β-acetoxyalkylsilanes which eliminate propylene by β-elimination. The amount of propylene formed would in each case depend upon the tendency of the silicon hydride to add beta to the acetoxy group and upon the ease of β-elimination in the adduct.

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A Study of the Mechanism of the Conversion of Aroyl Peroxides to Anhydrides by Tertiary Phosphines

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Three unsymmetrically substituted aroyl peroxides, which were specifically labeled with oxygen-18, were reduced with tributylphosphine to the corresponding unsymmetrical anhydrides. Systematic degradation of the anhydrides elucidated the distribution of oxygen-18 in these molecules. These data show that the peroxide oxygen attacked by the phosphine, either the α- or β-oxygen (see flow sheet), is governed to a very marked degree by the electron density at the attacked atom. It also has been shown that the ion pairs A and B do not undergo exchange with each other but collapse directly to the products.

It has been demonstrated recently that the reaction of aroyl peroxides with tertiary phosphines proceeds by attack on the peroxidic oxygens to give ion pairs such as A or B.[2,3] The purpose of the research reported here was to delineate more thoroughly the factors which control the formation of the ion pairs A and B. The three unsymmetrical peroxides *p*-nitrobenzoyl *p*-methoxybenzoyl peroxide-*p-nitrobenzoyl carbonyl-O*^{18} (IV), *p*-nitrobenzoyl benzoyl peroxide-*p-nitrobenzoyl carbonyl-O*^{18} (VII) and *p*-phenylbenzoyl benzoyl peroxide-*p-phenylbenzoyl carbonyl-O*^{18} (XIII) were prepared and allowed to react with tri-*n*-butylphosphine. The labeled anhydrides, *p*-nitrobenzoic *p*-methoxybenzoic (V), *p*-nitrobenzoic benzoic (VIII) and *p*-phenylbenzoic benzoic (XIV) obtained from these reactions were treated with liquid ammonia to give the amides *p*-nitrobenzamide (VI and IX) and *p*-phenylbenzamide (XV). Analysis of the amides gave the oxygen-18 content of the carbonyl and therefore that of the parent carbonyl in the anhydride.[4] Inspection of the flow sheet demonstrates that attack at the α-oxygen, which gives rise to ion pair A, will ultimately afford an amide with the same excess oxygen-18 content in the carbonyl as was in the original anhydride.

Attack at the β-oxygen leads to an amide which contains only one-half of the original excess oxygen-18. Table I contains the percentage α-attack. Table II contains the analytical data which were used in making these calculations.

It is immediately evident that a *p*-nitro substituent markedly controls the position of attack by the phosphine. The mechanism of this control is undoubtedly due to the ability of the nitro group to lower the electron density at the α-oxygen both by resonance and induction.[5] The creation of a partial positive charge in this region enhances the rate of attack of the phosphine relative to a neutral center. The *p*-methoxy group in IV tends to increase the electron density at the β-oxygen, and one finds a diminution in rate of attack at this position as compared to VII. It is important to note that in the reaction of IV and VII the ion pair A, which is formed practically exclusively, appears to be the least stable thermodynamically. The reasons for suggesting this are that in A the anion is derived from the weakest acid and the cation is destabilized by the nitro group. The fact that the least stable ion pair is formed indicates that this is a kinetically controlled process. Such control can arise easily if the transition state for ion pair formation resembles the starting materials rather than the products. A postulation of this kind is in complete harmony with the very marked directive powers of the *p*-nitro group. The fact that very little of the stable ion pair is formed indicates that the reaction is irreversible, or much less likely that collapse to products is much faster than ion pair return, and therefore equilibrium between A and B *via* the starting materials is never set up.

TABLE I

Peroxide	α-Attack[a], %
p-Nitro-*p*′-methoxybenzoyl peroxide (IV)	100
p-Nitrobenzoyl benzoyl peroxide (VII)	95
p-Phenylbenzoyl benzoyl peroxide (XIII)	50

[a] The % attack at a given position was calculated using the oxygen-18 values of the starting acid and amide and those obtained from the product amides.

