Bis-(di-2-ethylbutylphosphinyl)-methane was prepared using the 2-ethylbutyl Grignard and isolated in the same manner as the *n*-hexyl derivative.

Bis-(diphenylphosphinyl)-methane.—The preparation of this compound was the same as described for the *n*-hexyl derivative, substituting the phenyl Grignard. Isolation was different due to its low solubility in organic solvents and the stability of its hydrochloric acid adduct. The excess Grignard reagent was hydrolyzed and the magnesium hydroxide was dissolved with (1:1) hydrochloric acid. The aqueous and ether layers were decanted from the residue which contains the hydrochloric acid adduct. The hydrochloric acid adduct was recrystallized several times by the addition of a large volume of water to the residue dissolved in hot ethanol. A methanol solution of the adduct was then eluted through an anion exchange (Dowex-1-X8) column (1.5″ × 12″) in the hydroxide form. After evaporation of the methanol, the product was dissolved in hot acetone, which gave white needle-like crystals upon cooling.

Recently Issleib and Baldauf[27] have shown that bis-(diphenylphosphinyl)-methane, m.p. 183°, was obtained when the product, $[(C_6H_5)_2P(O)CH_2P(C_6H_5)_2]$, from the reaction between diphenylchlorophosphine and moist diazomethane was oxidized. The usefulness of this reaction for the preparation of the bis-(dialkylphosphinyl)-methanes is doubtful.

Bis-(dimethylphosphinyl)-methane.—Aside from using the methyl Grignard, this preparation was the same as described for the *n*-hexyl derivative; however, because the product is water soluble, different separation techniques were necessary. After hydrolysis of the excess Grignard reagent, the ether layer was discarded and the magnesium salts in the aqueous phase were precipitated by the addition of a 10% sodium hydroxide solution. The magnesium hydroxide was removed by centrifugation and the resulting solution was acidified with 6 *N* hydrochloric acid prior to removing the water by vacuum distillation at 50°. During the distillation, it was occasionally necessary to filter off the magnesium halides. The desired compound was obtained either by subliming the residue or extracting it into hot benzene and then crystallizing by the addition of petroleum ether, b.p. 30–60°, as white hygroscopic needles. It was not possible to remove all of the water from this compound; therefore, complete analytical determinations were not attempted. Additional identification was obtained by infrared analysis.

1,1-Bis-(di-*n*-hexylphosphinyl)-butane.—The potassium salt of bis-(di-*n*-hexylphosphinyl)-methane was alkylated with *n*-propyl bromide by the procedure of Kosolapoff.[13] Two fractions were obtained, 120–127° and 223° at 0.2 mm.

Infrared analysis of the lower boiling neutral fraction indicated a mixture of di-*n*-hexylmethylphosphine oxide with an ester. The mixture was heated for 8 hours with concentrated hydrochloric acid to hydrolyze the ester. The acid thus obtained was isolated and identified as di-*n*-hexylphosphinic acid. The ester presumably was propyl di-*n*-hexylphosphinate.

The higher boiling fraction was characterized as the monoalkylated compound. Due to an acidic contaminant, it was further purified by dissolving in diethyl ether and twice extracting with 5% NaOH, then with water. The ether was evaporated and the compound dried; $n^{25}D$ 1.4781.

4,4-Bis-(di-*n*-hexylphosphinyl)-heptane.—The potassium salt of 1,1-bis-(di-*n*-hexylphosphinyl)-butane was alkylated with *n*-propyl bromide by the same procedure mentioned above. Complete dissolution of the potassium required about 24 hours. The redistilled fraction boiling between 220–221° at 0.13 mm. was collected; $n^{25}D$ 1.4810.

Attempted Preparation of Bis-(di-*n*-hexylphosphino)-methane.—Reduction of bis-(di-*n*-hexylphosphinyl)-methane with lithium aluminum hydride gave two fractions boiling at 77–84° and 132–134° at 1 mm. The lower boiling fraction upon oxidation with air or neutral potassium permanganate gave di-*n*-hexylphosphine oxide,[28] m.p. 73–74°. The same fraction upon oxidation with acidic potassium permanganate gave di-*n*-hexylphosphinic acid. The lower boiling fraction was therefore identified as di-*n*-hexylphosphine.

The 132–134° fraction was di-*n*-hexylmethylphosphine oxide.

Acknowledgment.—The authors are indebted to Hiroshi Sakurai, a visiting research chemist from Mitsubishi Metal Mining Co., Tokyo, Japan, for his assistance in the determination of certain physical constants.

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[27] K. Issleib and L. Baldauf, *Pharm. Zentr.*, **99**, 329 (1960).

[28] R. H. Williams and L. A. Hamilton, *J. Am. Chem. Soc.*, **74**, 5418 (1952).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS, THE STATE UNIVERSITY, NEW BRUNSWICK, N. J.]

A Study of the Mechanism of the Reaction of *t*-Alkyl Peresters with Trisubstituted Phosphines[1]

BY DONALD B. DENNEY, WILLIAM F. GOODYEAR[2] AND BERNARD GOLDSTEIN

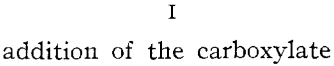
RECEIVED SEPTEMBER 9, 1960

The formation of *t*-alkyl esters and trisubstituted phosphine oxides from *t*-alkyl peresters and trisubstituted phosphines has been studied. A mechanism is proposed using data from oxygen-18 tracer studies, the kinetics of the reaction, the effect of additives, and some stereochemical results. The proposed mechanism involves initial formation of a pentacovalent phosphorus intermediate which decomposes by ion pair processes to the products.

Recently Horner and Jurgeleit[3] have presented the results of an extensive study of the reactions of organic peroxides with trisubstituted phosphines. They found that the general reaction is

$$R—O—O—R + R_3'P \longrightarrow R—O—R + R_3'P=O$$

The mechanism of the reaction of diaroyl peroxides with trisubstituted phosphines has been studied.[4] It was suggested that the reaction proceeds by initial displacement by the phosphine on one of the oxygens of the peroxidic link to give an ion pair (I). Decomposition of I most probably



$$[Ar—\overset{O}{\overset{\|}{C}}—O—\overset{+}{P}(R)_3 + ArCO_2^-]$$

I

occurs by addition of the carboxylate ion to the carbonyl carbon atom of the phosphonium salt followed by loss of the phosphine oxide and formation of an aromatic anhydride.

It was also shown by the use of suitably substituted peroxides that the phosphine displaces on the most electropositive oxygen of the aroyl per-

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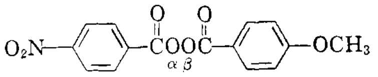
[1] Support of part of this work by Research Corporation is gratefully acknowledged.

[2] National Science Foundation Predoctoral Fellow, 1957–1959.

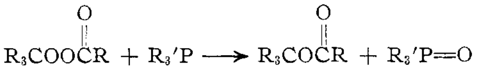
[3] L. Horner and W. Jurgeleit, *Ann.*, **591**, 138 (1955).

[4] (a) M. A. Greenbaum, D. B. Denney and A. K. Hoffman, *J. Am. Chem. Soc.*, **78**, 2563 (1956); (b) D. B. Denney and M. A. Greenbaum, *ibid.*, **79**, 979 (1957).

oxide. For example, the phosphine displaced on the α-oxygen of *p*-nitrobenzoyl *p*-methoxybenzoyl peroxide to the practical exclusion of the β-oxygen.



