Ozonization of Isoquinoline-2-oxide (42). In Methanol.—A pale yellow solution of 3.0 g. (16.6 mmoles) of **42** dihydrate in 200 ml. of methanol at $-78°$ was treated with 16.5 mmoles of ozone with no detectable color change. After flushing with nitrogen, 20 ml. of 10% sodium hydroxide solution was added, and the red-colored alkaline solution extracted with 4×50 ml. of chloroform. The chloroform extracts were evaporated to dryness and the residue, recrystallized from ethyl acetate, was unreacted **42**.

The alkaline solution was acidified and extracted with benzene for 24 hr.; evaporation of the benzene extract left <1% of the impure hydroxamic acid **43**. The acid fraction was neutralized and the whole oxidized with 20 ml. of 10% sodium hydroxide and 20 ml. of 30% hydrogen peroxide. After refluxing for 2 hr., the solution was acidified with hydrochloric acid (vapors of NO_2 evolved) and concentrated (Rinco) to 50 ml. On cooling, **44** precipitated, m.p. 195–200°.[62] Continuous ether extraction of the filtrate led to additional amounts of **44**.

When two or more (to a maximum of 2.6) molar ozone equivalents were used, only black tars were obtained on evaporation of the benzene extract. In similar experiments, sodium hydroxide and hydrogen peroxide were added directly to the ozonized methanolic solution. After evaporation of the methanol and refluxing several hours, the solution was acidified and extracted (continuously) with benzene for 24 hr. The benzene extract was evaporated to dryness, and the residue, recrystallized from 1:1 benzene–cyclohexane, gave monomethyl phthalate, m.p. 79–80°,[62] as white plates, lit.[68] m.p. 79°.

In solvent methylene chloride, quantities, ozonization procedure, and nitrogen purging were as in solvent methanol. The ozonized solution was extracted with 5×50 ml. of 1% sodium hydroxide; the methylene chloride fraction gave unreacted **42**.

The red alkaline extracts were acidified with concentrated hydrochloric acid to give a yellow, turbid solution which was continually extracted with benzene for 24 hr. Evaporation of the benzene extract left a brown paste which was dissolved in 5% ammonium hydroxide, heated to remove excess ammonia, treated with charcoal, and filtered. Acidification of the filtrate and cooling gave pale yellow needles of 2-hydroxyisocarbostyril (**43**), m.p. 184–185°[62] (sublimed).

The acidic solution, after extraction, was neutralized, and to it was added 20 ml. of 10% sodium hydroxide and 20 ml. of 30% hydrogen peroxide. Refluxing for 2 hr., followed by acidification, concentration to 50 ml. (Rinco), and charcoal treatment, gave **44** on cooling. When **42** was ozonized with 2.4 molar ozone equivalents, the methylene chloride extracts yielded a brown material, m.p. 115–117°, which on oxidation with alkaline hydrogen peroxide ultimately produced a white powder (∼1 g.), m.p. > 360°. Both of these products were not further identified.

Ozonization of 3-Methylisoquinoline-2-oxide (45). In Methylene Chloride.—Ozonolysis and alkaline extraction procedures were identical with those used in the ozonization of **42**. The methylene chloride extracts led to unreacted **45**. Acidification of the red alkaline extract with hydrochloric acid produced a brick-red precipitate which was filtered and recrystallized from carbon tetrachloride to give tan needles of 2-hydroxy-3-methylisocarbostyril (**46**), m.p. 172.5–173° (sublimed as white plates), lit. m.p.[33] 172.5–173°.

Anal. Calcd. for $C_{10}H_9NO_2$: C, 68.56; H, 5.18; N, 8.00. Found: C, 68.57; H, 5.21; N, 8.17.

(68) G. Koller and E. Shang, *Monatsh.*, **50**, 48 (1928).

As with **42**, neutralization of the acid filtrate followed by alkaline hydrogen peroxide oxidation and acidification led to **44**, separated both by precipitation and ether extraction.

The benzoate ester of **46** was prepared by treating a solution of 0.2 g. of **46** in 3 ml. of anhydrous pyridine with 0.3 g. of benzoyl chloride. The solution was warmed for a few minutes, then cooled, and added to 25 ml. of cracked ice. The N-benzoate ester was collected by filtration, washed with water, and recrystallized from 50% ethanol (60% yield); m.p. 167–168°,[62] lit.[33] m.p. 167–168°.

With 2.0–2.4 molar equivalents (max. ozone absorption) in methylene chloride, only small amounts (0.1%) of **46** could be isolated.

In solvent methanol, the absorption of one molar ozone equivalent led to **44** and a low yield of **46**. Increasing the amounts of ozone (to a maximum of 2.6 molar equivalents) led only to **44**.

Ozonization of 1-Methylisoquinoline-2-oxide (47).—Compound **47** was insoluble in methylene chloride. A suspension of 3.0 g. (1.90 mmoles) in 200 ml. of methylene chloride was treated with 22 mmoles of ozone. No reaction was observed; some 98% of **45** was recovered and approximately 95% of the ozone passed into the potassium iodide trap. Ozonization of **45** in methanol with 1.7 molar ozone equivalents led to a 70% recovery of unreacted **47**. Work-up procedures similar to those of **42** led to no identifiable products.

