vacuo to give a white solid. Recrystallization of this solid from C_6H_6–C_6H_{12} (1:3) afforded 3.1 g (30.1%) of the diester **5**: mp 129–131 °C; ir[18] (KBr) ν 1620, 1592 (aromatic), 1260, 1238, 1205, 1150, 1115, 1027, 963, 937, 885, 862, 849, 815, 752, 739, 696, and 640 cm^{-1}; ^1H NMR ($DCCl_3$) δ 7.06–7.84 (m, 2 $C_{10}H_7$ and C_6H_5, 17 H), 8.05 (m, C_6H_5 2 H); ^{31}P NMR ($DCCl_3$ + pyridine) −11.34 ppm relative to 85% H_3PO_4; mass spectrum (70 eV) *m/e* 410 (M^+). Peak matching for $C_{26}H_{19}O_3P$: 410.107175. Found: 410.128523. The ester is insoluble in H_2O and was recovered unchanged after being stirred in 8 N HCl for 3 h.

Registry No.—**2** (R = C_6H_5), 824-72-6; **2** (R = c-C_6H_4), 1005-22-7; **2** (R = n-C_3H_7), 4708-04-7; **2** (R = 2-C_3H_7), 1498-46-0; **2** (R = $ClCH_2$), 1983-26-2; **2** (R = CH_3), 676-97-1; **4** (R = C_6H_5; Ar = p-$O_2NC_6H_4$), 57885-61-7; **4** (R = C_6H_5; Ar = 2-$C_{10}H_7$), 57885-62-8; **4** (R = c-C_6H_4; Ar = p-$O_2NC_6H_4$), 57885-63-9; **4** (R = n-C_3H_7, Ar = p-$O_2NC_6H_4$), 57885-64-0; **4** (R = n C_3H_7, Ar = 2-$C_{10}H_7$), 57885-65-1; **4** (R = C_6H_5; Ar = p-$O_2NC_6H_4$) free acid, 57072-35-2; **4** (R = 2-C_3H_7; Ar = p-$O_2NC_6H_4$), 57885-66-2; **4** (R = 2-C_3H_7; Ar = 2-$C_{10}H_7$), 57885-67-3; **4** (R = $ClCH_2$; Ar = p-$O_2NC_6H_4$), 57885-68-4; **4** (R = $ClCH_2$; Ar = 2-$C_{10}H_7$), 57885-69-5; **4** (R = CH_3; Ar = p-$O_2NC_6H_4$), 57885-70-8; **4** (R = CH_3; Ar = 2-$C_{10}H_7$), 57885-71-9; **5**, 57885-72-0; dimethylformamide, 68-12-2; p-nitrophenol, 100-02-7; 2-naphthol, 135-19-3.

References and Notes

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(2) (a) Research Associate in Chemistry, 1973–1975; (b) Research Associate in Biochemistry, 1974–1975.

(3) S. J. Kelly and L. G. Butler, *Biochem. Biophys. Res. Commun.*, **68**, 316 (1975).

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(10) For a brief discussion on the synthesis of phosphonates, see G. M. Kosolapoff, "Organophosphorus Compounds", Wiley, New York, N.Y., 1950, Chapter 7, and references cited therein. Diesters may also be prepared by a variety of methods analogous to the synthesis of phosphate triesters; see E. Cherbuliez, "Organic Phosphorus Compounds", Vol. 6, G. M. Kosolapoff and L. Maier, Ed., Wiley-Interscience, New York, N.Y., 1973, Chapter 15.

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(12) This value is in good agreement with those previously reported for the ^{31}P NMR of the pure liquid; see V. Mark et al., *Top. Phosphorus Chem.*, **5**, 227 (1967), and references cited therein.

(13) J. R. Van Wazer, C. F. Callis, J. N. Shoolery, and R. C. Jones, *J. Am. Chem. Soc.*, **78**, 5715 (1956).