The purpose of this present work was to investigate the mechanism of the reaction of *t*-alkyl peresters with trisubstituted phosphines. The reaction in question is



$$R_3COO\overset{\overset{O}{\|}}{C}R + R_3'P \longrightarrow R_3CO\overset{\overset{O}{\|}}{C}R + R_3'P{=}O$$

The perester used in much of this work was *t*-butyl perbenzoate. In general varying amounts of benzoic acid were isolated from the reaction. It has not been established conclusively whether the benzoic acid is formed during the reaction of the phosphine with the perester or whether it arises during the isolation procedures. In a control experiment *t*-butyl benzoate was treated with tri-*n*-butylphosphine. Under these conditions the *t*-butyl benzoate was stable. This result suggests that the benzoic acid is formed during the reaction. It will be shown that its formation can be explained on mechanistic grounds.

Results and Discussion

Tracer Experiments.—In a preliminary series of experiments, benzoyl chloride, labeled with oxygen-18, was converted to carbonyl labeled *t*-butyl perbenzoate. The perester was reduced with triphenylphosphine in boiling ether. Reduction of the *t*-butyl benzoate with lithium aluminum hydride afforded benzyl alcohol which was converted to its phenylurethan and analyzed for oxygen-18. The urethan contained 62% of the excess oxygen-18 originally present in the starting benzoyl chloride. It has been shown that in the reduction of esters by lithium aluminum hydride the carbonyl oxygen is retained in the alcohol formed from the radical containing the carboxyl group.[5] Thus in this case the *t*-butyl benzoate contained 62% of the original excess oxygen-18 in its carbonyl group.

Since all of the products from the above series of experiments were not analyzed for oxygen-18, it was necessary to repeat the sequence. Another sample of carbonyl labeled *t*-butyl perbenzoate was prepared and reduced in benzene at 60°. The benzyl alcohol obtained in this series had 79% of the excess oxygen-18. The *t*-butyl alcohol contained the remainder of the excess oxygen-18.

Effect of Additives.—Several experiments were conducted in which substances were added to the reaction mixture. When the reaction was conducted in the presence of ethylene glycol, the product isolated in 91% yield appeared to be pure *t*-butyl benzoate. No β-hydroxyethyl benzoate could be detected. In another experiment *t*-butyl peracetate was allowed to react in methanol with triphenylphosphine. Gas phase chromatography of the volatile products showed that only trace amounts of methyl acetate were formed.

Reduction of *t*-butyl perbenzoate in 95% ethanol to which had been added a molar amount of *p*-nitrobenzoate ion gave a mixture of *t*-butyl benzoate and *t*-butyl *p*-nitrobenzoate. A nitrogen analysis of the mixture indicated that the *t*-butyl *p*-nitrobenzoate comprised *ca.* 8% of the product. In another experiment *t*-butyl perbenzoate was reduced in chloroform in the presence of acetate ion. Gas phase chromatography showed some *t*-butyl acetate was formed. Similarly reduction of *t*-butyl perbenzoate with tri-*n*-butylphosphine in 95% ethanol containing thiocyanate ion afforded both *t*-butyl thiocyanate and *t*-butyl isothiocyanate in addition to the expected *t*-butyl benzoate.

Kinetics.—A study of the kinetics of the reactions of several *p*-substituted *t*-butyl perbenzoates with triphenylphosphine in several solvents revealed that the reaction is bimolecular, first order in perester and triphenylphosphine. The data obtained in toluene for the substituted peresters fitted a conventional Hammett plot, ρ 1.24. Kinetic data from four *p*-substituted peresters were plotted to obtain ρ. These were *p*-nitro, *p*-chloro, *p*-hydrogen and *p*-benzyloxy. The value of the slope was obtained omitting the rate constant for *t*-butyl *p*-benzyloxyperbenzoate which was not in accord with the remainder of the data (see Experimental). There seems to be no logical reason for the *p*-benzyloxy group not to follow the close correlation to the Hammett relationship obtained for the other substituents. The discrepancy must then lie in either the rate constants obtained or in the reported σ-value. In view of the rather good consistency and constancy of the rate data it would seem that it is the σ-value that should be suspected. The value of -0.415 reported by Jaffé[6] was calculated solely on the basis of the spectroscopic data reported by Ingraham, *et al.*[7] Using the data obtained in this research a σ of -0.139 can be calculated for the *p*-benzyloxy group. This value is more in accord with the inductive power of the benzyloxy group and is suggested as a replacement for the older value.

From data obtained at 40 and 50° for the reaction of *t*-butyl perbenzoate with triphenylphosphine in toluene, it was possible to calculate the free energy, enthalpy and entropy of activation. These were found to be 24.6 kcal./mole, 17.9 kcal./mole and -21.2 e.u. Changes in the solvating power of the solvent did not have an appreciable effect on the rate of the reaction. The maximum effect observed was a 10-fold increase in rate in changing the solvent from toluene to 2-methyl-1-pentanol.[8]

Stereochemistry.—*trans*-9-Decalyl perbenzoate (II) was allowed to react with tri-*n*-butylphosphine in chloroform to give *trans*-9-decalyl benzoate (III) in 46% yield and 6-cyclodecanone hemiacetal benzoate (IV) in 18% yield. The formation of the latter compound is not unexpected.[9] The structure of *trans*-9-decalyl benzoate was proved by reducing it to *trans*-9-decalol with lithium aluminum hydride.

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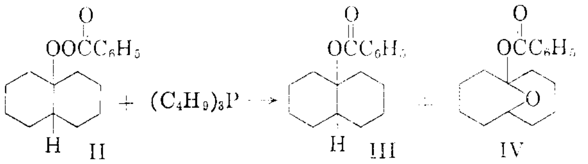
[5] D. B. Denney and D. G. Denney, *J. Am. Chem Soc.*, **79**, 4806 (1957).

[6] H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

[7] L. L. Ingraham, J. Corse, G. F. Bailey and F. Stitt, *J. Am. Chem. Soc.*, **74**, 2297 (1952).

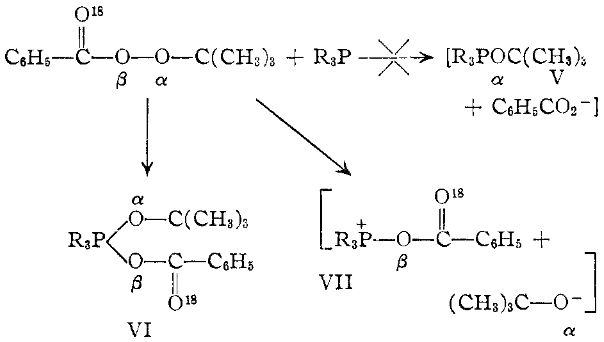
[8] A more detailed discussion of the kinetic data can be found in the Experimental section.

[9] R. Criegee and R. Kaspar, *Ann.*, **560**, 127 (1948).



II III IV

Mechanism.—Previous work has shown that trisubstituted phosphines react with peroxides by initial displacement on one of the oxygen atoms of the peroxide group by the phosphine.[4,10] A similar displacement in the phosphine–perester reaction seems quite reasonable. The oxygen-18 results obtained in ether and benzene exclude displacement on the α-oxygen to give V. The ester formed from V would necessarily have equal amounts of oxygen-18 in both positions.