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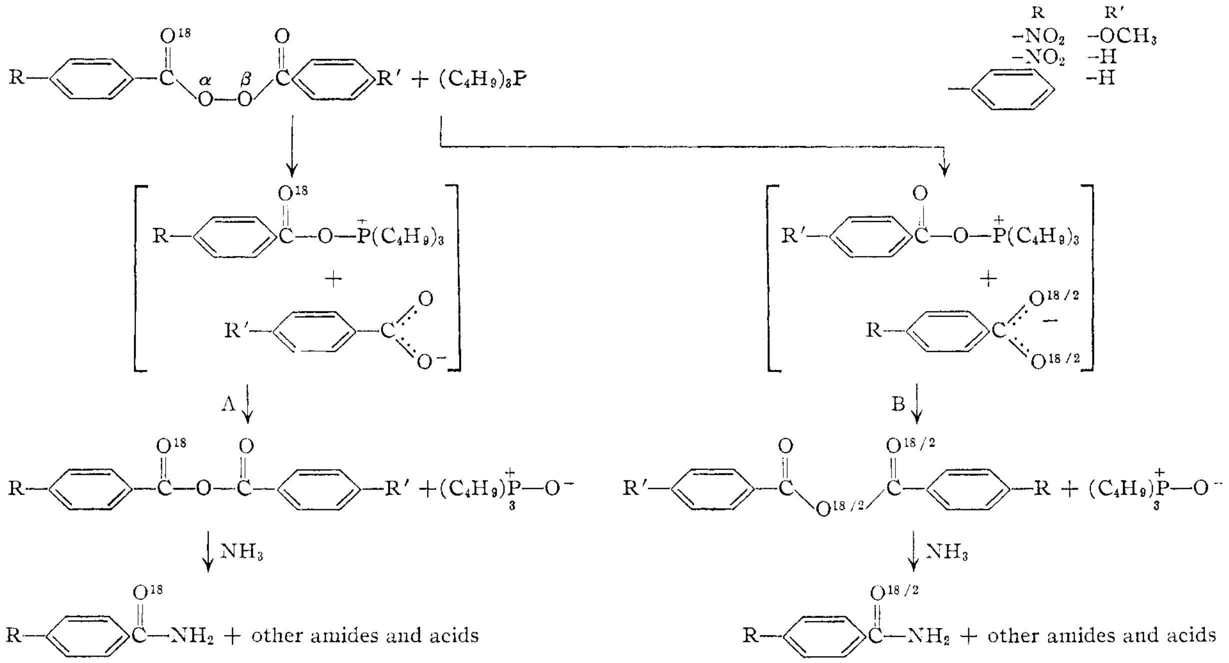
[1] Alfred P. Sloan Post-doctoral Fellow in Chemistry.

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

[3] L. Horner and W. Jurgeleit, *Ann.*, **591**, 138 (1955).

[4] The above is only true if in the reaction of the anhydrides with ammonia there is no equilibration of the three oxygens. Such is the case if the reaction is carried out in refluxing ammonia; however, at Dry Ice temperatures equilibration can occur. This has been demonstrated by allowing monolabeled benzoic anhydride to react with refluxing ammonia; under these conditions no equilibration occurs; at Dry Ice temperatures the benzamide isolated contains completely equilibrated oxygen. This most interesting observation will be the subject of an article now in preparation.

[5] Considerable evidence is available concerning the effect of substituents on the reactions of aroyl peroxides. A good discussion of these effects can be found in A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954, pp. 79–81.