(14) (a) Obtained in water; see M. L. Nielsen, J. V. Pustinger, Jr., and J. Strobel, *J. Chem. Eng. Data*, **9**, 167 (1964). (b) Obtained in water; see J. G. Riess, J. R. Van Wazer, and J. H. Letcher, *J. Phys. Chem.*, **71**, 1925 (1967).

(15) For a brief discussion on the effects of charge (generally negligible), electronegativity of other atoms, and configurational changes on the ^{31}P resonance of phosphorus moieties, see ref 12.

(16) The conversion of **6** to **10** in the absence of 2-$C_{10}H_7OH$ is necessitated by the appearance of only the two ^{31}P resonances, −1.0 and +1.0 ppm (sample C, Table III) after 10 min mixing. These same resonances are also present in the absence of both pyridine and 2-$C_{10}H_7OH$; see Table IV.

(17) The interaction of DMF and $POCl_3$ has been extensively investigated by nuclear magnetic resonance in the last decade. A few of the conclusions are (1) that the major cationic formylating specie has the tentative structure $(CH_3)_2NCHCl^+$ with the anion being either $^-O_2PCl_2$ or Cl^-; (2) extensive heteronuclear decoupling experiments on ^1H have shown that there is no P–OCH covalent structure to the intermediate cation. For more detailed discussion, see (a) G. J. Martin and S. Poignant, *J. Chem. Soc., Perkin Trans. 2*, 642 (1974); (b) S. Alummi et al., *ibid.*, 2070 (1972); (c) G. J. Martin and S. Poignant, *ibid.*, 1964 (1972); (d) G. J. Martin, S. Poignant, M. L. Filleux, and M. T. Quemeneur, *Tetrahedron Lett.*, 5061 (1970); (e) G. Martin and M. Martin, *Bull. Soc. Chim. Fr.*, 1637 (1963), and references cited therein.

(18) Owing to the complexity of the infrared spectra, detailed interpretations were not attempted.

A One-Step Synthesis of Epoxyphosphonates

Bleecker Springs and Paul Haake*

Department of Chemistry, Wesleyan University, Middletown, Connecticut 06457

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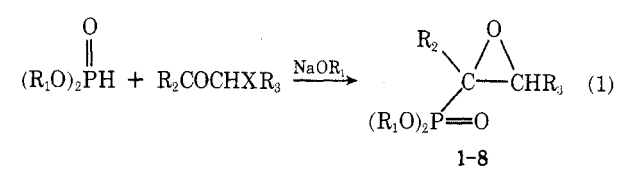
Owing to the recent interest in epoxyphosphonates generated by the newly discovered antibiotic fosfomycin, we have synthesized some epoxyphosphonates, $(R_1O)_2P(O)\overline{CR_2\text{–}O\text{–}CHR_3}$, by a facile one-step procedure. Our synthesis proceeds by the reaction of a stoichiometric amount of a dialkyl phosphonate, an α-halo ketone, and sodium alkoxide; the yields include (R_1, R_2, R_3, % yield) CH_3, CH_3, H, 84; C_2H_5, CH_3, H, 83; CH_3, $(CH_3)_3C$, H, 87. In addition, for the reaction with $R_1 = CH_3$, $R_2 = CH_3$, and $R_3 = H$, we have NMR evidence, a doublet at τ 8.5 (J_{PCCH} = 15 Hz), which indicates that the reaction proceeds via a phosphonate halohydrin intermediate (eq 6).