V VI VII

Displacement on the β-oxygen to give VII cannot be completely excluded; however, the available evidence does not favor this process. If VII was formed in an hydroxylic solvent or in the presence of an alcohol one would expect rapid proton exchange to give *t*-butyl alcohol and the alkoxide ion derived from the solvent. If this occurred an ester derived from this alkoxide ion might well be formed. Indeed the cation of VII would be expected to solvolyze rapidly in alcohol to an ester and the phosphine oxide.

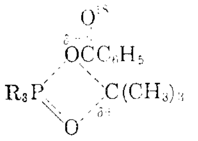
A mechanism which is consistent with the experimental data involves displacement on the β-oxygen of the perester to give the pentacovalent phosphorus compound VI. Attack on the β-oxygen rather than the α-oxygen is favored because of the steric effects.[10,11] The β-oxygen is more electropositive than the α-oxygen and is therefore more susceptible to attack by the nucleophile.

The kinetic data suggest that the displacement reaction involves a transition state in which there is little charge separation. The 10-fold increase in rate in changing the solvent from toluene to 2-methyl-1-pentanol is much smaller than has been found for ionic displacement reactions of triphenylphosphine. Bartlett and Meguerian[12] have shown that the rate of the reaction of triphenylphosphine with sulfur is markedly affected by small changes in the dielectric constant of the solvent. They also observed rate increases of several hundred-fold when small amounts of methanol or phenol were added to benzene solutions of the reactants. They concluded that the transition state for the reaction had about half of the ionic charge developed.

The entropy of activation found for the phosphine–perester reaction is also not in accord with a transition state involving much charge separation. Frost and Pearson[13] have tabulated data for many ionic displacement reactions. In solvents such as toluene the entropy of activation for these reactions is negative and usually about twice that observed in this case.

The formation of VI can occur *via* a transition state in which there is little charge separation. In the displacement process a partial negative charge develops on the α-oxygen. This charge can be neutralized by interaction and bond formation with a vacant sp^{3}d orbital on the phosphorus atom, thus leading to VI directly.

The conversion of VI to products is probably an ionic process. Several schemes can be envisioned for this transformation. One attractive hypothesis involves ion pairs. The oxygen-18 results show that in benzene and ether a completely free benzoate ion is not formed. These results can be accommodated by an internal ion pair decomposition path as represented by VIII. For simplicity only the preferred bonding of the β-oxygen to the *t*-butyl group is shown. The partial equilibration can occur by bonding of the carbonyl oxygen to the *t*-alkyl group in a similar ion pair.[14] The fact that more equilibration is observed in ether than in benzene is in accord with this hypothesis. Ether is a somewhat more polar solvent than benzene; therefore one would expect a less tightly bound ion pair which should lead to more equilibration. In more polar solvents complete equilibration of the label may well occur.



VIII

The reduction in chloroform of *trans*-9-decalyl perbenzoate to *trans*-9-decalyl benzoate shows that inversion does not take place at the tertiary center. The result does not prove that the reaction takes place with complete retention of configuration, since small amounts of *cis*-9-decalyl benzoate could have been lost in the isolation procedure.[15] Retention of configuration is in accord with the proposed ion pair decomposition process.[16]

The incorporation of added foreign anions into the products of the reaction is consistent with an

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[10] D. B. Denney, W. F. Goodyear and B. Goldstein, *J. Am. Chem. Soc.*, **82**, 1393 (1960).

[11] C. Walling, O. H. Basedow and E. S. Savas, *ibid.*, **82**, 2181 (1960), have found that di-*t*-butyl peroxide does not undergo an ionic reaction with triphenylphosphine. This must be due in part to the difficulty of approach to an oxygen of the peroxidic link.

[12] P. D. Bartlett and G. Meguerian, *ibid.*, **78**, 3710 (1956).

[13] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, Ch. 7.

[14] Incomplete equilibration of a label in other internal ion pair reactions has been observed before. For a thorough discussion of ion pairs in reactions similar to this, see S. Winstein and G. C. Robinson, *J. Am. Chem. Soc.*, **80**, 169 (1958).

[15] In order for an experiment of this type to be completely definitive, it is necessary to study the reaction using both geometrical isomers or better an optically active system. Experiments of this nature are in progress.

[16] D. J. Cram, J. L. Mateos, F. Havck, A. Langemann, K. R. Kopecky, W. D. Nielsen and J. Allinger, *J. Am. Chem. Soc.*, **81**, 5774 (1959).

ion pair decomposition. In the more polar solvents, *i.e.*, chloroform or alcohol, dissociation of VI may lead initially to IX which then decomposes to

$$[R_3\overset{+}{P}OC(CH_3)_3 + C_6H_5—CO_2^-]$$

IX

products. Anion exchange with the benzoate ion of IX explains the introduction of the foreign anions; IX can also decompose to olefin, phosphine oxide and benzoic acid.

Experimental[17]

Triphenylphosphine.—Following the procedure of Dodonon and Medox,[18] triphenylphosphine was prepared in crude yields of 65–80% by the action of phenylmagnesium bromide on phosphorus trichloride. The crude material was recrystallized four times from ethanol for ordinary use and, for use as a primary standard or in a kinetic run, it was recrystallized six times, powdered and dried in a vacuum desiccator to give a nearly odorless product, m.p. 80.5–81.0° (lit.[19] m.p. 79°).

***t*-Butyl Perbenzoates.**—The preparation of all peresters was accomplished from the appropriate acid chloride and *t*-butyl hydroperoxide following the method of Milas and Surgenor.[20] In many non-kinetic experiments commercial *t*-butyl perbenzoate was used without further purification.

By this method, the addition of benzoyl chloride (140.6 g., 1.0 mole) and 30% potassium hydroxide solution (243.1 g., 1.3 moles) to 60% *t*-butyl hydroperoxide (165.2 g., 1.1 moles) afforded, after removal of the solvent *in vacuo*, 175.2 g. (89.3%) of a liquid whose infrared spectrum corresponded closely to that of a known sample of *t*-butyl perbenzoate.

An attempt to purify further approximately 25 g. of the crude material by vacuum distillation resulted in a violent decomposition of the perester at about 125°. Molecular distillation afforded only limited quantities of pure perester.

A pure sample of *t*-butyl perbenzoate, for use in the kinetic study, was obtained by dissolving *ca.* 10 g. of the crude material in about 200 ml. of *n*-pentane and extracting with two 50-ml. portions of 5% sodium carbonate solution and two 50-ml. portions of water. After drying over anhydrous sodium sulfate, the perester was crystallized in a Dry Ice–acetone-bath, filtered rapidly and transferred to a flask where it was dried thoroughly over anhydrous sodium sulfate. After drying, the last traces of *n*-pentane were removed in a vacuum desiccator. The perester then was stored in a refrigerator until used.

Material thus purified was assayed to be nearly 98% pure by allowing it to react, undiluted, with an excess of analytic grade triphenylphosphine. After 48 hours the unreacted triphenylphosphine was determined iodimetrically.

***t*-Butyl *p*-Nitroperbenzoate.**—In a similar manner 92.8 g. (0.50 mole) of *p*-nitrobenzoyl chloride (recrystallized from hexane; m.p. 72°) in 500 ml. of dry ether, 122.0 g. (0.65 mole) of 30% potassium hydroxide solution and 82.6 g. (0.55 mole) of 60% *t*-butyl hydroperoxide afforded, after removal of the solvent *in vacuo*, 90.7 g. (70.8%) of yellow crystals, m.p. 77–78°. Two recrystallizations from hexane gave the desired perester, m.p. 77–78° (lit.[21] m.p. 79°).