When the phosphine reacts with mono-*p*-phenylbenzoyl peroxide (XIII), it does so in essentially a random manner. This finding is not unexpected as the *p*-phenyl substituent exerts a very negligible electronic effect in the ground state on the carboxyl group (Hammett's $\sigma = 0.009$). Careful attention was paid to the nature of the product from XIII. Since both ion pairs A and B are being formed at about the same rate, any exchange between the two should have led to a mixture of the three possible anhydrides XIV, benzoic anhydride and *p*-phenylbenzoic anhydride. Such is not the case as only XIV is isolated. It was demonstrated that XIV is thermodynamically unstable with respect to a mixture of the anhydrides. These findings are in agreement with those of Horner and Jurgeleit[3] who also found only mixed anhydrides from mixed peroxides. In an earlier paper[2] it was shown that when benzoyl peroxide was allowed to react with triphenylphosphine in the presence of *p*-nitrobenzoate ion, the *p*-nitrobenzoate ion was capable of entering into the reaction and a mixture of anhydrides was obtained. Little comparison is possible between these two experiments as in the latter the ion concentration is high at all times, whereas when no added ions are present, exchange depends on diffusion of two pairs together before either one can collapse to products.

TABLE II

Compound	Atom % oxygen-18[a]
p-Nitrobenzoic acid (I)	1.12, 1.10
p-Nitrobenzamide (III)	1.12
p-Nitro-*p'*-methoxybenzoic anhydride (V)	1.07, 1.07[b]
p-Nitrobenzamide (VI)	1.13, 1.10
p-Nitrobenzoic benzoic anhydride (VIII)	1.12, 1.09
p-Nitrobenzamide (IX)	1.07, 1.07
p-Phenylbenzoic acid (X)	0.97, 0.97
p-Phenylbenzamide (XII)	0.96
p-Phenylbenzoic benzoic anhydride (XIV)	0.98, 1.01
p-Phenylbenzamide (XV)	0.80, 0.78

[a] Normal isotopic abundance of oxygen-18 was taken at 0.204 atom %. [b] In the Experimental section the effect of increasing oxygen content on the analytical values in a series of compounds is discussed.

Acknowledgment.—We wish to thank the Esso Research and Engineering Corp. for making available the mass spectrometer used in this work.

Experimental[6]

Oxygen-18 Analytical Procedure and Calculations.—Doering and Dorfman[7] have shown that the usual oxygen determination procedure is satisfactory for the conversion of oxygen-18 containing substances to carbon dioxide. Recently Oita and Conway[8] have found that it is possible to lower the temperature of the combustion furnace from 1120 to 900° by using a carbon–platinum packing rather than carbon alone. We have extended the use of this packing to include oxygen-18 containing substances. The results obtained by analyzing several samples using both packings were identical. Several advantages are obtained by following this modification; they are, (1) the blanks are insignificant, (2) temperature control of the furnace is much less critical and (3) attrition of the tube and furnace is markedly reduced.

As yet no one has published a general formula for the calculation of the oxygen-18 content of a substance by using the data obtained from this analytical procedure. Within a given set of experiments, such as are reported here, it is usually not necessary to know the absolute amount of oxygen-18 in the molecules but rather only the relative amounts of the isotope are required. For this reason it is sufficient to consider only the 44, $C^{12}O^{16}O^{16}$, abundance and the 46, $C^{12}O^{16}O^{18}$, $C^{12}O^{17}O^{17}$ and $C^{13}O^{16}O^{17}$, abundance using as a reference standard the 44 and 46 abundances as obtained from normal CO_2. Using the published values for the relative abundances of the pertinent isotopes it is possible to set up the following equation for the calculation of the oxygen-18 in any organic molecule.

In the equation below the contribution of $C^{12}O^{17}O^{17}$ to the 46 peak has been ignored as it is insignificant. The excess oxygen-17 which is incorporated in the enriched H_2O^{18} has also been neglected, since it will remain constant throughout a series. It can be seen that the $C^{13}O^{16}O^{17}$ (second factor of the numerator) does not contribute materially to the 46 peak

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[6] Analysis by G. Robertson, Florham Park, New Jersey. Melting points are uncorrected.

[7] W. E. Doering and E. Dorfman, THIS JOURNAL, **75**, 5595 (1953).

