and the organic material was extracted with ether, dried, and distilled. This isomerization yielded some angelic acid but principally tiglic acid: b.p. 195–200°; m.p. 62–64° (lit., b.p. 198.5°[22]; m.p. 63.5–64.0°[10]).

trans-2-Butene-2-d. Tiglic acid-3-*d* was converted to the alkene by the method of Young, Dillon, and Lucas.[10] The tiglic acid hydriodide intermediate melted at 86–87.5° (lit.,[10] 86.2–86.3°). Treatment of the hydriodide with aqueous sodium carbonate at 75° yielded *trans*-2-butene-2-*d* in 67% yield. The product was at least 99.5% pure according to chromatographic analysis. The major contaminant was a trace of *cis*-2-butene-2-*d*.

RIVERSIDE, CALIF.

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[22] R. Fittig and H. Kopp, *Ann.*, **195**, 81 (1879).

[CONTRIBUTION FROM THE MONSANTO CHEMICAL CO., PLASTICS DIVISION]

Mechanism of the Michaelis-Arbuzov Reaction: Olefin Formation

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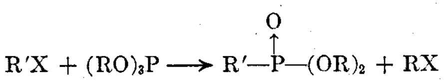
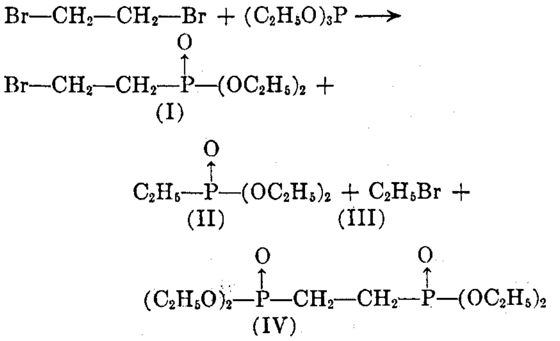
Support is given for the mechanism of the Michaelis-Arbuzov reaction in terms of the formation of a quasiphosphonium salt intermediate. The production of olefin and dialkyl phosphonate, $(RO)_2\overset{O}{\overset{\uparrow}{P}}—H$, is shown to be a general phenomenon when an *alpha*-haloalkane which has an activating group on the *beta* carbon is treated with a trialkyl phosphite. The formation of these products is explained in terms of an intramolecular *beta*-elimination involving the quasiphosphonium salt intermediate.

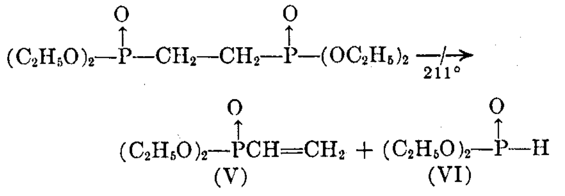
Introduction. During the preparation of diethyl β-bromoethylphosphonate (I) by the Michaelis-Arbuzov Reaction (1) using triethyl phosphite and 1,2-dibromoethane (2), it was found through the use of infrared spectroscopy and vapor phase chromatography that diethyl vinylphosphonate (V) and diethyl phosphonate (VI) are formed. In addition, diethyl β-bromoethylphosphonate (I), diethyl ethylphosphonate (II), ethyl bromide (III), and tetraethyl ethylenediphosphonate (IV) are found as reported previously by Ford-Moore and Williams[1a] and Kosolapoff.[1b] The most obvious explanation for the formation of these products is that the tetraethyl ethylenediphosphonate (IV) decomposes under the conditions of the reaction. This decomposition, however, has been shown not to take place. The diphosphonate (IV) is stable at 211° over a period of 5 hr., and the initial reaction was run at 150° to 170°.



$$R'X + (RO)_3P \longrightarrow R'—\overset{O}{\overset{\uparrow}{P}}—(OR)_2 + RX \qquad (1)$$

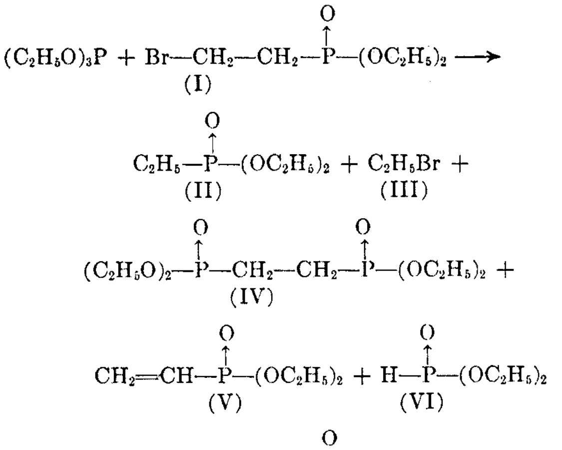


$$Br—CH_2—CH_2—Br + (C_2H_5O)_3P \longrightarrow \underset{(I)}{Br—CH_2—CH_2—\overset{O}{\overset{\uparrow}{P}}—(OC_2H_5)_2} + \underset{(II)}{C_2H_5—\overset{O}{\overset{\uparrow}{P}}—(OC_2H_5)_2} + \underset{(III)}{C_2H_5Br} + \underset{(IV)}{(C_2H_5O)_2—\overset{O}{\overset{\uparrow}{P}}—CH_2—CH_2—\overset{O}{\overset{\uparrow}{P}}—(OC_2H_5)_2} \qquad (2)$$