Cyclic Hydroxamic Acids

Ozonization of 1-Hydroxycarbostyril (25). In Methanol.—A solution of 644 mg. (4.0 mmoles) of **25** in 100 ml. of methanol at $-78°$ was subjected to a stream of 8 l. of ozone–oxygen. Treatment of the ozonized solution with 50 ml. of 2% sodium hydroxide solution and evaporation of the alcohol left a dark brown solution which was extracted with three 25-ml. portions of chloroform. The chloroform extracts were evaporated to dryness (Rinco) to leave a yellow residue. Recrystallization from 25% ethanol gave 7–10% of carbostyril (**28**), m.p. 198–199°.[62]

The alkaline solution was acidified to recover 8–11% of unreacted **25**. Alkaline peroxide oxidation of the acid filtrate yielded (after reacidification) a fine yellow solid (50 mg.), m.p. > 360°; the infrared spectrum of this material showed no sharp absorption bands. This product was not further investigated.

In methylene chloride, **25** did not yield any **28**. Only 5% of **25** was recovered, in addition to the high-melting yellow solid.

Attempted Ozonization of 2-Hydroxyisocarbostyril (43) and 2-Hydroxy-3-methylisocarbostyril (46).—Using ozonization–base decomposition procedures similar to those for **25**, no deoxygenation or bond cleavage products could be isolated from **43** or **46**. In both cases, alkaline peroxide oxidation of the ozonized isocarbostyrils led to unidentified, high melting, colored (cream, yellow) solids.

Ozonization of 10-Hydroxy-9-acridanone (33).—A suspension of 1.0 g. (4.7 mmoles) of **33** in 220 ml. of methanol or methylene chloride at 20° was ozonized in the usual manner with 1.0 molar ozone equivalent. Conventional nitrogen purge, the addition of 50 ml. of 1% sodium hydroxide, and the azeotropic removal of solvent were as previously described. The red solution was filtered while hot to leave a yellow residue which was washed with 3×30 ml. of hot water and then recrystallized from ethanol to give tiny pale yellow needles of 9-acridanone (**3**)[62] in 10% yield. Acidification of the red alkaline solution gave 60–72% of unreacted **33**. Two molar ozone equivalents (ozone–oxygen and ozone–nitrogen) addition to **33** led to 14–18% of **3** and 44–65% recovery of **33**.

Reactions of Lewis Acids with Diaroyl Peroxides[1]

BY DOROTHY Z. DENNEY, THOMAS M. VALEGA,[2] AND DONALD B. DENNEY[3]

The conversion of benzoyl peroxide to phenyl benzoate by antimony pentachloride has been studied by the oxygen-18 tracer technique. The reaction is shown to involve an initial carboxy-inversion process which gives benzoyl phenyl carbonate. The mixed carbonate is converted to phenyl benzoate and carbon dioxide rapidly by antimony pentachloride. An oxygen-18 tracer study of the formation of 2,4,6-trimethylphenyl p-nitrobenzoate (III) from labeled p,p'-dinitrobenzoyl peroxide, aluminum chloride, and mesitylene showed that partial equilibration of the label occurs during the transformation. It was found that bimesityl is a product of the reaction. Various mechanistic implications of these results are discussed.

A series of papers appeared, in 1927, in which Reynhart[4] described the reaction of benzoyl peroxide with a number of inorganic acid chlorides. Several reactions were reported, but only two are of concern here. The first involves the reaction of antimony pentachloride

(1) A portion of the material being reported appeared in *J. Am. Chem. Soc.*, **84**, 2455 (1962).

(2) National Defense Education Act Fellow, 1959–1962; Public Health Service Fellow, 1962–1963.

(3) Rutgers Research Council Faculty Fellow, 1963–1964.

(4) A. F. A. Reynhart, *Rec. trav. chim.*, **46**, 54, 62, 72 (1927).

with benzoyl peroxide which was reported to give

$$(C_6H_5\overset{O}{\overset{\|}{C}}O)_2 \xrightarrow{SbCl_5} C_6H_5\overset{O}{\overset{\|}{C}}OC_6H_5 + CO_2 \quad (1)$$

phenyl benzoate and carbon dioxide in excellent yield. The second involved the reaction of aluminum chloride with benzoyl peroxide in benzene which was said to give phenyl benzoate and benzoic acid in greater than 90% yield.

$$(C_6H_5\overset{O}{\overset{\|}{C}}O)_2 + C_6H_6 \xrightarrow{AlCl_3} C_6H_5\overset{O}{\overset{\|}{C}}OC_6H_5 + C_6H_5CO_2H \quad (2)$$

Apparently this work was little noted for it was only recently that further investigation of these transformations was undertaken.[5,6] Both groups reported that they could not duplicate reaction 2. Edward and co-workers did obtain the products but in much lower yields than those reported by Reynhart. Considerable quantities of carbon dioxide were also obtained. It was concluded[5,6] that benzoyl peroxide does not react with benzene in the presence of aluminum chloride by a substitution process but rather undergoes a carboxy-inversion reaction[7] which gives phenyl benzoate and carbon dioxide.

Edward, Chang, and Samad[6] reported that they could effect an apparent Friedel–Crafts substitution (reaction 2) when they used a peroxide, which was deactivated toward the carboxy-inversion reaction, e.g., p,p'-dinitrobenzoyl peroxide, in conjunction with a highly reactive aromatic substrate such as mesitylene.

It is the purpose of this report to present data obtained from oxygen-18 tracer studies of these reactions.