[8] I. J. Oita and H. S. Conway, *Anal. Chem.*, **26**, 600 (1954).

$$\frac{\left(\frac{46}{44}\right)_{\text{sample}}(0.00408)}{\left(\frac{46}{44}\right)_{\text{tank}}} = \frac{(2)(0.98892)[(2Z - 1)(0.00204) + X] + (2)(2Z)(0.01108)(0.00037)}{(0.98892)[(2Z - 1)(0.99759) + 0.99963 - X]}$$

X = atom % oxygen-18 for the labeled position (clearly the molecule may be labeled in a number of positions, and the further assignment of the oxygen-18 distribution must come from other knowledge).

Z = number of oxygens in the molecule combusted.

until Z becomes large. It is important to note that in this equation $(2Z - 1)$ is multiplied times the peak height ratios; this means that any errors in these ratios are increased as Z increases, consequently the inherent accuracy of the method decreases as one goes to more highly oxygenated substances.

***p*-Nitrobenzoic Acid-$\mathrm{CO^{18}O^{18}H}$ (I).**—This compound was prepared in connection with another project and its preparation will be described at a later date.

***p*-Nitrobenzamide-$\mathrm{CO^{18}NH_2}$ (III).**—Labeled *p*-nitrobenzoyl chloride-$\mathrm{CO^{18}Cl}$ (II) which had been prepared from I was added to ammonia. After crystallization from methanol–water, pure III, m.p. 199–201°, was obtained.

***p*-Nitro-*p′*-methoxybenzoyl Peroxide *p*-Nitrobenzoyl Carbonyl-$\mathrm{O^{18}}$ (IV).**—This compound's preparation will be described at a later date as it was prepared in connection with another project.

***p*-Nitrobenzoyl Peroxide *p*-Nitrobenzoyl Carbonyl-$\mathrm{O^{18}}$ (VII).**—This compound was prepared according to the procedure of Wieland and Rasuwajew.[9] From 9.22 g. (0.0496 mole) of *p*-nitrobenzoyl chloride-$\mathrm{CO^{18}Cl}$ (II) there was obtained 8.6 g. (64%) of the peroxide, m.p. 113–115°.

***p*-Phenylbenzoic Acid-$\mathrm{CO^{18}O^{18}H}$ (X).**—Crude *p*-phenylbenzoyl chloride, which had been prepared by refluxing 53.5 g. (0.27 mole) of unlabeled X with thionyl chloride for 4 hr., was added to 300 ml. of pure tetrahydrofuran to which had been added 20 ml. of $\mathrm{H_2O^{18}}$ (*ca.* 1.5 atom % $\mathrm{O^{18}}$). The mixture was stirred and refluxed for 36 hr. Most of the tetrahydrofuran was removed under reduced pressure. The resulting mixture partially solidified; filtration afforded 30 g. of very crude material which was crystallized from methanol to afford 20 g. of acid, m.p. 223–225°.

The pot residue and the mother liquors from the crystallization were refluxed with potassium hydroxide solution until complete solution had occurred. The cooled basic solution was acidified. Filtration afforded 18.5 g. of acid. During the exchange a considerable amount of ester was formed, and therefore this method cannot be recommended for this type of work.

***p*-Phenylbenzoyl Chloride-$\mathrm{CO^{18}Cl}$ (XI).**—Labeled X, 19.0 g. (0.0958 mole), was refluxed in 50 ml. of thionyl chloride for 3 hr. The thionyl chloride was removed *in vacuo*, and the residue was crystallized from hexane to yield 18.1 g. (87%) of XI, m.p. 114–115°.

The amide XII was prepared by adding the acid chloride to liquid ammonia. After crystallization from methanol, it had m.p. 221–222°.

***p*-Phenylbenzoyl Benzoyl Peroxide-*p*-Phenylbenzoyl Carbonyl-$\mathrm{O^{18}}$ (XIII).**—The method of preparation was that of Wieland and Rasuwajew.[9] From 17.0 g. (0.0785 mole) of XI there was obtained after crystallization from chloroform–methanol 19.0 g. (76%) of XIII, m.p. 138–141° dec.