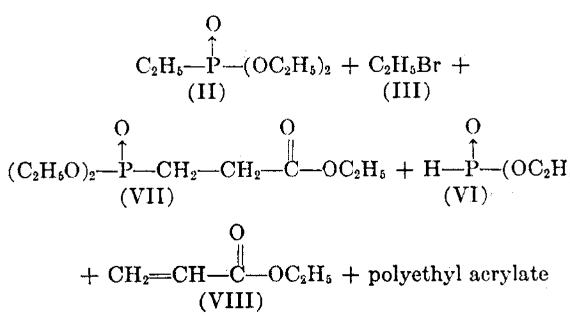


$$(C_2H_5O)_2—\overset{O}{\overset{\uparrow}{P}}—CH_2—CH_2—\overset{O}{\overset{\uparrow}{P}}—(OC_2H_5)_2 \underset{211°}{\not\longrightarrow} \underset{(V)}{(C_2H_5O)_2—\overset{O}{\overset{\uparrow}{P}}CH{=}CH_2} + \underset{(VI)}{(C_2H_5O)_2—\overset{O}{\overset{\uparrow}{P}}—H} \qquad (3)$$

The following reactions were run to determine the generality of this reaction as an olefin-forming



$$(C_2H_5O)_3P + \underset{(I)}{Br—CH_2—CH_2—\overset{O}{\overset{\uparrow}{P}}—(OC_2H_5)_2} \longrightarrow \underset{(II)}{C_2H_5—\overset{O}{\overset{\uparrow}{P}}—(OC_2H_5)_2} + \underset{(III)}{C_2H_5Br} + \underset{(IV)}{(C_2H_5O)_2—\overset{O}{\overset{\uparrow}{P}}—CH_2—CH_2—\overset{O}{\overset{\uparrow}{P}}—(OC_2H_5)_2} + \underset{(V)}{CH_2{=}CH—\overset{O}{\overset{\uparrow}{P}}—(OC_2H_5)_2} + \underset{(VI)}{H—\overset{O}{\overset{\uparrow}{P}}—(OC_2H_5)_2} \qquad (4)$$



$$(C_2H_5O)_3P + Br—CH_2—CH_2—\overset{O}{\overset{\|}{C}}—OC_2H_5 \longrightarrow \underset{(II)}{C_2H_5—\overset{O}{\overset{\uparrow}{P}}—(OC_2H_5)_2} + \underset{(III)}{C_2H_5Br} + \underset{(VII)}{(C_2H_5O)_2—\overset{O}{\overset{\uparrow}{P}}—CH_2—CH_2—\overset{O}{\overset{\|}{C}}—OC_2H_5} + \underset{(VI)}{H—\overset{O}{\overset{\uparrow}{P}}—(OC_2H_5)_2} + \underset{(VIII)}{CH_2{=}CH—\overset{O}{\overset{\|}{C}}—OC_2H_5} + \text{polyethyl acrylate} \qquad (5)$$

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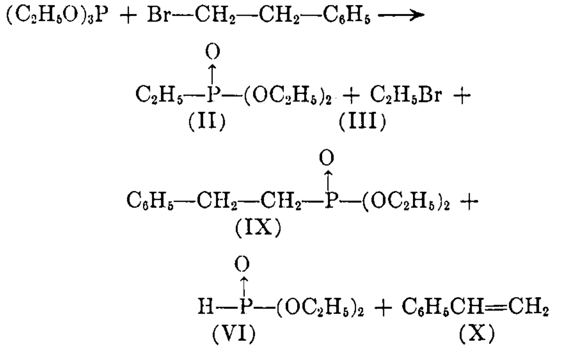
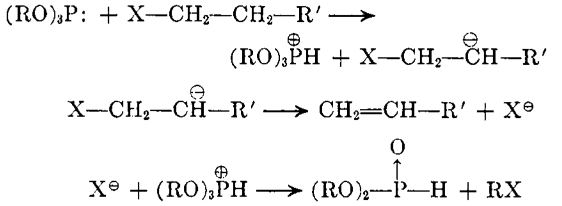
[1] (a) A. H. Ford-Moore and J. W. Williams, *J. Chem. Soc.*, 1467 (1945). (b) G. M. Kosolapoff, *J. Am. Chem. Soc.*, **66**, 109 (1944).