Before use, this and all other solid peresters were recrystallized twice from hexane, powdered, dried in a vacuum desiccator and stored in a refrigerator.

***t*-Butyl *p*-Chloroperbenzoate.**—Freshly distilled *p*-chlorobenzoyl chloride (b.p. 97° (11 mm.), 92.0 g., 0.53 mole) in 200 ml. of dry ether and 127.8 g. (0.63 mole) of 30% potassium hydroxide solution were added to 87.9 g. (0.58 mole) of 60% *t*-butyl hydroperoxide. Removal of the solvent *in vacuo* gave 126.0 g. of a viscous liquid. Solution of this liquid in 250 ml. of hexane, followed by cooling in a Dry Ice–acetone-bath, afforded a glassy solid. A threefold dilution of the solution with hexane and then cooling to −78° produced a white crystalline mass, 105.1 g. (87.6%), m.p. 47–48°. Recrystallization from *n*-pentane afforded colorless crystals, m.p. 48.0–48.5° (lit.[21] m.p. 49°).

***p*-Benzyloxybenzoic acid** was prepared according to the procedure of Cohen and Dudley[22] in 83% yield, m.p. 192–193° (lit.[22] m.p. 188–190°).

***p*-Benzyloxybenzoyl Chloride.**—*p*-Benzyloxybenzoic acid was converted to the acid chloride in 52% yield, m.p. 104–105° (lit.[22] m.p. 104–106°).

***t*-Butyl *p*-Benzyloxyperbenzoate.**—*p*-Benzyloxybenzoyl chloride (25.5 g., 0.10 mole) in 200 ml. of methylene chloride and 22.5 g. (0.12 mole) of 30% potassium hydroxide solution were added to 16.5 g. (0.11 mole) of 60% *t*-butyl hydroperoxide. Removal of the methylene chloride *in vacuo* afforded a viscous liquid in which a solid was suspended. Filtration afforded 0.88 g. of an acidic material, m.p. 195–196°.

Attempts to crystallize the liquid from a variety of solvents produced only a powdery substance, 22.0 g., m.p. 55–68°. This powder was chromatographed on 200 g. of alumina. Elution with benzene–hexane (2:1) gave 3.30 g. which, when recrystallized from hexane, afforded 1.45 g., m.p. 72.5–73.0°. Further elution with pure benzene gave another 6.50 g. which, upon recrystallization, afforded 3.5 g., m.p. 71–72°.

The column was washed with acetone and the material thus obtained was combined with the residues from the above recrystallizations and rechromatographed on 150 g. of fresh alumina. A similar elution afforded 2.62 g. which gave, upon recrystallization, 0.82 g., m.p. 72.5–73.0°. The above three recrystallized fractions were combined and recrystallized from hexane to give fine white needles, m.p. 72.5–73.0°. The infrared spectrum of this material was similar to the spectra of other *p*-substituted peresters and was entirely commensurate with the structure of the desired perester.

Anal. Calcd. for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71. Found: C, 71.73; H, 6.75.

Benzoic Acid-CO^{18}O^{18}H.—Benzotrichloride (240.4 g., 1.23 moles) and water (73.9 g. 3.69 moles, *ca.* 1.5 atom % O^{18}) were stirred on a steam-bath for 22 hours. The crude benzoic acid was filtered, washed with distilled water and dried. Recrystallization from benzene–hexane gave 110.6 g. (78%) of benzoic acid, m.p. 126.0–126.5°; oxygen-18 analysis, 1.30, 1.31 atom % excess oxygen-18 in each position.

Benzoyl Chloride-O^{18}.—Labeled benzoic acid (55.0 g., 0.45 mole) and thionyl chloride (67.5 g., 0.57 mole) were refluxed for 3 hours. The excess thionyl chloride was removed and the product was distilled *in vacuo* to give 51.0 g. (80.6%) of benzoyl chloride, b.p. 78–82° (18 mm.).

***t*-Butyl Perbenzoate-*carbonyl*-O^{18}.**—Following the previously outlined procedure, 46.0 g. (0.325 mole) of labeled benzoyl chloride and 79.5 g. (0.426 mole) of 30% potassium hydroxide solution were added to 54.1 g. (0.361 mole) of 60% *t*-butyl hydroperoxide. After removal of the solvent *in vacuo* and drying over anhydrous magnesium sulfate, there was obtained 63.8 g. (99.3%) of crude labeled perester.

Molecular distillation of 5.6 g. of the crude perester afforded 4.5 g. of liquid, block temperature 60° (0.3 mm.) (lit.[18] 77° (2 mm.)). The infrared spectrum of this material was identical with that of an authentic sample of *t*-butyl perbenzoate. Oxygen-18 analysis showed 1.26, 1.27 atom % excess oxygen-18.

The Reaction of Labeled *t*-Butyl Perbenzoate with Triphenylphosphine in Ether.—A sample of *t*-butyl perbenzoate prepared from benzoic acid containing 0.90 atom % excess oxygen-18 was used in this experiment. The perester (3.85 g., 0.0196 mole) in 10 ml. of dry ether was added to 5.80 g. (0.0216 mole) of triphenylphosphine and the mixture was refluxed for 40 hours. The triphenylphosphine oxide which had precipitated was filtered and washed with cold ether. The yield was 1.28 g. (23.5%), m.p. 148–149° (lit.[22a] 152–153°).

The filtrate was molecularly distilled to give a forerun, block temperature 40–70° (30 mm.), and a second fraction, 1.16 g. (33%), block temperature 70–75° (3 mm.). The

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(17) All melting points were taken on a Kofler hot-stage. Oxygen-18 analyses were carried out according to the procedure of W. E. Doering and E. Dorfman, *J. Am. Chem. Soc.*, **75**, 5595 (1953). Analyses were by G. Robertson, Florham Park, N. J.

(18) J. Dodonon and H. Medox, *Ber.*, **61**, 910 (1928).

(19) G. M. Kosolapoff, "Organophosphorus Compounds," J. Wiley and Sons, Inc., New York, N. Y., 1950, p. 32.

(20) N. A. Milas and D. M. Surgenor, *J. Am. Chem. Soc.*, **68**, 642 (1946).

(21) A. T. Blomquist and I. A. Berstein, *ibid.*, **73**, 5546 (1951).

(22) J. B. Cohen and H. W. Dudley, *J. Chem. Soc.*, **97**, 1746 (1910).

(22a) G. M. Kosolapoff, *J. Am. Chem. Soc.*, **64**, 2982 (1942).

infrared spectrum of this fraction was identical with that of an authentic sample of *t*-butyl benzoate.

The still residue, which had become too viscous for further distillation, was extracted several times with ether and with *n*-pentane, but no separation of ester and triphenylphosphine oxide could be effected. Further attempts to obtain more ester were abandoned.

Lithium Aluminum Hydride Reduction of Labeled *t*-Butyl Benzoate.—To a slurry of 0.29 g. (0.0077 mole) of lithium aluminum hydride in 5 ml. of dry ether was added 1.16 g. (0.007 mole) of *t*-butyl benzoate (from the reduction of the labeled perester) in 5 ml. of dry ether. The mixture was stirred at room temperature for 44 hours and hydrolyzed with 1 ml. of water. The mixture was filtered and the filtrate was dried over anhydrous magnesium sulfate.

Molecular distillation gave an initial fraction, 0.26 g., block temperature 70–85° (17 mm.), and a second fraction, 0.18 g., block temperature 85–120° (17 mm.). The infrared spectra of both fractions were identical with that of an authentic sample of benzyl alcohol. No *t*-butyl alcohol was recovered.