The novel structure of the newly discovered antibiotic fosfomycin [**1**, (−)-(1*R*,2*S*)-1,2-epoxypropylphosphonic acid] has generated interest in epoxyphosphonates.[1,2] Previous studies on epoxyphosphonates have been concerned primarily with either their potential as synthetic intermediates[3] or the mechanism of the reaction of dialkyl phosphonates, $(RO)_2P(O)H$, with α-halo ketones.[4] The discovery of fosfomycin and its mode of action as an analogue of phosphoenol pyruvate in its inhibition of the enzyme pyruval transferase has given epoxyphosphonates biochemical significance.[5]

We have synthesized epoxyphosphonates **2**–**8** by a facile, one-step procedure by the action of sodium alkoxide on a dialkyl phosphonate and an α-halo ketone (eq 1). In addition, we have NMR evidence concerning the mechanism of this reaction.



(1)

1–**8**

Experimental Section

We used the following instruments: Varian A-60 for NMR spectra, tetramethylsilane as internal standard; Perkin-Elmer 137 for infrared spectra; Hitachi RMU-6L for mass spectra. Analyses were determined by Spang Microanalytical Laboratory, Ann Arbor, Mich.

Materials. Chloroacetone and 2-chloro-4,4-dimethyl-3-pentanone were prepared by treating acetone and ethyl *tert*-butyl ketone, respectively, with sulfuryl chloride.[6,7] Chlorocyclohexanone and 1-chloro-3,3-dimethyl-2-butanone were prepared by the reaction

Table I. Yields of Epoxyphosphonates

Compd	R_1	R_2	R_3	Yield, %
1	H	H	CH_3	
2	CH_3	CH_3	H	84
3	C_2H_5	CH_3	H	83
4	$C_6H_5CH_2$	CH_3	H	48
5	CH_3	$(CH_3)_3C$	H	87
6	CH_3	$(CH_3)_3C$	CH_3	70
7	CH_3	CH_3	CH_3	53
8	CH_3	$(CH_2)_4$		33

of cyclohexanone and pinacolone, respectively, with Cl_2.[8,9] α-Chloroacetophenone and 3-bromo-2-butanone (Aldrich) were used as received. Ethyl *tert*-butyl ketone was prepared by chromic acid oxidation of 2,2-dimethyl-3-pentanol.[10] Dimethyl and diethyl phosphonate (Aldrich) were used as received for synthetic reactions; dimethyl phosphonate was distilled, bp 170–171 °C, for kinetic experiments.

Dimethyl 1,2-Epoxy-2-propylphosphonate (2). The following is illustrative for the synthesis of all epoxyphosphonates described below. A solution of sodium methoxide was prepared by dissolving 0.06 mol (1.37 g) of sodium in 25 ml of methanol. The sodium methoxide was then added dropwise over a period of 15 min to a mixture of 0.06 mol (5.55 g) of chloroacetone and 0.06 mol (6.60 g) of dimethyl phosphonate in 5 ml of methanol at room temperature. After stirring for 1 h the solution was filtered, distilled to remove methanol, and refiltered. Ether was then added to precipitate any remaining sodium chloride. The solution was filtered again and ether evaporated off. A short-path distillation gave **2**: bp 75–76 °C (0.7 mm); mol wt 166 by mass spectroscopy; ir (neat) 1260 (P=O), 1235 (epoxide), 1185 and 1035 ($POCH_3$), 855, 835, and 760 cm^{-1} (epoxide); NMR ($CDCl_3$) τ 8.52 (d, 3 H, J_{PCCH_3} = 11.3 Hz), 7.31 (t, 1, J_{HCH} = 5.0, J_{PCCH} = 5.0 Hz), 6.91 (t, 1, J_{HH} = 5.0, J_{PCCH} = 5.0 Hz), 6.21 (d, 6, J_{POCH} = 11.0 Hz).

Anal. Calcd for $C_5H_{11}O_4P$: C, 36.15; H, 6.69. Found: C, 35.74; H, 6.92.