$$(C_2H_5O)_3P + Br{-}CH_2{-}CH_2{-}C_6H_5 \longrightarrow \underset{(II)}{C_2H_5{-}\overset{\overset{O}{\uparrow}}{P}{-}(OC_2H_5)_2} + \underset{(III)}{C_2H_5Br} + \underset{(IX)}{C_6H_5{-}CH_2{-}CH_2{-}\overset{\overset{O}{\uparrow}}{P}{-}(OC_2H_5)_2} + \underset{(VI)}{H{-}\overset{\overset{O}{\uparrow}}{P}{-}(OC_2H_5)_2} + \underset{(X)}{C_6H_5CH{=}CH_2} \quad (6)$$

elimination reaction. In each case the products were as written. The major products were the expected Michaelis-Arbuzov products with the olefin and dialkyl phosphonate appearing to be products of a less favorable side reaction. Reaction (5) has been reported previously by McConnell and Coover,[2a] but the only products mentioned were III and VII. Likewise, Abramov and Pall[2b] do not report VI and VIII as products of this reaction. A further search of the literature yielded several references[3] to Michaelis-Arbuzov reactions involving α-haloalkanes containing an activating group on the β-carbon. These authors report olefin, dialkyl phosphonate, or both such products.

Discussion. The formation of olefin and dialkyl phosphonate can be explained through two mechanisms. The first of these mechanisms involves an ordinary base-catalyzed β-elimination with the trialkyl phosphite functioning as the base. Step



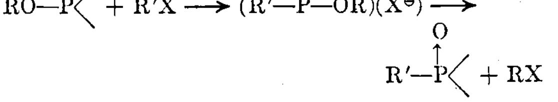
$$(RO)_3P\colon + X{-}CH_2{-}CH_2{-}R' \longrightarrow (RO)_3\overset{\oplus}{P}H + X{-}CH_2{-}\overset{\ominus}{C}H{-}R' \quad (1)$$

$$X{-}CH_2{-}\overset{\ominus}{C}H{-}R' \longrightarrow CH_2{=}CH{-}R' + X^{\ominus} \quad (2)$$

$$X^{\ominus} + (RO)_3\overset{\oplus}{P}H \longrightarrow (RO)_2{-}\overset{\overset{O}{\uparrow}}{P}{-}H + RX \quad (3)$$

(3) involves nucleophilic attack by halide ion on the alkyl carbon which is consistent with the last step of the Michaelis-Arbuzov reaction as pictured below. This mechanism, however, is unlikely in view of the relative weakness of trialkyl phosphites as bases compared with the bases usually used in β-eliminations, the high temperatures needed to make this reaction go and the well known nucleophilicity of phosphites.

Before discussing the second mechanism, a brief but pertinent review of the mechanism of the Michaelis-Arbuzov reaction must be given. The reaction was discovered first by Michaelis and Kähne[4] and was explored rather thoroughly later by Arbuzov.[5] These authors proposed a mechanism (4) which involves an addition reaction to form a quasiphosphonium intermediate which subsequently decomposes into the products. Myers, Preis, and Jensen[6] present the low reactivity of cyclohexyl tosylate with triethyl phosphite as being in accord with the low reactivity of cyclohexyl halides in SN_2 reactions and thus substantiating the initial stage of the Michaelis-Arbuzov reaction as an SN_2 displacement. Although Michaelis and Kähne[4] isolated an intermediate from triphenyl phosphite and methyl iodide which had saltlike properties, Abramov and Pekhman[7a] and Abramov and Karp[7b,c] obtained sirups from trialkyl phosphites and α-,β-dihaloalkyl ethers. Smith and Burger[7d] conclude that no quasiphosphonium compound is involved when bulky secondary alkyl halides are used. Arbuzov and Sazonova[8a] have recently isolated several more of these intermediates using triaryl phosphites and alkyl iodides. These compounds are crystalline salts. Similarly, Razumov and Bankovskaya[8b] report the isolation of saltlike intermediates from the reaction between alkyl phosphinites, $R_2{-}P{-}OR'$, and alkyl halides, Dimroth and Nurrenback[8c] report the isolation of several quasiphosphonium salts from the reaction of carbonium ions and trialkyl phosphites. Physico chemical evidence for the existence of these intermediates is presented by Arbuzov and Fuzhenkova.[9a,b]



$$RO{-}P\Big\langle + R'X \longrightarrow (R'{-}\overset{\oplus}{P}{-}OR)(X^{\ominus}) \longrightarrow R'{-}\overset{\overset{O}{\uparrow}}{P}\Big\langle + RX \quad (4)$$

The over-all mechanism of the Michaelis-Arbuzov reaction has been described by Jacobsen, Harvey,

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(2) (a) R. L. McConnell and H. W. Coover, *J. Am. Chem. Soc.*, **78**, 4453 (1956). (b) V. S. Abramov and S. Pall, *Trudy Kazan, Khim. Teknol. Inst. im S. M. Kirova*, **23**, 105 (1957); *Chem. Abstr.*, **52**, 9949d (1958).