To 2 ml. of phenyl isocyanate (*ca.* 3 g., 0.025 mole) in 2 ml. of dry hexane was added fraction I of the benzyl alcohol obtained in the distillation, 0.26 g. (0.0234 mole) in 3 ml. of dry hexane. The mixture was allowed to stand at room temperature for several hours and then was refrigerated overnight. Filtration of the precipitate which had formed afforded 0.30 g. (56.5%) of a crystalline material, m.p. 72–76°. Recrystallization from petroleum ether (90–120°) yielded 0.24 g., m.p. 72–74° (lit.[22b] m.p. 75.5–76.0°). A mixed melting point determination with a previously prepared authentic sample of benzyl phenylurethan showed no depression. The infrared spectra of the two urethans were identical. Oxygen-18 analysis showed 0.55, 0.56 atom % excess oxygen-18.

The Reaction of Labeled *t*-Butyl Perbenzoate with Triphenylphosphine in Benzene.—The crude labeled perester, 1.27 atom % excess oxygen-18 (58.2 g., *ca.* 0.30 mole), in 250 ml. of dry benzene was added slowly to a stirred solution of 78.6 g. (0.30 mole) of triphenylphosphine in 250 ml. of dry benzene. After the addition was complete the reaction mixture was heated to 55–60° for 18 hours. The benzene was then removed *in vacuo* and the triphenylphosphine oxide which had precipitated was removed by filtration and washed with ether. The addition of the ether to the filtrate caused more oxide to precipitate and this was also filtered and washed with ether. In this manner 44.8 g. of triphenylphosphine oxide, m.p. 152–155°, was obtained.

Continued extraction of the semi-liquid residue with ether and with pentane afforded an additional 22.1 g. of the oxide, m.p. 142–147°, total yield 66.9 g. (80%).

The ether and pentane were removed from the filtrate *in vacuo* and the ester was distilled to give 21.2 g. (39.7%) of crude material, b.p. 77° (2 mm.) (lit.[23] b.p. 75–79° (2–3 mm.)). At this point the still residue became too viscous for convenient distillation. The infrared spectrum of the residue indicated, *via* comparison with those of authentic samples, that it was chiefly a mixture of triphenylphosphine oxide and *t*-butyl benzoate.

Redistillation of the crude ester afforded 19.1 g., b.p. 77° (2 mm.). The infrared spectrum of this distillate was essentially identical to a spectrum of an authentic sample of *t*-butyl benzoate.

A 5.0-g. portion of this distillate was molecularly distilled and a center cut, 2.44 g., block temperature 70° (0.1 mm.), was retained for oxygen-18 analysis. The oxygen-18 content was found to be 1.23, 1.23 atom % excess oxygen-18. These values are lower by 0.03 atom % than those found for the perester. This could be due to some loss of oxygen-18 or to oxygenated impurities in the *t*-butyl benzoate. The later explanation probably is more nearly correct. In subsequent calculations 1.26 atom % was used.

Lithium Aluminum Hydride Reduction of Labeled *t*-Butyl Benzoate.—To a slurry of 1.68 g. (0.0444 mole) of lithium aluminum hydride in 100 ml. of dry ether was added 15.8 g. (0.0887 mole) of *t*-butyl benzoate (from the reduction of the labeled perester in benzene) in 150 ml. of dry ether. The reaction mixture was stirred overnight and then hydrolyzed with a minimum amount of water (*ca.* 0.75 g.). The resultant suspension was filtered and the filtrate was dried over anhydrous magnesium sulfate. Distillation through a packed column gave a forerun (34–46°) whose infrared spectrum indicated the presence of a hydroxyl group. A second fraction, 0.40 g., b.p. 46–54°, was also obtained.

The undistilled residue was then molecularly distilled to give 8.63 g. of a liquid, block temperature 147–152° (14 mm.). The infrared spectrum of this distillate was almost identical with that of an authentic sample of benzyl alcohol.

The fraction which had distilled at 46–54° (0.40 g.), was dissolved in 5 ml. of dry hexane and added to 0.71 g. (0.0060 mole) of phenyl isocyanate in 3 ml. of dry hexane. After standing overnight, the resultant precipitate was filtered to give 0.34 g. (32.7%) of pinkish crystals, m.p. 133–134°, with a small residue, m.p. 245–247°. Recrystallization from petroleum ether (60–90°) gave 0.27 g., m.p. 126–133°. Sublimation at 100° (14 mm.) gave an initial sublimate, 0.02 g., m.p. 115–118°, and a second, 0.20 g., m.p. 134–137°. Recrystallization of the latter from petroleum ether (60–90°) afforded 0.16 g. of the desired *t*-butylphenylurethan, m.p. 135–136° (lit.[24] m.p. 136°). A mixed melting point determination with an authentic sample of *t*-butylphenylurethan gave no depression. The infrared spectra of the two materials were identical. Oxygen-18 analysis showed 0.27, 0.27 atom % excess oxygen-18.

In a manner identical with the one previously described 1.34 g. (0.0124 mole) of benzyl alcohol obtained above and 1.61 g. (0.0135 mole) of phenyl isocyanate gave 0.70 g. (24.8%) of product, m.p. 70–73°. Four recrystallizations from petroleum ether (60–90°) gave 0.21 g. of benzylphenylurethan, m.p. 76–77°. The infrared spectrum of this derivative was identical to that of an authentic sample of benzyl phenylurethan and a mixed melting point determination showed no depression. Oxygen-18 analysis showed 0.98, 0.99 atom % excess oxygen-18. The total excess oxygen-18 accounted for is then 0.27 + 0.99 = 1.26 atom % excess oxygen-18. These values were used in the calculation of percentage equilibration in this series.

The Reaction of *t*-Butyl Perbenzoate with Triphenylphosphine in the Presence of Triethylammonium Acetate.—Triethylammonium acetate (8.06 g., 0.05 mole) was prepared by adding 3.0 g. (0.05 mole) of glacial acetic acid to 5.06 g. (0.05 mole) of triethylamine dissolved in 50 ml. of chloroform. This solution then was added to a solution of 13.12 g. (0.05 mole) of triphenylphosphine and 9.72 g. (0.05 mole) of *t*-butyl perbenzoate in 70 ml. of chloroform. The solution was allowed to remain at room temperature for 60 hours and refluxed on a steam-bath for 10 hours.

The volatile material was distilled at atmospheric pressure until a pot temperature of 120° was reached. The residue was then distilled at 18 mm. with a Dry Ice condenser in the system to trap the volatile material. The infrared spectrum of this second fraction showed a carbonyl peak at 5.75 μ which was not removed by extraction with 5% sodium bicarbonate solution. After drying over anhydrous magnesium sulfate the liquid was chromatographed in a vapor phase chromatography apparatus using a 2-foot silicone grease column at 27°. Peaks were obtained after 3.1 min. (chloroform) and after 8.9 min. (*t*-butyl acetate). The identity of these peaks was confirmed by chromatographing a solution of *t*-butyl acetate (10%) and chloroform (90%) in which case peaks were obtained after 3.17 min. (chloroform) and 9.0 min. (*t*-butyl acetate). All other volatile materials which could have arisen during the reaction were also chromatographed as chloroform solutions and found to have retention times which were sufficiently different from the ones in question to avoid any confusion.