Diethyl 1,2-epoxy-2-propylphosphonate (3): bp 69–72 °C (0.5 mm) [lit.[4] 75 °C (0.6 mm)]; mol wt 194 by mass spectroscopy; ir (neat) 1260 (P=O), 1225 (epoxide), 1170 and 1030 (POC_2H_5), 855, 800, and 750 cm^{-1} (epoxide); NMR ($CDCl_3$) τ 8.69 (d, 3, J_{PCCH_3} = 11.3 Hz), 8.54 (t, 6, $J_{H_2CCH_3}$ = 7 Hz), 7.29 and 6.90 (t, 1, J_{HH} = 5.0, J_{PCCH} = 5.0 Hz), 5.82 (qq, 4, $J_{H_3CCH_2}$ = 7.0, J_{POCH} = 7.0 Hz).

Dimethyl 1,2-epoxy-3,3-dimethyl-2-butylphosphonate (5) was made starting from pinacolone: bp 75–77 °C (0.75 mm); mol wt 208 by mass spectroscopy; ir (neat) 1260 (P=O), 1235 (epoxide), 1185 and 1050 ($POCH_3$), 870, 830, and 750 cm^{-1} (epoxide); NMR ($CDCl_3$) τ 8.91 [s, 9, $(CH_3)_3C$], 7.15 and 7.01 (t, 1, J_{HCH} = 5.0, J_{PCCH} = 5 Hz), 6.21 (d, 6, J_{POCH_3} = 10.5 Hz); NMR (neat) two triplets become a doublet at τ 7.09 (J_{HCH} = 5 Hz).

Anal. Calcd for $C_8H_{17}O_4P$: C, 46.16; H, 8.23. Found: C, 45.95; H, 8.14.

Dimethyl 2,3-epoxy-4,4-dimethyl-3-pentylphosphonate (6) was made from 2-chloro-4,4-dimethyl-3-pentanone: bp 75–77 °C (0.75 mm); mol wt 222 by mass spectroscopy; ir (neat) 1260 (P=O), 1220 (epoxide), 1185 and 1030 ($POCH_3$), 835, 810, and 755 cm^{-1} (epoxide); NMR ($CDCl_3$) τ 8.92 [s, 9, $(CH_3)_3C$], 8.49 (d, 3, J_{HCCH_3} = 5.5 Hz), 6.22 (d, 6, J_{POCH} = 10.5 Hz).

Anal. Calcd for $C_9H_{19}O_4P$: C, 48.66; H, 8.64. Found: C, 48.68; H, 9.06.

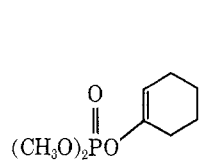
Compounds **4**, **7** and **8**, although new, were not verified by elemental analysis. **Dibenzyl 1,2-epoxy-2-propylphosphonate (4)** was prepared by the addition of sodium benzyloxide to dibenzyl phosphonate and chloroacetone in benzene. After filtration benzyl alcohol was removed by distillation. The pot residue containing **4** was passed through two silica gel columns for purification. The first column was eluted with benzene–chloroform–methanol (10:14:1) and the second column 15:15:1. Fractions with the appropriate NMR for the epoxide also have peaks in the NMR due to an impurity, probably $PhCH_2OH$. NMR ($CDCl_3$) τ 8.55 (d, 3, J_{PCCH_3} = 11.3 Hz), 7.40 and 6.93 (t, 1, J_{HCH} = 5.0, J_{PCCH} = 5.0 Hz, CH_2), 4.95 (d, 3, J_{POCH_2} = 8 Hz), 2.69 (s, 17, C_6H_5), 5.48 (s, 1.5, impurity). **Dimethyl 2,3-epoxy-2-butylphosphonate (7)** was made from 3-bromo-2-butanone: bp 59–62 °C (0.7 mm); ir (neat) 1260 (P=O), 1185 and 1030 ($POCH_3$), 855, 833, and 760 cm^{-1} (epoxide); NMR ($CDCl_3$) τ 8.65 (two doublets for cis and trans, 2, J = 5.5 Hz, $CHCH_3$), 8.55 (d, 3, J = 11.3 Hz, CH_3), 6.60 (qq, 1, J_{HH} = 5.5, J_{PCCH} = 5.5 Hz, $CHCH_3$), 6.23 [d, 7, J_{POCH} = 10.5 Hz, $P(OCH_3)_2$]; mass spectrum *m/e* 180. The analysis was low in carbon. **Dimethyl 1,2-epoxy-1-cyclohexylphosphonate (8)** was made from chlorocyclohexanone. The reaction mixture after distillation appeared by NMR to give a 50:50 mixture of the epoxyphosphonate **8** and dimethyl cyclohexenyl phosphate **9** (total yield of 66%): bp 84–87 °C (0.25 mm); ir (neat) 1670 (C=C), 1260 (P=O), 1190 and 1020 ($POCH_3$), 850, 830, and 785 cm^{-1} (epoxide); NMR (neat) τ 8.8–7.7 (m, 8, cyclohexyl), 6.65 (m, 1, epoxide), 6.21 (d, 6, J_{POCH} = 10.5 Hz), 4.5 (m, 1, vinyl proton).