(3) (a) A. N. Podovik and N. P. Denisova, *Sbornik Statei Obshchei Khim. Akad. Nauk S.S.S.R.*, *1*, 388 (1953); *Chem. Abstr.*, **49**, 8386 (1955). (b) B. A. Arbuzov and B. P. Lugovkin, *Zhur. Obshchei Khim.*, **21**, 99 (1951); *Chem. Abstr.*, **45**, 7002 (1951). (c) V. S. Abramov and N. A. Ilina, *Zhur. Obshchei Khim.*, **26**, 2014 (1956); *Chem. Abstr.*, **51**, 1822 (1957). (d) G. Kamai and V. A. Kukhtin, *Trudy Kazan. Khim. Tekhnol. Inst. im. S. M. Kirova*, No. 21, 147 (1956); *Chem. Abstr.*, **51**, 11983 (1957). (e) V. S. Abramov and N. A. Ilvina, *J. Gen. Chem., U.S.S.R.*, **26**, 2245 (1956).

(4) A. Michaelis and R. Kähne, *Ber.*, **31**, 1048 (1898).

(5) A. E. Arbuzov, *J. Russ. Phys. Chem. Soc.*, **38**, 687 (1906).

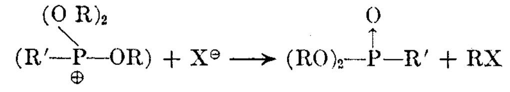
(6) T. C. Myers, S. Preis, and E. V. Jensen, *J. Am. Chem. Soc.*, **76**, 4172 (1954).

(7) V. S. Abramov and A. P. Pekhman, *J. Gen. Chem., U.S.S.R.*, **26**, #1, 171 (1956). (b) V. S. Abramov and G. A. Karp, *Doklady Akad. Nauk S.S.S.R.*, **91**, 1095 (1953); *Chem. Abstr.*, **48**, 9906g (1954). (c) V. S. Abramov and G. A. Karp, *J. Gen. Chem.*, **24**, 1823 (1954). (d) B. E. Smith and A. Burger, *J. Am. Chem. Soc.*, **75**, 5891 (1955).

(8) (a) A. E. Arbuzov and N. N. Sazonova, *Doklady Akad. Nauk S.S.S.R.*, **115**, 1119 (1957); *Chem. Abstr.*, **52**, 6239f (1958). (b) A. I. Razumov and N. N. Bankovskaya, *Doklady Akad. Nauk S.S.S.R.*, **116**, 2411 (1957); *Chem. Abstr.*, **52**, 6164i (1958). (c) K. Dimroth and A. Nurrenback, *Angew. Chem.*, **70**, 26 (1958).

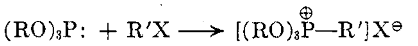
(9) (a) B. A. Arbuzov and A. V. Fuzhenkova, *Doklady Akad. Nauk. S.S.S.R.*, **113**, 1269 (1957). (b) B. A. Arbuzov and A. V. Fuzhenkova, *Doklady Akad. Nauk S.S.S.R.*, **114**, 89 (1957).

and Jensen[10a] and by Kharasch and Bengelsdorf[10b] and pictured by Saunders[11] as a displacement of halogen by phosphite to form a quasiphosphonium compound which, on attack by halide ion, eliminates RX to form the phosphonate (5). That the

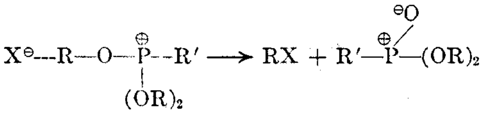


$$(R'-\underset{\oplus}{\overset{(OR)_2}{P}}-OR) + X^{\ominus} \longrightarrow (RO)_2-\overset{O}{\overset{\uparrow}{P}}-R' + RX \quad (5)$$

final stage of the reaction involves nucleophilic attack by halide ion on the alkyl carbon of the ester has been demonstrated experimentally. First, Landauer and Rydon[12] isolated the intermediate from methyl iodide and triphenyl phosphite and treated this material with optically active 2-octanol. The 2-iodooctane which was obtained as a product was inverted showing clearly that a bimolecular nucleophilic substitution had taken place, presumably preceded by a rapid ester interchange between the octanol and the phosphonium salt. Attacking the problem in the reverse manner, Gerrard and Jeacocke[13] reacted trioctyl phosphite containing 2-octyl residues from optically active 2-octanol with bromine and likewise obtained the inverted 2-bromooctane. On the basis of the above experimental evidence, the mechanism of the Michaelis-Arbuzov reaction can be pictured as follows:

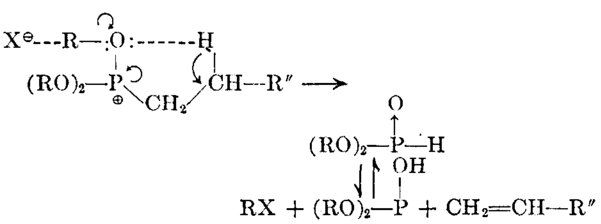


$$(RO)_3P: + R'X \longrightarrow [(RO)_3\overset{\oplus}{P}-R']X^{\ominus} \quad (a)$$



$$X^{\ominus}\text{---}R-O-\underset{(OR)_2}{\overset{\oplus}{P}}\text{--}R' \longrightarrow RX + R'-\overset{\ominus O}{\overset{\oplus}{P}}-(OR)_2 \quad (b)$$

In the case under discussion where the alkyl halide has an activating group on the β-carbon atom, the quasiphosphonium intermediate can be pictured as going through a less favorable breakdown involving a cyclic transition state which leads to an intramolecular β-elimination similar to that proposed for ester pyrolysis and Chugaev eliminations.[14]



The formation of styrene during the thermal decomposition of quarternary phosphonium hydroxides and ethoxides which contained β-phenethyl groups has been shown by Fenton and Ingold[15] and Hey and Ingold.[16] Further, the hydrogen bonding ability of the phosphoryl group has been shown clearly by Kosolapoff and McCullough[17] and Arbuzov and Razumova.[18] Baumgarten and Setterquist[19] have demonstrated recently that alkyl phosphates, like carboxylic acid esters, undergo pyrolysis to give an olefin and the acid.

To test the formation of olefin by means of an intramolecular β-elimination through the quasiphosphonium salt, triphenoxy-β-phenethylphosphonium iodide, $(C_6H_5O)_3\underset{I_{\ominus}}{P_{\oplus}}\text{-}CH_2\text{-}CH_2\text{-}C_6H_5$ (XI), was prepared and heated to decomposition at 210–222° and 0.15 mm. Vapor phase chromatographic analysis of the volatile products showed the presence of styrene and iodobenzene. The solid residue was identified as diphenyl β-phenethylphosphonate, $(C_6H_5O)_2-\overset{O}{\overset{\uparrow}{P}}-CH_2-CH_2-C_6H_5$ (XII), the major product and the usual Michaelis-Arbuzov product. To show that the styrene was not produced as a consequence of the pyrolysis of the ester (XII), the diphenyl β-phenethylphosphonate was heated at 240° and 0.15 mm. for 2 hr. without decomposition. The phosphonate finally decomposed at 390°. In support of the experimental evidence for the olefin formation from the quasiphosphonium salts, the models of these compounds show that the hydrogen atoms which are *alpha* to the activating group help to form a perfect five-membered ring with one of the oxygens that is attached to the phosphorus atom. In fact, these two atoms virtually touch each other.

With the positive charge on the phosphorus, the activated β-hydrogens and the close proximity of the hydrogen and oxygen in a five-membered ring, one might expect olefin formation to be more predominant. Since there are three alkoxyl groups attached to the phosphorus, the chances of the incoming negative ion attacking the same alkoxyl group which forms the ring is made even less favorable by the fact that the other alkyoxyl or aryloxyl groups are thrown outward into space where they are more susceptible to attack.

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(10) (a) H. I. Jacobsen, R. G. Harvey, and E. V. Jensen, *J. Am. Chem. Soc.*, **77**, 6064 (1955). (b) M. S. Kharasch and I. S. Bengelsdorf, *J. Org. Chem.*, **20**, 1356 (1955).

(11) B. C. Saunders, *Some Aspects of the Chemistry of and Toxic Action of Organic Compounds Containing Phosphorus and Fluorine*, Cambridge University Press, Cambridge, 1957, p. 95.

(12) S. R. Landauer and H. N. Rydon, *Chem. & Ind. (London)*, 313 (1951).

(13) W. Gerrard and G. J. Jeacocke, *J. Chem. Soc.*, 3647 (1954).