The Reaction of *t*-Butyl Peracetate with Triphenylphosphine in Methanol.—Triphenylphosphine (13.12 g., 0.05 mole) in 80 ml. of methanol and 40 ml. of chloroform was added to 8.25 g. (0.05 mole) of *t*-butyl peracetate (75% in benzene) in 20 ml. of methanol. The solution was allowed to stand at room temperature for 60 hours and then refluxed on a steam-bath for 10 hours. The volatile material was removed by distillation and then chromatographed using a 2-foot silicone grease column at 27°. Peaks were obtained after 0.75 min. (methanol), a small shoulder at 1.75 min. (methyl acetate) and after 3.67 min. (chloroform). The identity of each peak was confirmed by chromatographing several known solutions. A solution of methanol, methyl acetate and *t*-butyl acetate (1:1:1) gave peaks after 0.9 min.

(22b) F. Straus and H. Grindel, *Ann.*, **439**, 312 (1924).

(23) R. Altschul, *J. Am. Chem. Soc.*, **68**, 2605 (1946).

(24) E. Knoevenagel, *Ann.*, **297**, 148 (1897).

(methanol), 1.75 min. (methyl acetate) and 8.9 min. (*t*-butyl acetate). A solution of methanol (65%), chloroform (30%) and methyl acetate (5%) gave peaks after 0.75 min. (methanol), 1.75 min. (methyl acetate) and 3.1 min. (chloroform).

The area of the methyl acetate peak obtained in the chromatography of the distillate was considerably smaller than that obtained from the known solution in which methyl acetate represented 5% of the mixture. From this it was apparent that the methyl acetate in the distillate represented only a trace amount.

***t*-Butyl Perbenzoate and Tri-*n*-butylphosphine in the Presence of *p*-Nitrobenzoate Ion.**—To a solution of 1.94 g. (0.010 mole) of *t*-butyl perbenzoate, 1.67 g. (0.010 mole) of *p*-nitrobenzoic acid and 1.01 g. (0.010 mole) of triethylamine in 40 ml. of 95% ethanol was added 4.04 g. (0.020 mole) of tri-*n*-butylphosphine. The solution was refluxed for 1 hour and then allowed to stand at room temperature for 24 hours. The reaction mixture was poured into 100 ml. of water and extracted with pentane. The pentane extract was washed with two 40-ml. portions of 10% sodium bicarbonate solution and then with three 50-ml. portions of 6 *N* hydrochloric acid. The pentane solution was dried over sodium sulfate, and the solvent was evaporated to yield 0.82 g. of an oil whose infrared spectrum was entirely commensurate with that of a mixture of *t*-butyl benzoate and *t*-butyl *p*-nitrobenzoate. The two characteristic peaks of the nitro group were present at 6.10 and 7.60 μ. All of the other peaks were present in the spectra of *t*-butyl benzoate and *t*-butyl *p*-nitrobenzoate. The mixture was analyzed for nitrogen. It can be calculated from the analytical data that the mixture contained *ca.* 8% of *t*-butyl *p*-nitrobenzoate.

Anal. Found: N, 1.04.

Several other reductions of *t*-butyl perbenzoate were conducted in the presence of *p*-nitrobenzoate ion. In all of these cases the presence of *t*-butyl *p*-nitrobenzoate in the product was demonstrated by infrared analysis.

***t*-Butyl Perbenzoate and Tri-*n*-butylphosphine in the Presence of Thiocyanate Ion.**—To a solution of 4.00 g. (0.049 mole) of sodium thiocyanate and 2.05 g. (0.010 mole) of tri-*n*-butylphosphine in 30 ml. of 95% ethanol was added 1.50 g. (0.0072 mole) of *t*-butyl perbenzoate. The solution was refluxed for 3 hours and then added to 100 ml. of water. The aqueous solution was extracted with pentane. The pentane was washed with 10 ml. of 10% sodium bicarbonate and 10 ml. of 6 *N* hydrochloric acid. The pentane was dried over magnesium sulfate, and then evaporated to yield an oil which consisted of *t*-butyl benzoate, sharp band at 5.83 μ, *t*-butyl thiocyanate and *t*-butyl isothiocyanate, broad band at 4.75 μ. The mixture was evaporatively distilled to yield 0.91 g. of material which still contained *t*-butyl thiocyanate and *t*-butyl isothiocyanate, broad band at 4.75 μ. A known sample of *t*-butyl isothiocyanate and *t*-butyl thiocyanate also had a broad band at 4.75 μ.

***t*-Butyl Perbenzoate and Tri-*n*-butylphosphine in the Presence of Ethylene Glycol.**—To a solution of 1.94 g. (0.01 mole) of *t*-butyl perbenzoate and 1.24 g. (0.02 mole) of ethylene glycol in 20 ml. of acetonitrile was added 4.04 g. (0.02 mole) of tri-*n*-butylphosphine. The reaction mixture was refluxed for 1 hour and then allowed to stand at room temperature for 24 hours. The mixture was poured into 100 ml. of water and the aqueous solution was extracted with pentane. The pentane extract was washed with three 20-ml. portions of 6 *N* hydrochloric acid, 20 ml. of water and three 20-ml. portions of 10% sodium bicarbonate solution. The pentane was dried over sodium sulfate and then evaporated to afford 1.05 g. (91%) of *t*-butyl benzoate. The infrared spectrum of this sample was identical in every respect with that of a known sample. Acidification of the sodium bicarbonate extract yielded 0.12 g. (9.8%) of benzoic acid, m.p. 121–122°.

***trans*-9-Decalyl Perbenzoate and Tri-*n*-butylphosphine.**—To a solution of 1.00 g. (0.0037 mole) of *trans*-9-decalyl perbenzoate, m.p. 65.5–66.5° (lit.[25] 67–68°), in 10 ml. of chloroform was added 3.7 g. (0.018 mole) of tri-*n*-butylphosphine. The mixture was allowed to stand at room temperature for 48 hours. The solution was washed with 3 *N* hydrochloric acid and water and then dried over sodium sulfate. The chloroform was removed *in vacuo*, and the residue, 2.50 g., was chromatographed on silica gel, 11.8 g., with benzene as the eluent. The product obtained was crystallized from hexane to yield 0.39 g. (41%) of *trans*-9-decalyl benzoate (III), m.p. 90–91°.

Anal. Calcd. for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 79.07; H, 8.87.

In another reaction 2.13 g. (0.0078 mole) of II was reduced with 4.71 g. (0.023 mole) of tri-*n*-butylphosphine. The yield of III, m.p. 89–91°, was 46%. There was also isolated by chromatography 0.39 g. (18%), m.p. 94–96° (lit.[25] 95.5–97°), of 6-cyclodecanone hemiacetal benzoate (IV).

Lithium Aluminum Hydride Reduction of III.—To a stirred slurry of 0.020 g. (0.00052 mole) of lithium aluminum hydride in 3 ml. of dry ether was added 0.135 g. (0.00052 mole) of III in 3 ml. of dry ether. The reaction mixture was stirred and refluxed for 7 hours, and then hydrolyzed with water and 6 *N* hydrochloric acid. The aqueous solution was extracted with ether and the combined ether extracts were dried over magnesium sulfate. The solvent was removed to afford 0.102 g. of crude product which was chromatographed on silica gel, 4 g., using benzene as the eluent. In this manner there was obtained 0.043 g. (53%) of *trans*-9-decalol, m.p. 53–54° (lit.[26] 52–53°). A mixed melting point with an authentic sample prepared by tri-*n*-butylphosphine reduction of *trans*-9-decalyl hydroperoxide showed no depression.