Reaction of α-Chloroacetophenone with Dimethyl Phosphonate. In an attempt to make the corresponding epoxide, dimethyl 1,2-epoxy-2-phenyl-2-ethylphosphonate, the only apparent product by NMR was the vinyl phosphate **10**. No attempt was made to isolate this product.

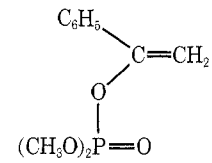
Results

Our synthetic method (eq 1) is a modification of two previously existing methods: reaction of a phosphonate halohydrin with base to give the epoxide, and reaction of a sodium dialkylphosphonate with an α-chloro ketone. The yields are in Table I.

This reaction appears to give only the epoxide with aliphatic α-halo ketones. The reaction of α-chloroacetophenone with dimethyl phosphonate gave only dimethyl 1-phenylvinylphosphate. Attempts to form the epoxide from the corresponding phosphonate halohydrin also resulted in the formation of **10**. However, the addition of sodium diethylphosphonate to α-chloroacetophenone has been reported to give a mixture of the benzyl epoxide and the vinyl phosphate.[11] The reaction of chlorocyclohexanone with dimethyl phosphonate appeared by NMR to give an equimolar ratio of the epoxide **8** and the vinyl phosphate **9**.



9

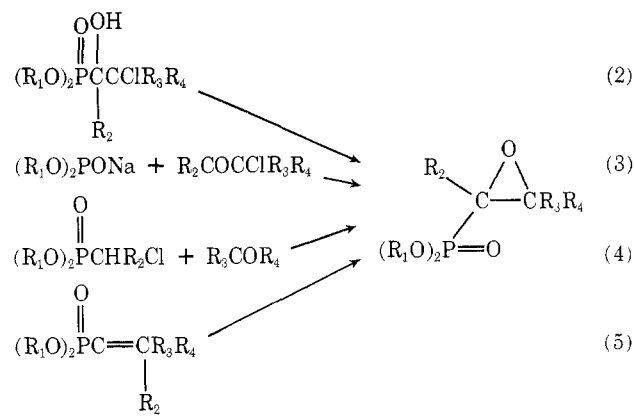


10

NMR Spectra of the Synthetic Reaction. The reaction solution for the synthesis of dimethyl 1,2-epoxy-2-propylphosphonate was made up as described and the NMR spectra in Figure 1 were obtained after successive additions of 0.25 equiv of sodium methoxide. The CH_3 group in chloroacetone is replaced by two doublets at τ 8.5; the one with the larger coupling is due to the halohydrin and the one with the smaller coupling is due to epoxyphosphonate. These assignments are based on spectra of authentic samples of each.