Carboxy-Inversion Reaction.—Benzoyl peroxide labeled with oxygen-18 in the carbonyl groups was allowed to react with 10 mole % of antimony pentachloride in petroleum ether. From this reaction a 90% yield of phenyl benzoate was obtained. Treatment of the phenyl benzoate with hydrazine afforded phenol, which contained no excess oxygen-18, and benzoic acid hydrazide, which contained essentially all of the excess oxygen-18 originally present in the peroxide.

$$(C_6H_5\overset{O^{18}}{\overset{\|}{C}}O)_2 \xrightarrow{SbCl_5} C_6H_5\overset{O^{18}}{\overset{\|}{C}}OC_6H_5 \xrightarrow{NH_2NH_2}$$
$$C_6H_5\overset{O^{18}}{\overset{\|}{C}}NHNH_2 + C_6H_5OH$$

The results of this study demonstrate that the label remains in the carbonyl group during the transformation. The tracer results coupled with the Lewis acid character of the catalyst and with the migratory aptitude studies of Huisgen and Edl[5] leave little doubt that the reaction involves an initial carboxy-inversion. Coordination by the Lewis acid with a carbonyl oxygen seems eminently reasonable.[8] Rearrangement through a transi-

$$\left[\begin{array}{c} \overset{18}{\overset{+}{O}}\text{—}\overset{-}{SbCl_5} \quad \overset{O^{18}}{\overset{\|}{}} \\ C_6H_5\overset{}{\overset{}{C}}\text{—}O\text{—}O\text{—}\overset{}{\overset{}{C}}C_6H_5 \end{array} \leftrightarrow \begin{array}{c} \overset{18}{\overset{-}{O}}\text{ }\overset{-}{SbCl_5} \quad \overset{O^{18}}{\overset{\|}{}} \\ C_6H_5\overset{}{\overset{}{C}}=\overset{+}{O}\text{—}O\text{—}\overset{}{\overset{}{C}}C_6H_5 \end{array} \leftrightarrow etc. \right]$$

$$\downarrow$$

$$C_6H_5\overset{O^{18}}{\overset{\|}{C}}\text{—}O\text{—}\overset{O^{18}}{\overset{\|}{C}}OC_6H_5 \underset{I}{\leftarrow} \left[\begin{array}{c} \overset{18}{\overset{-}{O}}\text{-}SbCl_5 \quad O^{18} \\ C_6H_5\overset{}{\overset{}{C}}\text{---}O \cdots \overset{C}{\underset{O}{\cdots}} \end{array} \right]^{\ddagger}$$
$$I \quad + SbCl_5 \qquad\qquad A$$

tion state depicted schematically by A is in accord with previous tracer studies on the carboxy-inversion reaction of p-methoxy-p'-nitrobenzoyl peroxide.[9] In the earlier work it was shown that the p-methoxyphenyl group migrated exclusively to a peroxidic oxygen[9a]; however, some randomization of the label did occur in the p-nitrobenzoyloxy group.[9b] That no randomization is found in the antimony pentachloride catalyzed reaction is explainable on the basis that coordination occurs on the carbonyl oxygen and is retained in this position during the reaction. Whether or not the mixed carbonate I is formed as such or remains complexed with the antimony pentachloride is not known. The postulation of I or its complex as an intermediate is supported by the finding that a sample of I was rapidly decomposed by antimony pentachloride in petroleum ether to give phenyl benzoate; no benzoic anhydride was detected.[10] Intramolecular decomposition (B)

$$C_6H_5\overset{O}{\overset{\|}{C}}\text{—}O\text{—}\overset{O}{\overset{\|}{C}}OR \xrightarrow{SbCl_5} \left[\begin{array}{c} O\text{—}\overset{-}{SbCl_5} \\ C_6H_5\overset{}{\overset{}{C}}\text{—}O \\ \overset{+}{\underset{O}{\diagdown}}C=O \\ B \quad R \end{array} \right]$$

$$\begin{array}{l} I, \ R = C_6H_5 \\ II, \ R = C_2H_5 \end{array}$$

$$\rightarrow C_6H_5CO_2R + CO_2$$

accommodates the tracer results.

Because of the inherent instability of I and the rather marked modification of the reaction course by antimony pentachloride it seemed of interest to investigate further the action of this Lewis acid on these mixed carbonates. Ethyl benzoyl carbonate (II) is stable at room temperature but decomposes at 150° to give ethyl benzoate, diethyl carbonate, benzoic anhydride, and carbon dioxide.[11] In the presence of molar amounts of boron trifluoride only ethyl benzoate and carbon dioxide were obtained.[11c] Treatment of II in petroleum ether, at room temperature, with antimony pentachloride led to fairly rapid decomposition, ca. 5 hr. Carbon dioxide was evolved. Ethyl benzoate contaminated with ca. 5% of benzoyl chloride was the only product detected. No diethyl carbonate or benzoic anhydride could be found. A mixture of diethyl carbonate, benzoic anhydride, and antimony pentachloride in petroleum ether did not give carbon dioxide or ethyl benzoate. These results demonstrate that antimony pentachloride is a remarkably efficient catalyst for the decomposition of these mixed carbonates. The formulation of the reaction path as involving intramolecular decomposition is in accord with these observations. A similar mechanism has been proposed by Boschan[12] to explain the decomposition of the mixed carbonate from trifluoroacetic acid and cholesterol.

The Lewis acid-catalyzed decomposition of diaroyl peroxides by the carboxy-inversion path is now well established. It constitutes a remarkably specific peroxide reaction.[13]

the same conditions, about 3 days is required. In diethyl ether very little, if any reaction occurred after 3 days. Presumably these striking solvent effects are due to deactivation of the catalyst by competitive complexing with the solvent. See H. Meerwein, E. Battenberg, H. Gold, E. Pfeil, and G. Wilfang, *J. prakt. Chem.*, **154**, 112 (1940).

(9) (a) D. B. Denney, *J. Am. Chem. Soc.*, **78**, 590 (1956); (b) D. B. Denney and D. G. Denney, *ibid.*, **79**, 4806 (1957).

