COMMUNICATIONS

Synthesis of Dialkyl Epoxyethylphosphonates

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The synthesis of dialkyl 1,2-epoxyalkylphosphonates has been dealt with in only a few papers. Martynov and Timofeev¹ reported the preparation of a dialkyl 2,2-disubstituted epoxyethylphosphonate by the Darzens reaction of cyclohexanone with ethyl chloromethylphosphonate. The chloromethylphosphonyl chloride used as starting material in this procedure is, however, difficult to obtain; furthermore, the 2,2-disubstituted epoxyethylphosphonates readily rearrange to carbonyl compounds upon heating²:

HCHO + PCl₃
$$\longrightarrow$$
 Cl-CH₂-P Cl $\xrightarrow{R^1\text{OH}}$

Cl-CH₂-P OR¹ $\xrightarrow{R^2\text{C=O}}$
 $\xrightarrow{R^2\text{C}}$
 $\xrightarrow{R^2\text{C}}$
 $\xrightarrow{R^3\text{C}}$
 $\xrightarrow{R^$

In this paper, we report the synthesis of diethyl epoxyethylphosphonate (2) from chloroacetaldehyde and diethyl phosphite. In the presence of triethylamine, these components react readily to give diethyl 2-chloro-1-hydroxyethylphosphonate (1); treatment of 1 with aqueous or ethanolic potassium hydroxide or with ethanolic sodium hydroxide produces diethyl epoxyethylphosphonate (2) in 23-56% yield:

$$H_2C - CH - P OC_2H_5$$

In the dehydrochlorination step, some polymeric material was also formed, probably by anionic polymerization of 2. In addition, a 4% yield of an oxo compound was obtained, to which the structure 3 was assigned on evidence of the spectral characteristics:

$$0 = CH - CH_2 - P \begin{vmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix}$$

Neither the vinyl compound 4 nor the isomeric oxo compound 5 was found in the reaction mixture. Compounds 4 and 5 could be expected to be formed in the reaction in analogy to the dehydrochlorination of dimethyl 2,2,2-trichloro-1-hydroxyethylphosphonate, which gives rise to a vinyl and an oxo compound corresponding to 4 and 5 respectively³.

Analogous to the procedure described, other dialkyl epoxyethylphosphonates (dibutyl, bis-[2-ethylhexyl], bis-[2-chloroethyl], and dicyclohexyl) were prepared, although their purification proved to be difficult. In the case of the diphenyl ester, only polymeric material was obtained.

Diethyl 2-Chloro-1-hydroxyethylphosphonate (1): A mixture of diethyl phosphite (27.6 g) and chloroacetaldehyde (15.6 g) was stirred at room temperature for 3 hr in the presence of a few drops of triethylamine. Distillation in vacuo of the resultant reaction mixture gave 23.7 g (63%) of 1; b. p. $116-118^{\circ}/0.06$ mm; n_D^{20} : 1.4574.

I. R. (neat): 3280 cm⁻¹ (OH). C₆H₁₄ClO₄P calc. OH 7.87 Cl 16.4 P 14.32 found 7.44 16.8 14.08

Diethyl Epoxyethylphosphonate (2):

Method A: An ethanolic solution of 32 g of potassium hydroxide was added dropwise with stirring to a solution of the chlorohydrin 1 (124 g) in ethanol (300 ml) at 4–6°. Stirring was continued at room temperature for 10 hr. The mixture was then filtered, concentrated, and distilled in vacuo; yield: 57.6 g (54%). Method B: An ethanolic solution of 19.2 g sodium ethoxide was added dropwise with stirring to a solution of the chlorohydrin 1 (60 g) in ethanol (300 ml) at 10–18°. Stirring was continued at room temperature for 7 hr. The mixture was then filtered, concentrated, and distilled in vacuo; yield: 28.6 g (56%). Method C: An aqueous solution of 10 g of potassium hydroxide was added dropwise with stirring to the chlorohydrin 1 (30.5 g) at room temperature. Stirring was continued for 5 hr. The mixture was then concentrated, extracted with ether, the ether distilled, and the residue distilled in vacuo; yield: 5.7 g (23%).

b. p. $86-89^{\circ}/2 \text{ mm}$; n_D^{20} : 1.4341.

I. R. (neat): 880 cm⁻¹ (oxirane group).

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N.M.R. (CCl₄): δ 1.37 (t, 6, J=6.8 Hz, C \underline{H} ₃), 4.12 (2 q, 4, J_{H-H}=6.8 Hz, J_{H-P}=8.0 Hz, C \underline{H} ₂—CH₃), 2.89 (2 d, 2, J_{H-H}=3.5 Hz, J_{H-P}=5.3 Hz, ring C \underline{H} ₂), 2.52 (m, 1, J_{H-H}=3.5 Hz, J_{H-P}=31.5 Hz, CH).

The general method of determination of oxirane content⁴ was not applicable to the epoxide 2.

C₆H₁₃O₄P calc. C 40.00 H 7.27 P 17.19 found 39.24 7.24 16.85

From the reaction mixture, the carbonyl compound 3 was isolated by distillation in 4% yield; b.p. $28-29^{\circ}/0.04$ mm.

I. R. (neat) 1640 cm⁻¹ (CO).

N. M. R. (CCl₄): δ 1.39 (t, 6, J_{H-H} = 7.2 Hz, CH₃), 4.14 (2 q, 4, J_{H-H} = 7.2 Hz, J_{H-P} = 7.5 Hz, CH₂—CH₃), 4.95 (2 d, 2, J_{H-H} = 6.5 Hz, J_{H-P} = 22.5 Hz, CH₂—P), 6.59 (2 t, 1, J_{H-H} = 6.5 Hz, J_{H-P} = 13.7 Hz, CHO).

Dialkyl Epoxyethylphosphonates: The reactions were carried out in a similar manner as described above; Method B was used in the dehydrochlorination step.

Dibutyl Epoxyethylphosphonate; yield: 53%; b.p. 81-87°/0.1 mm.

Bis-/2-ethylhexyl/Epoxyethylphosphonate; yield of crude product; 68% (undistillable).

Dicyclohexyl Epoxyethylphosphonate; yield: 13%; b.p. 105-110°/0.06 mm.

Bis-[2-chloroethyl] Epoxyethylphosphonate; yield: 36%; b.p. $72-82^{\circ}/0.06$ mm.

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