***t*-Butyl Benzoate and Tri-*n*-butylphosphine.**—A solution of 0.50 g. (0.0028 mole) of *t*-butyl benzoate and 0.63 g. (0.0031 mole) of tri-*n*-butylphosphine in 10-ml. of chloroform was refluxed for 1 hour, and then allowed to remain at room temperature for 24 hours. The reaction mixture was poured into water and extracted with four 40-ml. portions of 6 *N* hydrochloric acid, 40 ml. of water and two 40-ml. portions of 10% sodium bicarbonate solution. The solution was dried over sodium sulfate. Evaporation of the solvent afforded a residue whose infrared spectrum was identical with that of *t*-butyl benzoate. No benzoic acid was obtained when the sodium bicarbonate extract was acidified.

Solvents for the Kinetic Study.—Reagent grade toluene was dried over sodium wire and distilled. The fraction boiling at 110.5–111.0° (uncor.) was collected for use in the kinetic solutions.

2-Methyl-1-pentanol was dried over anhydrous sodium sulfate, the fraction boiling at 146–147° (uncor.) being retained for use in the kinetic solutions.

Cyclohexanone was dried over anhydrous magnesium sulfate and distilled. The fraction boiling at 155–156° was collected for use as a kinetic solvent.

Kinetic Procedure.—Solutions of triphenylphosphine and of the peresters were individually prepared in volumetric flasks at 20° and were preheated in the bath to the reaction temperature before they were mixed. The bath temperature was controlled to ±0.1°.

The concentrations of the solutions were corrected to the reaction temperature using the density–temperature relationship of the solvent. The reactants were mixed by transferring an equal amount of each preheated solution to a 50-ml. glass-stoppered erlenmeyer flask, using the same pipet for each transfer.

After the addition of the second reactant, each flask was shaken thoroughly and finely crushed Dry Ice was added to provide an inert atmosphere. In a blank determination a standard solution of triphenylphosphine in toluene, similarly treated and sampled intermittently over a 24-hour period, showed no appreciable change in concentration.

Samples for analysis were removed by means of pipets which previously had been calibrated for their delivery with a standard solution, having a concentration similar to the reaction mixture, at the same temperature and using the same solvent.

The reaction mixture was analyzed for its phosphine content by quenching the sample with an excess of ice-cold standard iodine solution, followed by back-titration with standard triphenylphosphine solution. This method utilizes this general reaction of tertiary phosphines

$$R_3P\colon + X_2 \longrightarrow R_3PX_2 \xrightarrow{H_2O} R_3\overset{+}{P}\overset{-}{O} + 2HX$$

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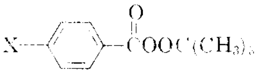
(25) A. C. Cope and G. Holzman, *J. Am. Chem. Soc.*, **72**, 3062 (1950).

(26) R. Criegee, *Ber.*, **77B**, 22 (1944).

TABLE I

SUMMARY OF KINETIC DATA FOR THE REACTION OF  WITH TRIPHENYLPHOSPHINE

$X-C_6H_4-\overset{O}{\overset{\|}{C}}OOC(CH_3)_3$

X	Solvent	Temp., °C.	P_0[a]	E_0[b]	k,[c] l. mole^{-1} hr.$^{-1}$	Av. k
H	Toluene	40	0.3035	0.3500	0.173	
			.3040	.2533	.175	
			.2500	.2991	.164	
			.2499	.2998	.166	
			.1035	.0993	.178	
			.2000	.0998	.178	0.172 ± 0.005
H	Toluene	50	.1062	.0491	.430	
			.1001	.1216	.425	
			.1001	.0608	.442	0.432 ± 0.006
NO_2	Toluene	40	.1035	.0996	1.67	
			.1035	.0996	1.67	
			.0911	.1002	1.62	1.65 ± 0.02
Cl	Toluene	40	.0614	.1002	0.354	
			.1250	.1513	.361	
			.1513	.0805	.372	
			.1522	.1002	.376	0.366 ± 0.008
$C_6H_5CH_2O$	Toluene	40	.3987	.2991	.118	
			.1504	.2991	.116	
			.3035	.1546	.119	0.118 ± 0.001
NO_2	2-Methyl-1-pentanol	40	.0795	.0702	6.58	
			.0399	.0508	6.56	6.57 ± 0.01
NO_2	Cyclohexanone	40	.0490	.0402	4.06	
			.0490	.0539	3.02	
			.0592	.0541	3.07	3.38 ± 0.45
H	2-Methyl-1-pentanol	40	.0989	.0819	1.305	
			.0504	.0378	2.06	
			.0907	.0503	1.13	
			.0590	.0312	1.57	
			.0306	.0615	1.87	1.59 ± 0.30

[a] Initial concentration of triphenylphosphine in moles per liter. [b] Initial concentration of perester in moles per liter. [c] Rate constant obtained by least squares method.

The standard titrating solutions were prepared in a solvent mixture consisting of 75% benzene and 25% ethanol (95%), which contained sufficient water to hydrolyze all of the triphenylphosphine diiodide produced. In order to minimize the reoxidation of the hydrogen iodide to iodine by atmospheric oxygen, 5 g. of pyridine was added to each liter of iodine solution. Additionally, finely crushed carbon dioxide was added to each sample throughout the titration. The solutions were standardized using triphenylphosphine as a primary standard and employing the same reaction sequence as in the analysis. The disappearance of the yellow color of the iodine was used as the end-point.

It is stated by Frost and Pearson[13] that the most accurate points in second-order kinetics are obtained near the mid-point in the reaction. With this in mind the majority of the rate constants were determined in the range from 40 to 60% of reaction completion and in no case were points obtained at less than 25% or more than 75% of reaction completion considered in the calculations. Once the approximate value of the rate constant was known, the conditions of subsequent runs were adjusted so that ten to twelve points could be taken in the 40–60% range. Sufficient time was allowed between points so that a significant increment in reaction could occur. The reaction was found to be bimolecular, first order in each reactant. The rate constants were determined by a least squares plot of

$$t \text{ vs. } \frac{2.303}{P_0 - E_0} \log \frac{P_0E}{E_0P}$$

where E_0 and P_0 are the initial concentrations of perester and phosphine, respectively, and E and P are the respective concentration after t hours had elapsed. The rate data are summarized in Table I.

Since t-butyl perbenzoate undergoes a unimolecular decomposition it was necessary to determine whether the rate of decomposition was great enough to warrant a correction. Using the rate data of Blomquist and Ferris[27] it was determined that for an average run the maximum concentration change would be of the order of 0.2%. This change in concentration was neglected in the calculation of the rate constant.

In the quest for a solvent of high dielectric constant and solvating power it was discovered that 2-methyl-1-pentanol would dissolve triphenylphosphine in sufficient concentration for the study. However the data obtained for this solvent, and for cyclohexanone which was used prior to it, are far less satisfactory than those obtained in toluene. No specific explanation is apparent for this. The solutions in cyclohexanone and the alcohol were rather

TABLE II

KINETIC DATA FOR THE REACTIONS OF p-SUBSTITUTED t-BUTYL PERBENZOATE WITH TRIPHENYLPHOSPHINE IN TOLUENE AT 40°

	p-Substituent			
	H	NO_2	Cl	$C_6H_5CH_2O$
k, l. mole^{-1} hr.$^{-1}$	0.172	1.65	0.366	0.118
Hammett σ[a]	0	0.778	0.227	(−0.415)
Hammett ρ	1.24			
Std. devn. of ρ	0.033			
σ (calcd.)[b]				−0.139
ΔF^* 40–50°	24.6 kcal./mole			
ΔH^* 40–50°	17.9 kcal./mole			
ΔS^* 40–50°	−21.2 cal./mole-deg.			