(10) The mixed carbonate was prepared from phenyl chloroformate and benzoic acid in the presence of triethylamine. It decomposes at room temperature to give phenyl benzoate, carbon dioxide, benzoic anhydride, and presumably diphenyl carbonate.

(11) (a) E. T. Longosz and D. S. Tarbell, *J. Org. Chem.*, **26**, 2161 (1961); (b) D. S. Tarbell and E. T. Longosz, *ibid.*, **24**, 774 (1959); (c) T. Windholz, *ibid.*, **25**, 1703 (1960).

(12) R. Boschan, *J. Am. Chem. Soc.*, **81**, 3341 (1959).

(13) Very little is known about the carboxy-inversion reaction of diacyl peroxides and mixed acyl aroyl peroxides. N. Sherman has demonstrated (unpublished work from this laboratory) that such reactions can be ef-

(5) R. Huisgen and W. Edl, *Angew. Chem.*, **74**, 588 (1962).

(6) J. T. Edward, H. S. Chang, and S. A. Samad, *Can. J. Chem.*, **40**, 804 (1962).

(7) J. E. Leffler, *J. Am. Chem. Soc.*, **72**, 67 (1950).

(8) In this connection it should be mentioned that in petroleum ether the reaction is complete at room temperature in *ca.* 5 hr. In toluene under

The Substitution Reaction.—Attempts to duplicate Reynhart's[4] reaction (2) have been fruitless.[5,6,14] There was an indication that very small amounts of cresyl benzoates were formed when molar amounts of benzoyl peroxide and aluminum chloride were allowed to react in toluene. When the ratio of benzoyl peroxide to aluminum chloride was changed from 1:1 to 1:10 there was a slight increase in the yield of cresyl benzoates and no phenyl benzoate could be detected. Interestingly, the amount of benzoic acid formed was changed from an average of 0.74 mole per mole of peroxide to 1.75 moles per mole of peroxide. Acids derived from the peroxide appear in all of these reactions.[6]

It was felt that some insight into the mechanism of the substitution process could be obtained by an oxygen-18 tracer experiment. The system chosen was one studied by Edward and co-workers,[6] namely, that of *p,p'*-dinitrobenzoyl peroxide, mesitylene, and aluminum chloride. In some initial experiments, with unlabeled material, it was found that 2,4,6-trimethylphenyl *p*-nitrobenzoate (III) and *p*-nitrobenzoic acid were formed

IV
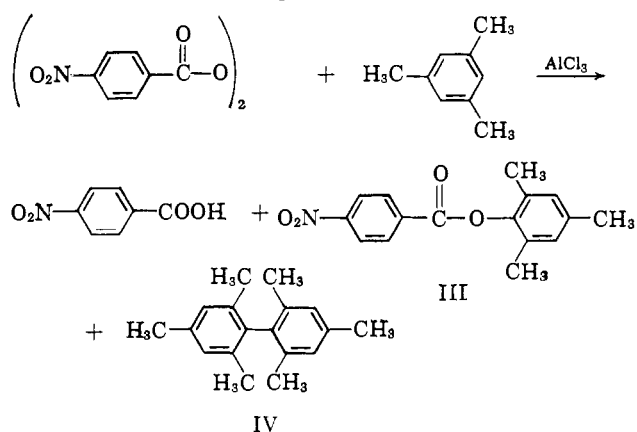
as reported. It was possible to isolate a 15% yield (based on one mole per mole of peroxide) of 2,4,6,2',4',6'-hexamethylbiphenyl (IV). This substance has not been found by the earlier workers,[6] although they had found *p,p'*-dimethoxybiphenyl when benzoyl peroxide was allowed to react with a mixture of nitrobenzene and anisole in the presence of aluminum chloride.

Treatment of oxygen-18 carbonyl labeled *p,p'*-dinitrobenzoyl peroxide and mesitylene with aluminum chloride at room temperature yielded labeled III which was degraded to 2,4,6-trimethylphenol and *p*-nitrobenzoic acid hydrazide by treatment with anhydrous hydrazine. It was found that the hydrazide contained 75% of the excess oxygen-18 originally present in the carbonyl group of the peroxide. Essentially all (21%) of the remaining excess oxygen-18 was found in the 2,4,6-trimethylphenol. These results show quite clearly that some scrambling of the label occurred during the substitution process or as an adjunct to the substitution process. In another experiment unreacted labeled peroxide was recovered and converted to methyl *p*-nitrobenzoate by treatment with methoxide ion. The ester contained all of the excess oxygen-18 originally present in the peroxide. This experiment shows that

the partial equilibration did not occur by some sort of reversible dissociation of the peroxide.

Partial equilibration of the label points strongly to there being two paths by which substitution occurs. One is necessarily specific, *i.e.*, label retained in the carbonyl group, and the other leads to randomization of the label. The data indicate that if two processes are competing in this way they must be proceeding at practically the same rate.[15]