(14) For a complete discussion of Intramolecular Eliminations see M. S. Newman, *Steric Effects in Organic Chemistry*, New York, John Wiley & Sons, Inc., 1956, pp. 305–14.

(15) G. W. Fenton and C. K. Ingold, *J. Chem. Soc.*, 2342 (1929).

(16) L. Hey and C. K. Ingold, *J. Chem. Soc.*, 531 (1933).

(17) G. M. Kosolapoff and J. M. McCullough, *J. Am. Chem. Soc.*, **73**, 5392 (1951).

(18) A. E. Arbuzov and N. A. Razumova, *Doklady Akad. Nauk S.S.S.R.*, **97**, 445 (1954); *Chem. Abstr.*, **49**, 9538 (1955).

(19) H. E. Baumgarten and R. A. Setterquist, *J. Am. Chem. Soc.*, **79**, 2605 (1957).

Although it has no bearing on the mechanism of the Michaelis-Arbuzov reaction or olefin formation, it should be mentioned here that a large portion of the products of this reaction is a nondistillable sirup. This material is always acidic, is water soluble, and, presumably, is easily hydrolyzed. All evidence to date indicates that these materials are polypyrophosphonates which contain (P—O—P) linkages formed by olefin and alohol elimination during the long heating periods of the reaction.

EXPERIMENTAL

The β-bromoethylbenzene and the ethyl β-bromopropionate were obtained from Matheson, Coleman, and Bell, the 1,2-dibromoethane from Eastman Kodak Co., and the triethyl phosphite and diethyl phosphonate from Virginia-Carolina Chemical Corp.

β-Iodoethylbenzene. A mixture of 92.5 g. (0.5 m.) of β-bromoethylbenzene, n_D^{25} 1.5543, 74.9 g. (0.5 m.) of sodium iodide and 50 ml. of acetone was refluxed on a steam bath overnight. The resultant red liquid was separated by filtration and the solvent was stripped. Distillation of the heavy oily residue gave 92.0 g. (79.3%) of material, b.p. 71°/1.1 mm., n_D^{25} 1.5945.

Diphenyl β-phenethylphosphonate. A 5.0 g. sample (0.009 m.) of triphenoxy-β-phenethylphosphonium iodide was allowed to stand overnight in excess 10% aqueous NaOH. A white solid formed. The solid was filtered and recrystallized from *n*-hexane to give 2.5 g. (65.2%) of fine, white needles, m.p. 75–76°.

Anal. Calcd. for $C_{20}H_{19}PO_3$: C, 71.0; H, 5.62; P, 9.17. Found: C, 71.13; H, 5.44; P, 9.38.

The infrared spectrum of this material was recorded as a melt on NaCl plates.

Triphenoxy-β-phenethylphosphonium iodide. A mixture of 73.0 g. (0.3 m.) of freshly prepared β-phenethyl iodide and 146.2 g. (0.5 m.) of triphenylphosphite was heated at 128° for 5 days. The reaction mixture was protected from moisture by "Drierite" tubes. When the resultant, dark red-brown mixture was mixed with absolute ether, a dark solid fraction precipitated. The ether was decanted and a fresh portion was added and the solid became more firm. The material was mixed with an absolute ether, C.P. acetone solution, in several portions until the color became canary yellow. Then the solid was extracted in a Soxhlet extractor with a mixture of 10 ml. of C.P. acetone and 250 ml. of absolute ether until the solid was almost cream color, and the solvent no longer became yellow. Removal of the solvent and drying under vacuum left 28.3 g. of material which melted in a sealed tube at 154–157°. The solid with silver nitrate gave an immediate precipitate which was insoluble in dilute nitric acid.

Anal. Calcd. for $C_{26}H_{24}PO_3I$: C, 57.57; H, 4.43; P, 5.72; I, 23.42. Found: C, 56.86; H, 4.63; P, 5.60; I, 23.46

Reaction of triethyl phosphite with 1,2-dibromoethane. Seven hundred fifty-two g., (4.0 m.) of 1,2-dibromoethane was heated to reflux at 131°. Then 183.0 g. (1.1 m.) of freshly distilled triethyl phosphite was added dropwise under nitrogen pressure over a period of 1.5 hr. During the addition of the phosphite and subsequent heating of the mixture to a final temperature of 145° over a period of 3.5 hr., 110.8 g. (1.08 m.) of ethyl bromide was distilled from the reaction mixture through an 8-in. Vigreux and was collected in an attached cold trap. The reaction mixture was fractionated through a 15-in. Vigreux column after removal of 509.6 g. of unreacted dibromide at atmospheric pressure.