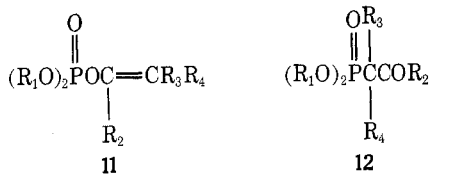
Discussion

Epoxyphosphonate Synthesis. Present methods for the synthesis of epoxyphosphonates have recently been reviewed.[12] These methods include (a) the reaction of a dialkyl phosphonate halohydrin with base (eq 2); (b) the reac-

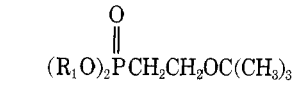


tion of a sodium dialkylphosphonate with an α-halo ketone (eq 3); (c) Darzen's reaction of dialkyl chloromethylphosphonates with carbonyl compounds (eq 4); and (d) direct epoxidation of unsaturated phosphonates with a peroxide and catalyst or a peracid (eq 5).

In general the yields for these reactions are at best 60–70%. In addition, they are subject to limitations. (a) The reaction of a sodium dialkylphosphonate has been reported to also give the isomeric enol or vinyl phosphate 11 and β-ketophosphonate 12;[11,13] the α-halo carbon cannot be tertiary.[13] (b) The Darzen's reaction is without side reactions, but is limited to ketones and aryl aldehydes; R_3 and R_4 = alkyl or R_4 = aryl and R_3 = H; in addition, this reaction has, as yet, been carried out only with the methyl and ethyl esters of chloromethylphosphonic acid (R_2 = H). (c) Epoxidation of the unsaturated phosphonate can result in side reactions: in a buffered solution trifluoroperacetic acid, when used as the oxidant, may cause ring opening of the epoxide when formed,[14] and the use of *tert*-butyl peroxide has been shown to result in the Michael addition product 13 of the butoxide to the olefin.[3] (d) Epoxidation has two distinct advantages. First, the formation of the intermediate, unsaturated phosphonate in the synthetic sequence permits an acid-catalyzed ester hydrolysis prior to epoxidation. Once the epoxide is formed, as in the other reactions discussed, the esters can be removed by hydrogenation if $R_1 = CH_2C_6H_5$.[15] Second, if R_3 or $R_4 \neq H$, then there will be two isomeric unsaturated phosphonates formed which can be separated. Epoxidation of the appropriate isomer can then take place in the presence of a resolving agent in order to isolate the product with the desired absolute stereochemistry.[16]



11 12



13

In our attempt to synthesize analogues of fosfomycin, our attention was directed to the reaction of a phosphonate halohydrin with base. Phosphonate halohydrins are readily formed from the reaction of a dialkyl phosphonate with an α-chloro ketone,[13,17,18] so we examined the reaction of chloroacetone and dimethyl phosphonate with 1 equiv of sodium methoxide. The addition of 1 equiv of sodium methoxide to the reactants resulted in the immediate precipitation of sodium chloride. After stirring for 1 h, an NMR spectrum indicated the presence of only the epoxide. Refinement of the reaction work-up has led to reproducible yields of 84% for both **2** and **3**. These yields represent a significant improvement over the yields of 30 and 63% reported for the one-step reaction of chloroacetone with sodium diethyl phosphonate.[4,13] This procedure avoids formation of the sodium dialkyl phosphonate salt which tends to precipitate out and coat the sodium as it dissolves in a solution of the dialkyl phosphonate in ether.[4] We have extended this reaction to a variety of α-halo ketones and two other phosphonates. The procedure seems facile and convenient.

Esterification of fosfomycin causes a marked decrease in its biological activity.[15] The synthesis of any analogue therefore requires the free acid as a final product. Since it has been shown that a dibenzyl epoxyphosphonate can be hydrogenated to give the free acid,[15] we extended our reaction to include that of chloroacetone with dibenzyl phosphonate; although we did not succeed in preparing an analytical sample, free from benzyl alcohol, the NMR demonstrated that this method is successful with benzyl esters.