The portion of ester which is formed with equilibration could be derived by attack of a *p*-nitrobenzoyloxy radical on mesitylene. Thermal decomposition of *p,p'*-dinitrobenzoyl peroxide in mesitylene at 100–135° yielded III (39%), thus demonstrating the feasibility
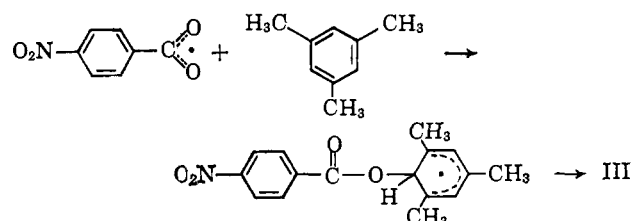
of this path. One possible way by which the *p*-nitrobenzoyloxy radical could be formed is by an oxidation–reduction reaction of mesitylene with a complex of the peroxide and aluminum chloride. This reaction would also lead to the radical-cation V derived from mesitylene. Formation of V and its subsequent
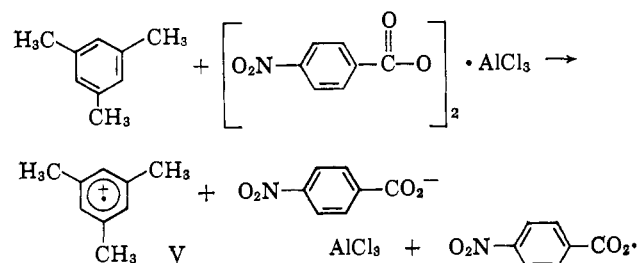
reaction with mesitylene accounts ultimately for the formation of bimesityl (IV). Indeed it is difficult to rationalize formation of IV without the intervention of
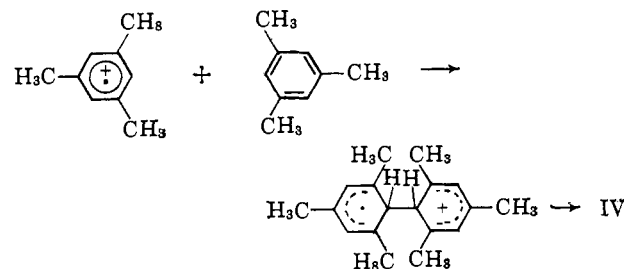
V.[16,17] The radical-cation could also react with *p*-nitrobenzoate ion and/or *p*-nitrobenzoyloxy radical to give equilibrated III.

Formation of the specifically labeled ester could occur by attack of V on peroxide. This would be an induced decomposition so attack on a peroxidic oxygen would be expected.[18] It should be noted that this involves a

fected and may even constitute a synthetic method of converting an acid to an alcohol with the loss of one carbon atom. Further work on this aspect of the carboxy-inversion reaction is now in progress.

(14) Discussion of the many experiments conducted by this group can be found in the dissertation of Thomas M. Valega, Ph.D. Thesis, 1963, Rutgers, The State University, New Brunswick, N. J. In this connection the early tracer experiment reported by D. B. Denney and H. M. Weiss, *Chem. Ind.* (London), 818 (1962), in which Reynhart's stoichiometry was taken at face value is now known to represent a study of the carboxy-inversion reaction. The results agree with those found for the antimony pentachloride catalyzed reaction.

(15) It seems unlikely that a direct reaction between peroxide, mesitylene, and aluminum chloride would lead to partial equilibration, although such a process is not ruled out by the available data. It is also unlikely that equilibration occurs after the ester is formed.

(16) M. Das and S. Basu, *Spectrochim. Acta*, **17**, 897 (1961), claim to have observed the spectrum of V.

(17) P. Kovacic and C. Wu, *J. Org. Chem.*, **26**, 759 (1961), have observed that treatment of mesitylene with ferric chloride yields IV. They suggest a mechanism which does not involve V; however, the referee (footnote 10) has made this suggestion.

(18) (a) E. H. Drew and J. C. Martin, *Chem. Ind.* (London), 925 (1959); (b) D. B. Denney and G. Feig, *J. Am. Chem. Soc.*, **81**, 5322 (1959); (c) W. von E. Doering, K. Okamoto, and H. Krauch, *ibid.*, **82**, 3579 (1960).
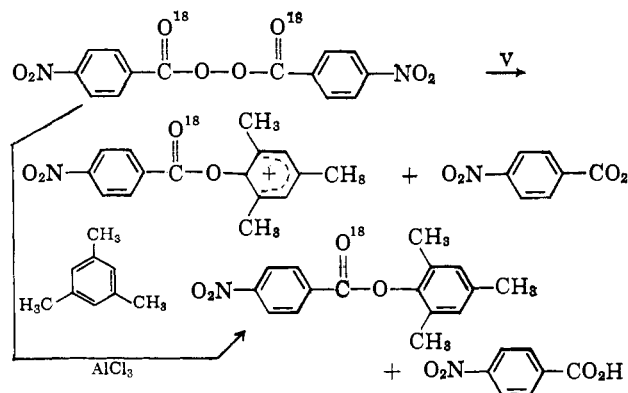
positively charged species so strict analogy to other induced decomposition may not hold. A direct Friedel–Crafts reaction which proceeds with retention of the label is of course not ruled out by the present data. Indeed, other somewhat more tortuous routes can be devised to rationalize the formation of the products and the distribution of the label. It is hoped that studies now in progress will clarify this situation. It is quite clear now that a simple substitution process cannot account effectively for all of the products and may not be operating at all.

Experimental[19]

Benzoyl Peroxide-*carbonyl*-O^{18}.—Benzoyl peroxide was prepared according to the method of Doering, Okamoto, and Krauch[18c] using benzoyl chloride-*carbonyl*-O^{18}. The peroxide was obtained in a yield of 82%, m.p. 105–106° (lit.[20] 108°).

Rearrangement of Benzoyl Peroxide-*carbonyl*-O^{18}.—There was added to a stirred suspension of 7.26 g. (0.03 mole) of benzoyl peroxide-*carbonyl*-O^{18} in 75 ml. of petroleum ether (30–60°) at ice bath temperature 0.3 g. (0.001 mole) of antimony pentachloride. The mixture was allowed to come to room temperature. After stirring for 4 hr. the reaction mixture was washed with two 50-ml. portions of water and dried with magnesium sulfate. After removing the solvent, by distillation, there was obtained 5.4 g. (90%) of white crystals, m.p. 69–70° (lit.[21] 70–71°). Recrystallization from ethanol–water afforded phenyl benzoate, m.p. 71–72°, no depression upon admixture with an authentic sample. The infrared spectrum was identical with that of an authentic sample of phenyl benzoate.

