is the predominant if not exclusive path for the induced decomposition of benzoyl peroxide. The maximum amount of decomposition which can be taking place by the addition–dissociation path is 20%. Most probably there is not attack on the carbonyl oxygen. The value of 80% oxygen-18 could be due to a number of factors mentioned earlier.

A preference for displacement over addition by the radical is not unreasonable since the oxygen–oxygen bond is the weakest bond in the molecule; also analogous reactions of benzoyl peroxide with nucleophiles such as trisubstituted phosphines,[12] phenols[13,14] and amines[14] all proceed by initial displacement on one of the peroxide oxygens. The preference for displacement by the radical is explicable if one considers that considerable stabilization of the transition state can be afforded by ionic contributors[15] such resonance stabilization of the transition state by ionic contributors is evidently of considerable importance in these induced decompositions since those radicals which can form stable carbonium ions cause the most rapid induced decomposition of benzoyl peroxide.



Acknowledgment.—It is a pleasure to acknowledge the financial assistance given by the Colgate–Palmolive Co. to G. F. We are also indebted to Dr. P. R. Schleyer and the Colgate–Palmolive Co. for the mass-spectral analyses.

Experimental[16]

Reaction of Benzoyl Peroxide-carbonyl-O^{18} in Diethyl Ether.—A solution of 4.92 g. (0.20 mole) of benzoyl peroxide-carbonyl-O^{18} (1.31 atom % excess oxygen-18 per carbonyl group) in 125 ml. of anhydrous ether was refluxed for 7 days. The ether solution of II was extracted three times with 50-ml. portions of aqueous sodium bicarbonate and dried over magnesium sulfate. The sodium bicarbonate extracts, upon acidification, afforded 1.8 g. (74%) of benzoic acid, m.p. 118–121°.

Reduction of II.—The dried ether solution of II obtained above was added dropwise to a stirred solution of 1.52 g. (0.04 mole) of lithium aluminum hydride in 50 ml. of anhydrous ether. The mixture was refluxed with stirring for 3 hours. The excess lithium aluminum hydride was decomposed by adding the minimum amount of water. The resulting hydroxides were removed by filtration and the ether solution was dried over magnesium sulfate. The ether was removed by distillation and the residue was molecularly distilled to afford 1.0 g. (46%) of benzyl alcohol, b.p. block temperature 92–105° (27 mm.), $n^{26.5}\mathrm{D}$ 1.5230. The infrared spectrum of this material was identical to that of a known sample.

The phenylurethan was prepared by allowing 0.65 g. (0.0055 mole) of phenyl isocyanate to react with 0.53 g. (0.005 mole) of benzyl alcohol in 6 ml. of hexane. The urethan was purified by crystallization from hexane, m.p. 76.5–77.3° (lit.[17] 78°). Analyses of this material for oxygen-18 showed that it had 0.74, 0.72 atom % excess oxygen-18.

Reaction of II with Benzoic Acid-carboxyl-O^{18}.—A solution of 3.66 g. (0.03 mole) of benzoic acid, containing 1.30 atom % excess oxygen-18 in each position, and 5.83 g. (0.03 mole) of II in 100 ml. of anhydrous ether was refluxed for 61 hr. The ether solution was extracted with three 100-ml. portions of 5% sodium bicarbonate, washed twice with 100-ml. portions of water and dried over sodium sulfate. After removal of the ether, the residue was distilled to afford 2.15 g. of II, b.p. 92° (2.6 mm.), $n^{29.5}\mathrm{D}$ 1.4852 (lit.[2] b.p. 57–58° (0.2 mm.), $n^{25}\mathrm{D}$ 1.4868). Oxygen-18 analysis showed this compound had 0.24, 0.28 atom % excess oxygen-18.

Reaction of Benzoyl Peroxide with Diethyl Ether in the Presence of Sodium Hydride.—A mixture of 9.69 g. (0.04 mole) of benzoyl peroxide-carbonyl-O^{18} (1.31 atom % excess oxygen-18 per carbonyl group), 1.20 g. (0.05 mole) of sodium hydride and 120 ml. of anhydrous ether was refluxed for 7 days with stirring. The excess sodium hydride was decomposed by the slow addition of a mixture of 40 parts water and 60 parts *t*-butyl alcohol. Additional water was then added to dissolve the salts. The ether layer was separated, washed twice with 100-ml. portions of water and dried over sodium sulfate. After removal of the ether, the residue was distilled to yield 4.4 g. (57%) of II, b.p. 72–74° (0.4 mm.), $n^{23.5}\mathrm{D}$ 1.4887. The infrared spectrum of this material was identical with that of a sample prepared in a large scale reaction of unlabeled materials.

Reduction of II.—Compound II was reduced with lithium aluminum hydride as described above to give benzyl alcohol, 67%, b.p. block temperature 83–88° (22 mm.), $n^{24}\mathrm{D}$ 1.5345. The infrared spectrum of this material was identical to that of a known sample. The phenylurethan was prepared as before, m.p. 76.5–77.5°. Oxygen-18 analysis showed that the material had 1.03, 1.05 atom % excess oxygen-18.

NEW BRUNSWICK, N. J.

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

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

[14] D. G. Denney, unpublished work.

[15] C. G. Swain, W. H. Stockmayer and J. J. Clarke, *ibid.*, **72**, 5426 (1950).

[16] Oxygen-18 analyses were carried out using the method of W. E. Doering and E. Dorfman, *ibid.*, **75**, 5595 (1953), as modified by D. B. Denney and M. A. Greenbaum, *ibid.*, **79**, 979 (1957).

[17] R. Shriner, R. Fuson and D. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 281.