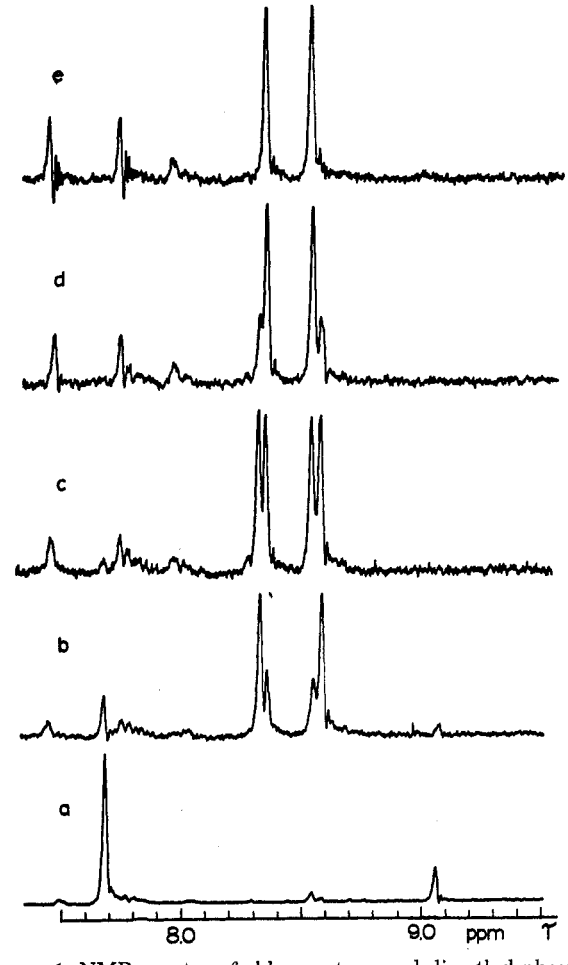
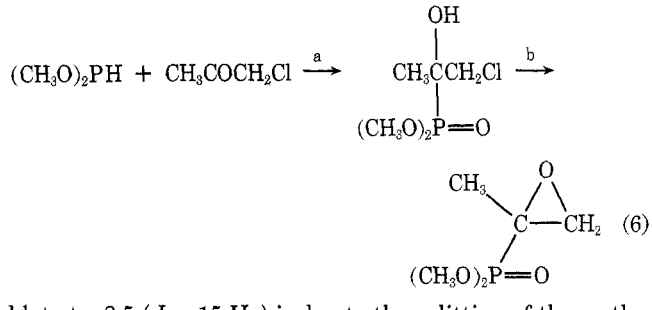


Figure 1. NMR spectra of chloroacetone and dimethyl phosphonate before (a) and after the addition of 0.25 (b), 0.50 (c), 0.75 (d), and 1.0 (e) equiv of sodium methoxide.

Mechanism of the Reaction. The NMR spectra in Figure 1 indicate that the reaction proceeds by a two-step mechanism (eq 6) through the chlorohydrin; the outer doublet at τ 8.5 (J = 15 Hz) is due to the splitting of the methyl group in the phosphonate halohydrin by the phosphorus. The inner doublet (J = 11.3 Hz) is due to the splitting of the methyl group of the epoxide by the phosphorus. Therefore, the spectra demonstrate formation and disappearance of chlorohydrin as sodium methoxide is added.

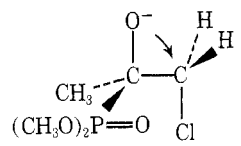


(6)

Formation of the vinyl phosphate in the case of both α-chloroacetophenone and α-chlorocyclohexanone is not unexpected. The similar reaction of sodium dialkyl phosphonates with α-halo ketones has been reported to give the epoxide alone, the vinyl phosphate alone, a mixture of the epoxide and vinyl phosphate, or a mixture of the epoxide

and β-ketophosphonate.[4,11,13] Similarly, the reactions of trialkyl phosphites with α-halo ketones give a variety of products depending on reaction conditions. Investigations of the mechanism of these reactions have led to little conclusive evidence about their mechanism.[19] Formation of the vinyl phosphate, epoxyphosphonate, and phosphate halohydrin is believed to result from attack by the phosphorus at the carbonyl carbon. Formation of the β-ketophosphonate results from attack at the α-halo carbon.