In a similar experiment the crude reaction mixture was subjected to gas–liquid chromatographic analysis on a 2-ft. silicone gum rubber column programmed at 15°/min. from 150°. The chromatogram indicated that phenyl benzoate was the major product and that no benzoic anhydride was formed. The retention times were 2.8 min. for phenyl benzoate and 4.5 min. for benzoic anhydride.

Cleavage of Phenyl Benzoate-O^{18}.—To 3.2 g. (0.016 mole) of phenyl benzoate-O^{18} suspended in 35 ml. of absolute ethanol was added 0.7 g. (0.022 mole) of anhydrous hydrazine. The mixture was heated under reflux for 2 hr. and then allowed to stand overnight. Most of the ethanol was removed by distillation and the white semisolid which formed was triturated with ether. The solid was removed by filtration and thoroughly washed with ether. The combined ether fractions were dried with magnesium sulfate.

The white solid, 1.4 g. (67%), m.p. 105–108° (lit.[22] 112°), was recrystallized from benzene to yield benzoic acid hydrazide, m.p. 113–114°. The infrared spectrum of this material was commensurate with its assigned structure.

The ether was removed by distillation to yield 2.0 g. of a semisolid which was thoroughly dried in a vacuum desiccator over calcium chloride. One gram of this was heated on a steam bath with 1 g. of phenyl isocyanate and 2 drops of pyridine. After recrystallization from carbon tetrachloride there was obtained the crude phenyl phenylurethan, m.p. 110–113°. This was recrystallized from benzene–hexane, m.p. 125.5–126° (lit.[23] 126°)

with no depression upon admixture with an authentic sample. The infrared spectrum was identical with that of a known sample of phenyl phenylurethan.

Table I

| | ⎯Atom % excess oxygen-18⎯ | |
Compound	Run 1	Run 2
Benzoic acid	1.56	0.76
Benzoyl peroxide	1.60	.75
Phenyl benzoate	1.59	.72
Benzoic acid hydrazide	1.47	.71
Phenyl phenylurethan	0.07[a]	.00

[a] The analytical results in run 1 are inferior to those in run 2. The 0.07 atom % excess oxygen-18 found in the phenyl phenylurethan probably is due to a memory effect. An unlabeled sample combusted at the same time showed 0.04 atom %. The combustion apparatus was refurbished before the analyses for run 2 were conducted.

Benzoyl Phenyl Carbonate.—There was added over a period of 1 hr. 6.24 g. (0.04 mole) of phenyl chloroformate to a stirred mixture of 4.88 g. (0.04 mole) of benzoic acid and 4.04 g. (0.04 mole) of triethylamine in 200 ml. of anhydrous ether at 0°. The mixture was permitted to come to room temperature and was stirred overnight. After the solid was removed by filtration the ether solution was washed with two 100-ml. portions of dilute hydrochloric acid, four 100-ml. portions of water, and was dried with magnesium sulfate. The ether was removed by vacuum distillation at room temperature to yield 5.0 g. (52%) of a semisolid which was recrystallized from pentane; m.p. 55–58°. The infrared spectrum had carbonyl bands at 5.45 and 5.65 μ.

After standing at room temperature for 2 days the material appeared to have decomposed; it was no longer a solid and its infrared spectrum indicated the presence of both benzoic anhydride and phenyl benzoate. This was verified by g.l.p.c.

Decomposition of Benzoyl Phenyl Carbonate.—There was added to a suspension of 2.42 g. (0.01 mole) of freshly prepared I in 75 ml. of petroleum ether (30–60°) at ice bath temperature 0.2 g. (0.0007 mole) of antimony pentachloride. The evolution of carbon dioxide was immediately observed and the reaction was complete in about 30 min. After washing with dilute hydrochloric acid, 5% sodium bicarbonate solution, and water, the petroleum ether solution was dried with magnesium sulfate. The solvent was removed by distillation to yield 2.0 g. (100%) of phenyl benzoate, m.p. 65–67°; no depression upon admixture with an authentic sample. The infrared spectrum was identical with that of an authentic sample of phenyl benzoate.

Benzoyl Ethyl Carbonate.—According to the procedure of Tarbell and Price,[24] benzoyl ethyl carbonate was prepared in 88% yield. The infrared spectrum was consistent with the assigned structure.

Decomposition of Benzoyl Ethyl Carbonate.—To a stirred solution of 1.94 g. (0.01 mole) of benzoyl ethyl carbonate in 75 ml. of petroleum ether (30–60°) at 0° was added 0.3 g. (0.001 mole) of antimony pentachloride. After reaching room temperature the reaction mixture was allowed to stir for 12 hr. The solution was washed with dilute hydrochloric acid, 5% sodium bicarbonate solution, water, and dried with magnesium sulfate. After removing the solvent by distillation there was obtained 1.5 g. of material. The infrared spectrum had carbonyl absorption at 5.65 (w) and 5.82 (s) μ. Molecular distillation, b.p. 40–63° (block) (12 mm.), left little residue and gave no change in the infrared spectrum. A mixture of 92% ethyl benzoate–8% benzoyl chloride had essentially the same infrared spectrum as the distillate; g.l.p.c. analysis, 6-ft. silicone grease column, programmed 100–300°, 15°/min., showed two components, retention times 5.8 and 6.5 min. Under the same conditions benzoyl chloride had a retention time of 5.8 min. and ethyl benzoate 6.5 min. The percentage of benzoyl chloride appeared to be around 5%.