[a] H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953). [b] See discussion concerning the σ-value of the p-benzyloxy group.

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(27) A. T. Blomquist and A. F. Ferris, *J. Am. Chem. Soc.*, **73**, 3408 (1951).

viscous, a factor which made accurate pipetting of samples more difficult, but this does not explain the deviations between separate runs. It was felt that perhaps the solvent used for each run was not uniform, but redistillation and immediate use of the alcohol in simultaneous runs did not offer a solution and as yet the problem has not been resolved. It is evident however that the data can be used, in a qualitative sense, to indicate the nature and extent of the effect of solvent dielectric and ionizing power upon the reaction.

Table II shows the effect of *p*-substituents on the reaction rate.

From the rate data obtained at 40° and 50° in toluene solution, the free energy, enthalpy and entropy of activation were calculated and are listed in Table II.

In addition to the rate data reported, several runs were discarded or not continued, especially in the alcohol and ketone solvents, because it was obvious that a gross discrepancy was present.

[CONTRIBUTION FROM ROHM AND HAAS CO., PHILADELPHIA 37, PENNA.]

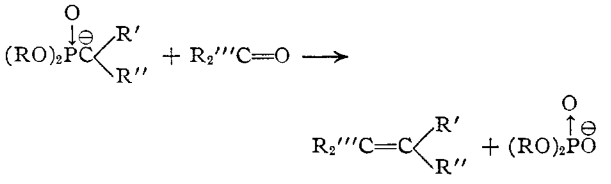
The Utility of Phosphonate Carbanions in Olefin Synthesis

BY WILLIAM S. WADSWORTH, JR., AND WILLIAM D. EMMONS

RECEIVED OCTOBER 28, 1960

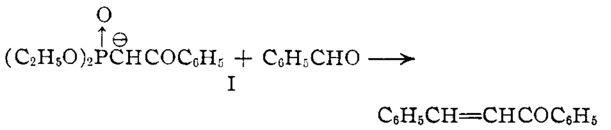
The reaction of phosphonate carbanions containing electron-withdrawing groups with aldehydes or ketones in an aprotic solvent constitutes a useful olefin synthesis. These reagents were, in general, more reactive than the analogous triarylphosphoranes or "Wittig" reagents and have a number of special features which enhance their utility.

In connection with another problem we have studied the reaction of phosphonate carbanions with ketones and aldehydes to produce olefins. The reaction proceeds smoothly under mild conditions to give fair to excellent yields of olefins and, indeed, this synthesis is a very useful supplement to the well known "Wittig" reaction.[1] The structures of the olefins were in every case deduced from their physical properties, infrared spectra and, where appropriate, by analysis.



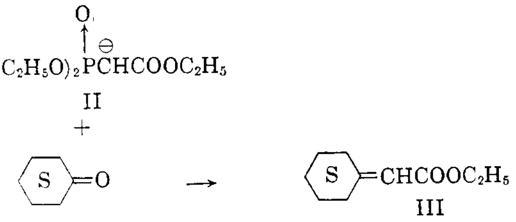
$$(RO)_2\overset{\overset{O}{\downarrow\ominus}}{P}C\begin{smallmatrix}R'\\R''\end{smallmatrix} + R_2'''C{=}O \longrightarrow R_2'''C{=}C\begin{smallmatrix}R'\\R''\end{smallmatrix} + (RO)_2\overset{\overset{O}{\uparrow\ominus}}{P}O$$

The phosphonate anions have in many instances a number of advantages over the triarylphosphoranes or "Wittig" reagents. They are in most cases much less expensive and they react with a wider variety of ketones and aldehydes, usually under much milder conditions. The reaction, for example, of triphenylphenacylidenephosphorane with benzaldehyde has been carried out by refluxing the reagents in tetrahydrofuran for thirty hours.[2] The analogous reaction using diethyl phenacylphosphonate anion (I) was exothermic at room temperature and gave comparable yields of olefin after immediate workup.



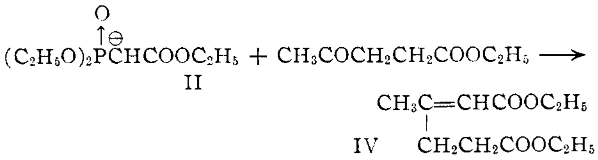
$$\underset{\text{I}}{(C_2H_5O)_2\overset{\overset{O}{\uparrow\ominus}}{P}CHCOC_6H_5} + C_6H_5CHO \longrightarrow C_6H_5CH{=}CHCOC_6H_5$$

Also, whereas triphenylcarbethoxymethylidenephosphorane reacts with benzaldehyde it fails to react with cyclohexanone in a normal manner.[3,4] Carbethoxymethylphosphonate anion (II) on the other hand, reacted exothermically with cyclohexanone to give the olefin III in good yield.



$$\underset{\text{II}}{(C_2H_5O)_2\overset{\overset{O}{\uparrow\ominus}}{P}CHCOOC_2H_5} + \text{S}{=}O \longrightarrow \underset{\text{III}}{\text{S}{=}CHCOOC_2H_5}$$

Unlike the triarylphosphoranes which give undesirable side products with keto esters,[5] the phosphonate anions react in a normal manner without reverse addition.



$$\underset{\text{II}}{(C_2H_5O)_2\overset{\overset{O}{\uparrow\ominus}}{P}CHCOOC_2H_5} + CH_3COCH_2CH_2COOC_2H_5 \longrightarrow \underset{\text{IV}}{\begin{matrix}CH_3C{=}CHCOOC_2H_5\\ |\\ CH_2CH_2COOC_2H_5\end{matrix}}$$

Horner and co-workers[6] recently have reported the preparation of olefins from phosphine oxides and aldehydes. The conditions for the reaction were relatively rigorous, requiring the use of refluxing toluene over a period of ten to twelve hours in the presence of potassium *t*-butoxide. These workers also reported that diethyl benzylphosphonate (V) reacted with benzaldehyde under comparable conditions to give stilbene. Obviously, only the most stable ketones or aldehydes could be used under these conditions. The use of a preformed phosphonate anion, on the other hand, allows all but the most hindered ketones to be used with equal ease.

A convenient method for preparing the anion consists of adding the phosphonate at room temperature to a slurry of sodium hydride in 1,2-dimethoxyethane. Elevated temperatures were detrimental, due to the facile self-condensation of the anion. Indeed, simple alkyl phosphate anions which did not contain an activating group could not be prepared, for the anions once formed were unstable at the elevated temperatures needed for

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(1) For an excellent review of the "Wittig" reagent see U. Schöllkopf, *Angew. Chem.*, **71**, 260 (1959).

(2) F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 41 (1957).

(3) G. Wittig and W. Haag, *Chem. Ber.*, **88**, 1654 (1955).

(4) M. Vilkas and N. A. Abraham, *Compt. rend.*, **246**, 1434 (1958).

(5) F. Bohlmann and E. Inhoffen, *Chem. Ber.*, **89**, 1276 (1956).

(6) L. Horner, H. Hoffmann, H. G. Wippel and G. Klahre, *ibid.*, **92**, 2499 (1959).