For the aliphatic α-halo ketones, formation of the epoxide is the favored course of the reaction. The phosphorus can attack the carbonyl carbon to form the intermediate halohydrin. The α carbon is free to rotate around its bond to the carbonyl carbon, positioning the halide trans to the oxygen which is involved in nucleophilic attack.



In the case of chlorocyclohexanone, the α carbon is not free to rotate. The preferred conformation of the molecule has the chlorine in an equatorial position. Attack by the phosphorus can result in chlorohydrin with hydroxyl and chlorine having either cis or trans stereochemistry; the trans can lead to epoxide through the axial–axial conformer (which has the phosphonate group equatorial), but the cis isomer cannot achieve the proper stereochemistry to generate epoxide so it would give vinyl phosphate by attack at phosphorus; we found a 50:50 mixture of epoxyphosphonate and vinyl phosphate.

For α-chloroacetophenone, the α carbon is free to rotate in epoxide formation. However, attack of the oxygen at phosphorus is also favorable owing to the formation of a conjugated system. Meisters and Swan, who found that sodium diethylphosphonate and α-chloroacetophenone in liquid ammonia gave a mixture of the epoxide and vinyl compounds, suggested that the polarity of the solvent was the determining factor.[11] They proposed that a more polar solvent would favor epoxide formation; however, our reaction in methanol gives no epoxide.

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Registry No.—**2,** 36432-35-6; **3,** 1445-84-7; **4,** 58074-07-0; **5,** 58074-08-1; **6,** 58074-09-2; **7,** 58074-10-5; **8,** 13176-31-3; chloroacetone, 78-95-5; 2-chloro-4,4-dimethyl-3-pentanone, 40955-58-6; chlorocyclohexane, 822-87-7; 1-chloro-3,3-dimethyl-2-butanone, 13547-70-1; α-chloroacetophenone, 532-27-4; 3-bromo-2-butanone, 814-75-5; dimethyl phosphonate, 868-85-9; diethyl phosphonate, 762-04-9; sodium methoxide, 124-41-4; sodium benzyloxide, 20194-18-7; dibenzyl phosphonate, 17176-77-1.

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Conformation and Electronic Structure of the Lithium Adduct of Methylenephosphoranes

Thomas A. Albright* and E. E. Schweizer*

Department of Chemistry, University of Delaware, Newark, Delaware 19711

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NMR evidence is presented to show that lithium adducts are formed upon addition of *n*-butyllithium to methyltriphenylphosphonium iodide. The geometry of the lithium adduct to methylenephosphorane was examined by means of CNDO/2 molecular orbital calculations. The electronic structure of this molecule is compared to several other related molecules. The calculations suggest that the lithium does not perturb the electron distribution or conformation about the methylene group significantly compared to methylenephosphorane, with the exception that the phosphorus atom loses electron density in the adduct. Calculations of P–C couplings by the finite perturbation method support the proposed conformation.

It has been previously established that lithium salts can bond to phosphorus–carbon ylides.[1] These compounds are the simplest type of a rich variety of organometallic compounds formed where the methylene carbanion of a phosphorus ylide bonds to a metal.[1a] However, there is very little reported on the nature of these adducts. From a proton NMR investigation it was proposed[1b] that the conformation of these lithium adducts was 1 since the C–H coupling of the methylene group was approximately the same as that found for phosphonium salts (see Table I). The C–H coupling for the salt-free ylide was, however, 15 Hz larger than that obtained for the lithium adduct.[1b] Evidence of both