No diethyl carbonate or benzoic anhydride was detected by g.l.p.c. or infrared analysis.

There was added 0.2 g. (0.0007 mole) of antimony pentachloride to a stirred solution of 1.18 g. (0.01 mole) of diethyl carbonate and 2.26 g. (0.01 mole) of benzoic anhydride in 75 ml. of petroleum ether (30–60°). No carbon dioxide was evolved. After stirring for 24 hr., the mixture was washed with water, dilute hydrochloric acid, 5% sodium bicarbonate solution, and water; the ether solution was dried with magnesium sulfate. Analysis, by g.l.p.c., indicated that the reactants diethyl carbonate and benzoic anhydride were both present and that no ethyl benzoate was formed.

Isolation of 2,2',4,4',6,6'-Hexamethylbiphenyl (IV).—*p,p'*-Dinitrobenzoyl peroxide (7.00 g., 0.0211 mole) was added as the solid in 15 portions over 1 hr. to a stirred mixture of 5.61 g.

(19) Oxygen-18 analyses were carried out using the method of W. von E. Doering and E. Dorfman, *J. Am. Chem. Soc.*, **75**, 5595 (1953), as modified by D. B. Denney and M. A. Greenbaum, *ibid.*, **79**, 979 (1957). The atom % excess oxygen-18 reported is an average of at least two separate analyses; accuracy estimated as ±0.01 atom %. The melting points were taken in capillary tubes and are uncorrected.

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

(21) Reference 20, p. 598.

(22) T. Curtius, *Ber.*, **23**, 3023 (1890).

(23) "Tables for Identification of Organic Compounds," Chemical Rubber Publishing Co., Cleveland, Ohio, 1960, p. 41.

(24) D. S. Tarbell and J. A. Price, *J. Org. Chem.*, **22**, 245 (1957).

(0.0422 mole) of aluminum chloride in 175 ml. of mesitylene. The reaction mixture was stirred at room temperature for 24 hr. and then hydrolyzed by adding 100 ml. of 10% hydrochloric acid slowly with cooling. The two phases were separated and the organic layer was washed with three 100-ml. portions of 5% sodium bicarbonate solution, 100 ml. of 10% sodium hydroxide solution, and 100 ml. of water. Acidification of the aqueous extracts afforded 2.96 g. of p-nitrobenzoic acid, m.p. 240–242°.

The organic extracts were dried (magnesium sulfate) and the solvent was removed to give a semisolid brown material (4.0 g.). A portion, 2.4 g., was sublimed at 30–90° (bath) and 0.02 mm. to give 1.52 g. of a yellow crystalline material which was crystallized from ethanol. Further recrystallization, four times, of a portion, 0.4 g., of this material gave 0.14 g., m.p. 103–104° (lit.[25] 100°). The n.m.r. spectrum of this material in carbon tetrachloride with tetramethylsilane as internal standard had three sharp peaks at 3.19, 7.73, and 8.18 τ. The ratio of the areas under these peaks was 4:6:12.

Anal. Calcd. for $C_{18}H_{22}$: C, 90.70; H, 9.30. Found: C, 90.26; H, 9.41.

p,p′-**Dinitrobenzoyl Peroxide-*carbonyl*-O[18].**—The peroxide was prepared from labeled *p*-nitrobenzoyl chloride[26]; m.p. 156.5–158° dec. (lit.[26] 158°).

Reaction of Labeled *p,p′*-Dinitrobenzoyl Peroxide with Mesitylene.—Essentially the same procedure was followed as outlined, except that 12.0 g. (0.0362 mole) of peroxide, 9.63 g. (0.0724 mole) of aluminum chloride, and 250 ml. of mesitylene were used. After the reaction mixture was processed there was obtained 8.53 g. of *p*-nitrobenzoic acid and 8.5 g. of neutral product. A mixture of 6.0 g. of the neutral material and 1.04 g. (0.0324 mole) of anhydrous hydrazine in 85 ml. of absolute ethanol was boiled for 5 hr. The solution was concentrated (72 ml. of ethanol removed), 40 ml. of benzene was added, and distillation was continued; 40 ml. was collected. The remainder of the solvent was removed *in vacuo*. The residue was triturated with 100 ml. of dry ether. The precipitate, 0.81 g., had m.p. 207–212° (lit.[27] 210°). The infrared spectrum was identical with that of an authentic sample of *p*-nitrobenzoic acid hydrazide. The material was recrystallized several times from ethanol and ethanol–benzene; m.p. 207.5–211°.

A portion of the ether solution (50 ml.) was extracted with two 20-ml. portions of 10% sodium hydroxide solution and 10 ml. of water. The combined aqueous extracts were extracted with 20 ml. of hexane and acidified (pH 1) and then extracted with three 20-ml. portions of methylene chloride. The residue obtained after evaporating the dried methylene chloride solution was sublimed at 60° (bath) to give 0.068 g. of material, m.p. 68–71.5° (lit.[28] 72°). The remainder of the ether solution was processed in the same way to give essentially the same amount of 2,4,6-trimethylphenol. The urethan was prepared; after recrystallization from benzene–hexane it had m.p. 145–146° (lit.[28] 140–142°).

TABLE II

Compound	Atom % excess oxygen-18
p-Nitrobenzoic acid	0.77
p-Nitrobenzanilide[a]	.76
p,p′-Dinitrobenzoyl peroxide	.76
p-Nitrobenzoic acid hydrazide	.56
2,4,6-Trimethylphenol	.16
2,4,6-Trimethylphenyl phenylurethan	.16

[a] Prepared from the acid chloride used to prepare the peroxide.