The first low boiling fractions of 33.7 g. consisted of a mixture of diethyl vinylphosphonate, diethyl phosphonate, and diethyl ethylphosphonate as shown by infrared analysis and vapor phase chromatography. Subsequently, 127.0 g. of diethyl β-bromoethylphosphonate, b.p. 90°/1 mm., n_D^{25} 1.4564 was obtained. Seven and seven-tenths grams of an intermediate fraction, n_D^{25} 1.4473, which contained some tetraethyl ethylenediphosphonate was followed by the sudden evolution of 13.4 g. of material which dropped the head temperature to 30°/2 mm. and had n_D^{25} 1.4250 which along with its infrared spectrum showed it to be pure diethyl vinylphosphonate.

Reaction of triethyl phosphite with diethyl β-bromoethylphosphonate. Diethyl β-bromoethylphosphonate, 50.7 g. (0.17 m.), was heated to 157° and 35.3 g. (0.21 m.) of distilled triethyl phosphite was added dropwise over a 3-hr. period. During the heating over a total of 6 hr., 17.9 g. (0.16 m.) of ethyl bromide distilled. The final reaction temperature was 198°. Vacuum distillation of the pale yellow, nonviscous mixture yielded 28.8 g. of a low boiling mixture of approximately 64.5% diethyl phosphonate, 25.8% diethyl vinylphosphonate, 6.9% diethyl ethylphosphonate, and 2.9% of an unknown as determined by infrared and vapor phase chromatographic analyses. A higher boiling fraction consisted of 16.2 g. of tetraethyl ethylenediphosphonate, b.p. 151–157°/1 mm., n_D^{25} 1.4397.

Reaction of ethyl β-bromopropionate with triethyl phosphite. Ninety g. (0.54 m.) of distilled triethyl phosphite was added dropwise over a period of 3 hr. to 100.0 g. (0.55 m.) ethyl β-bromopropionate at 155°. The initial addition of the phosphite caused the temperature to drop to 137° which temperature held throughout the reaction. The reaction mixture was heated for 5 hr. after the complete addition of the phosphite and 48.4 g. (0.44 m.) of ethyl bromide was distilled during the heating.

Vacuum distillation of the mixture yielded 21.9 g. of material, b.p. 66–86°/4–7 mm., which infrared showed to be diethyl phosphonate and probably diethyl ethylphosphonate, 80.0 g. of ethyl 3-diethylphosphonopropionate, b.p. 114–115°/2 mm., n_D^{25} 1.4301 and 24.1 g. of polyethylacrylate, n_D^{25} 1.4662. The distillation cold trap yielded 6.84 g. of ethyl acrylate, n_D^{25} 1.3975. The acrylate monomer and polymer were identified by their infrared spectra.

Reaction of triethyl phosphite with β-bromoethylbenzene. One hundred g. (0.54 m.) of β-bromoethylbenzene was heated to 165°, then 90.9 g. (0.54 m.) of distilled triethyl phosphite was added dropwise. The temperature rose slightly and maintained itself at 166–155° when the heat was lowered. The heat was maintained for approximately 20 hr. During this period, 33.6 g. (0.31 m.) of ethyl bromide distilled from the mixture. The reaction mixture was vacuum distilled through an 8-in. Vigreux.

The first fraction of 43.9 g. was shown by infrared to contain diethyl phosphonate, diethyl ethylphosphonate, and unreacted β-bromoethylbenzene. The second fraction was mostly diethyl ethylphosphonate, 3.9 g., and the third fraction consisted of 68.8 g. of diethyl β-phenethylphosphonate, b.p. 144–147°/2.3 mm., n_D^{25} 1.4925. The residue in the pot was dissolved in benzene and 3.2 g. of polystyrene was precipitated in methanol. The cold trap contained 10.4 g. of material which decolorized bromine in carbon tetrachloride and was shown by its infrared spectrum to be mostly styrene.

Test for thermal stability of tetraethyl ethylenediphosphonate. A sample of tetraethyl ethylenediphosphonate was heated at 211° for 5.5 hr. The material was pumped down and heated. No low boiling materials were distilled at 70°/2 mm.

Pyrolysis of diphenyl β-phenethylphosphonate. An 8.1 g. sample of diphenyl β-phenethylphosphonate was heated for 2 hr. at 240°/0.15 mm. with no decomposition. This material was heated again for 4.5 hr. at 250–305°/5 mm. still without decomposition. The material was recovered, recrystallized, and the melting point checked. Then the sample was heated at atmospheric pressure up to 390° to give a trace of water and a viscous, brown residue which was strongly acidic. The odor of styrene was strong in the attached dry ice trap, but no styrene was isolated. The infrared spectrum of the viscous, brown residue showed polystyrene to be absent.