Labeled-*p*-Nitro-*p′*-methoxybenzoic Anhydride (V).—To a solution of 1.0 g. (0.0032 mole) of IV in 50 ml. of methylene chloride was added a solution of 0.71 g. (0.0035 mole) of tri-*n*-butylphosphine in 25 ml. of methylene chloride. After standing 24 hr., the mixture was concentrated to one-quarter of its original volume. The anhydride crystallized from this mixture at −80°. After crystallization from acetone–hexane, 0.75 g. (78%) of V, m.p. 158–159° was obtained.

An authentic sample of unlabeled V was prepared by allowing *p*-nitrobenzoyl chloride, 15.2 g. (0.10 mole), anisic acid, 18.6 g. (0.10 mole), and pyridine, 15.8 g. (0.20 mole), to react in 250 ml. of ether. The precipitated anhydride was washed with acid and water. The dried material was recrystallized from acetone–hexane to afford unlabeled V, m.p. 159–160°.

Anal. Calcd. for $\mathrm{C_{15}H_{11}NO_6}$: C, 59.80; H, 3.65. Found: C, 59.44; H, 3.75.

***p*-Nitrobenzamide (VI).**—Labeled V, 0.65 g. (0.00216 mole), was added to 10 ml. of boiling liquid ammonia. After the ammonia had evaporated, the residue was washed with 5% sodium bicarbonate solution and then crystallized twice from methanol to yield 0.30 g. (84%) of VI, m.p. 200–201°.

Labeled *p*-Nitrobenzoic Benzoic Anhydride (VIII).—Labeled VII, 4.1 g. (0.014 mole), in a mixture of 150 ml. of ether and 50 ml. of chloroform was treated with a solution of 3.2 g. (0.016 mole) of tri-*n*-butylphosphine in 35 ml. of chloroform. The mixture was allowed to stand for 24 hr. and then concentrated to give a semi-solid mass which was recrystallized from acetone–hexane to yield 3.1 g. (77%) of VIII, m.p. 126–127°.

***p*-Nitrobenzamide (IX).**—Treatment of VIII with liquid ammonia followed by the usual workup afforded IX, m.p. 200.5–201.5°.

Labeled *p*-Phenylbenzoic Benzoic Anhydride (XIV).—To a solution of 3.18 g. (0.010 mole) of XIII in 100 ml. of methylene chloride was added 2.03 g. (0.010 mole) of tri-*n*-butylphosphine in 25 ml. of methylene chloride. After 24 hr. the solvent was removed to afford a pale yellow oil which was washed three times with water. The oil crystallized on standing. Recrystallization from acetone–hexane afforded 2.1 g. (70%) of XIV, m.p. 149–150°.

An authentic sample of unlabeled XIV was prepared by allowing 7.0 g. (0.0353 mole) of *p*-phenylbenzoic acid, 2.8 g. of pyridine and 5.0 g. (0.0356 mole) of benzoyl chloride to react in 100 ml. of N,N-dimethylformamide. The solution was poured into dilute hydrochloric acid. The precipitated product was filtered, dried and then recrystallized from acetone–hexane to give 6.1 g. (57%) of XIV, m.p. 151–152°.

Anal. Calcd. for $\mathrm{C_{20}H_{14}O_3}$: C, 79.47; H, 4.63. Found: C, 79.27; H, 4.53.

Labeled *p*-Phenylbenzamide (XV).—Labeled XIV, 1.8 g. (0.00906 mole), was converted to the mixture of amides in liquid ammonia. After treating the crude reaction product with two 25-ml. portions of boiling water to remove the benzamide, the residue was crystallized from methanol to afford 0.40 g. of XV, m.p. 221–222°.

Equilibration of *p*-Phenylbenzoic Benzoic Anhydride (XIV).—XIV, 2.0 g., was allowed to stand at room temperature for three days in 25 ml. of pyridine. Acidification of the reaction mixture produced an oil which was taken up in chloroform. The dried chloroform solution was evaporated and the residue was extracted with two 25-ml. portions of boiling hexane. The hexane extracts on cooling deposited 0.40 g. of benzoic anhydride, m.p. 39–41°.

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[9] H. Wieland and G. Rasuwajew, *Ann.*, **480**, 157 (1930).