Recovery of *p,p′*-Dinitrobenzoyl Peroxide.—The peroxide (5.0 g., 0.0151 mole) was added portionwise to 2.0 g. (0.0151 mole) of aluminum chloride and 125 ml. of mesitylene. The mixture was stirred for 3 hr. at room temperature. After hydrolysis with 10%

(25) G. Egloff, "Physical Constants of Hydrocarbons," Vol. III, Reinhold Publishing Corp., New York, N. Y., 1946, p. 337.

(26) "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 649.

(27) J. P. Horwitz and V. A. Grakauskas, *J. Org. Chem.*, **19**, 194 (1954).

(28) D. R. Boyd, *J. Chem. Soc.*, **107**, 1538 (1915).

hydrochloric acid, 100 ml., there was obtained 3.5 g. of solid which was triturated with hot toluene. Cooling of the toluene gave 0.92 g. of material, m.p. 157–158° dec., whose infrared spectrum was nearly identical with that of *p,p′*-dinitrobenzoyl peroxide. Extraneous peaks at 5.90 (w), 7.1 (w), 10.8 (m), and 11.5 (m) μ were present.

The recovered peroxide was dissolved in 150 ml. of chloroform and added to a solution of sodium methoxide in methanol. Water, 100 ml., was added and the chloroform solution was extracted with several 100-ml. portions of water, dried over magnesium sulfate, and evaporated to give 0.77 g. of crude methyl *p*-nitrobenzoate, m.p. 85–94°. Recrystallization from 95% ethanol gave 0.51 g. of material, m.p. 95–97° (lit.[29] 96°). The infrared spectrum was identical with that of a known sample of methyl *p*-nitrobenzoate. The atom % excess oxygen-18 was found to be 0.78.

Reaction of *p,p′*-Dinitrobenzoyl Peroxide with Mesitylene.—A solution of 10.0 g. (0.0302 mole) of the peroxide in 100 ml. of mesitylene was heated at 100–135° (bath) for 4 hr. After cooling and filtration, 4.22 g. of *p*-nitrobenzoic acid, m.p. 232–238°, was obtained. Extraction with aqueous bicarbonate solution and acidification afforded 1.12 g. of *p*-nitrobenzoic acid, m.p. 230–235°. The neutral fraction, 6.92 g. of oil, had a strong band at 5.75 and a weak band at 5.85 μ. The oil was treated with 1.0 g. (0.03 mole) of anhydrous hydrazine in 50 ml. of absolute ethanol. Isolation as before afforded 1.90 g. of crude *p*-nitrobenzoic acid hydrazide, m.p. 200–211°. The infrared spectrum was identical with that of an authentic sample. 2,4,6-Trimethylphenol, 0.178 g., m.p. 69–73°, was obtained. The infrared spectrum was essentially identical with that of the sample obtained from the aluminum chloride reaction.

Reaction of Benzoyl Peroxide with Toluene in the Presence of Aluminum Chloride.—To a cooled stirred mixture of 133 g. (1.0 mole) of aluminum chloride and 107 ml. (1.0 mole) of toluene was added over 2 hr. 24.2 g. (0.10 mole) of benzoyl peroxide in 250 ml. of toluene. After stirring 7 hr. at ice bath temperature and 11 hr. at room temperature the mixture was hydrolyzed by pouring it onto 1 kg. of ice followed by the addition of 200 ml. of concentrated hydrochloric acid. The resulting emulsion was broken by filtering through Filter-Cel. The organic phase was washed with four 100-ml. portions of 5% sodium bicarbonate solution and 100 ml. of water. The combined aqueous extracts were washed with 200 ml. of pentane and acidified to pH 1. There was isolated 20.3 g. of benzoic acid (infrared spectrum identical with that of a known sample).

The toluene–pentane mixture was evaporated to give 8.6 g. of a red-brown liquid; g.l.p.c. analysis, 3.5-ft. Apiezon T column at 250°, showed phenyl benzoate was not present but the presence of cresyl benzoates was indicated. Several other materials were also present. A solution of 2.0 g. of the oil and 0.8 g. of sodium hydroxide in 50 ml. of ethanol was boiled for 5 hr. The ethanol was evaporated; 25 ml. of water was added and the pH was brought to 7. The solution was extracted with three 35-ml. portions of ether. After drying and evaporating the extracts, there was obtained 1.37 g. of material which had a weak band at 2.7 (hydroxyl) and a strong band at 6.0 μ (*p*-methylbenzophenone).[30] The mixture was taken up in 75 ml. of ether which was extracted with four 25-ml. portions of 5% sodium hydroxide solution which were in turn acidified (pH 1) and extracted with three 35-ml. portions of ether. Removal of the ether gave 0.1 g. of material which had a phenolic odor; g.l.p.c. analysis, 10-ft. Apiezon L column at 150°, showed two components with retention times of 14.0 and 14.5 min. Phenol had a retention time of 8.8 min. and *o*-cresol, *m*-cresol, and *p*-cresol, 13.8, 14.5, and 15.0 min., respectively.

In another experiment a portion of the neutral material was treated with hydrazine which gave benzoic acid hydrazide, m.p. 113–115°, and a phenolic fraction which showed three components on the Apiezon L column at 150°, retention times 13.7, 14.2, and 14.9 min. The relative areas were 6:41:53.

When molar quantities of benzoyl peroxide and aluminum chloride were allowed to react in toluene, there was obtained 9.6 g. of benzoic acid and 10.8 g. of neutral material which was *ca.* 50% phenyl benzoate by g.l.p.c. analysis.

(29) Reference 20, p. 554.

(30) In another experiment *p*-methylbenzophenone was isolated from the neutral fraction.