Pyrolysis of triphenoxy-β-phenethylphosphonium iodide. A 10.0 g. sample of triphenoxy-β-phenethylphosphonium iodide was dried overnight under vacuum and then was heated at 210–220°/0.15 mm. over a period of 4 hr. The dry ice traps which were attached to the pyrolysis apparatus contained a small amount of liquid which smelled of iodobenzene. The infrared spectrum of this material confirmed the presence of iodobenzene and hinted at the presence of styrene. Vapor phase chromatographic analysis of this material showed the presence of a small amount of styrene.

The dark solid residue in the pyrolysis tube was recrystallized from *n*-hexane as long white needles, m.p. 75.1–75.6°. A mixed melting point with authenticated diphenyl β-phenethylphosphonate of m.p. 75.0–75.3° was 75.0–75.6°.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF MOREHOUSE COLLEGE AND THE ATLANTA UNIVERSITY]

Reactions of Methyl and Ethoxy Free Radicals in Chlorohydrocarbons: A Comparative Study of the Use of Diacetyl Peroxide and Diethylperoxydicarbonate as Agents for Linking Alpha Carbon to Alpha Carbon in Some Chloro-Substituted Aralkyls[1]

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Diacetyl peroxide reacts with approximately equal facility with the chloro-substituted aralkyls, 3,4-dichlorotoluene, 2,6-dichlorotoluene, and α,α-dichlorotoluene (benzal chloride) to give the corresponding chloro-substituted bibenzyls derived from the dimerizations at the alpha positions. Diethyl peroxydicarbonate reacts with 3,4-dichlorotoluene in the same manner as does diacetyl peroxide, producing 1,2-bis(3,4-dichlorophenyl)ethane (3,4,3′,4′-tetrachlorobibenzyl), and with essentially equal yield. Diethyl peroxydicarbonate gives a poorer yield of the same dimer, 2,6,2′,6′-tetrachlorobibenzyl, as obtained from the reaction of diacetyl peroxide with 2,6-dichlorotoluene. Practically none of the dimer, tetrachlorotolane, obtained from the reaction of benzal chloride with diacetyl peroxide, is produced when diethyl peroxydicarbonate is used as the linking agent. Diacetyl peroxide links *p*-isopropylbenzal chloride unsymmetrically with itself to produce 1,1-dichloro-1-*p*-isopropylphenyl-2-methyl-2-(ω,ω-dichloro-*p*-tolyl)propane exclusively, while diethylperoxydicarbonate links *p*-isopropylbenzal chloride symmetrically with itself to produce exclusively 2,3-di-(ω,ω-dichloro-*p*-tolyl)-2,3-dimethylbutane.

Of the several possible modes of reaction available to free radicals generated in solution, the one taken by a given free radical depends only in part upon the nature of the free radical itself. External factors of importance are temperature and the nature of the coreactant. It must be kept in mind that there is competition between solvent and parent substance, despite its low concentration in dilute solution, as coreactants for the free radical. Several factors determining the relative effectiveness of the solvent molecule in such competition have been disclosed. The relative strengths of the bonds holding the univalent atoms in the solvent molecule, which strength largely determines the ease with which the bonds holding these univalent atoms succumb to cleavage by free radicals, has been termed the *energy factor.*[2] The nature and the positions of the substituents in the solvent molecule have a pronounced effect upon the ease with which said molecule yields an univalent atom to the cleaving action of *ethoxy free radicals*, but these factors seem to have little or no effect upon the analogous action of such molecule toward *methyl free radicals.* A previous paper[3] reports that hydrogen atoms are readily cleft from solvent molecules by methyl and by ethoxy free radicals when these hydrogens are attached to the same carbon atom with methyl and/or phenyl groups. The substitution of carbomethoxy groups for the methyl and/or phenyl groups produces no noticeable effect upon the tendency of the solvent to donate a hydrogen atom to *methyl* free radical but greatly reduces its tendency to yield hydrogen to the *ethoxy* free radical. This unusual effect of the carbomethoxy group upon the course of these free radical reactions has been termed the *repulsion factor.*[3] This paper reports a continuation of these studies. It attempts to show that the introduction of chlorine atoms into positions adjacent to the "preferred" seat of attack for the cleavage reactions of these free radicals has little or no effect on the percentage of cleavage exhibited by the *methyl* free radical and no effect whatever on the site of its cleavage attack. On the other hand, the immediate proximity of these chlorine atoms to the preferred seat of attack *decreases* the percentage

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(1) Presented in part before the Organic Division of the American Chemical Society at the 128th National Meeting, New York, September 1954.

(2) H. C. McBay and O. Tucker, *J. Org. Chem.*, **19**, 869 (1954).

(3) H. C. McBay, O. Tucker, and A. Milligan, *J. Org. Chem.*, **19**, 1003 (1954).