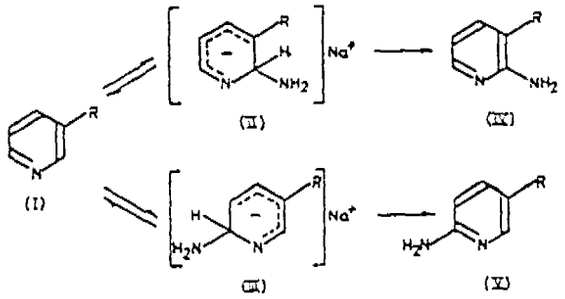
pyridine-3*d* mixture was the same as that of the starting material, agreeing with an addition-elimination mechanism and ruling out a rate-determining elimination of a hydride-ion from *C*(3) to give the



2,3-pyridyne intermediate. (ii) The reaction of 3-picoline with sodamide in boiling toluene gave a mixture of (IV) and (V) (R = Me) in the ratio of 90 : 10 (product analysed by gas chromatography). The isomer ratio was unchanged within experimental error when 3-picoline-2*d* was used instead. This could be taken as evidence that the addition step leading to (II) and (III) is the rate-determining one, which is unlikely. By analogy with the mechanism of the reaction of phenyllithium with 3-picoline[1] it seems more probable that the hydride-ion elimination is the slower of the two steps, but that the addition stages are virtually irreversible so that the ratio of (IV) to (V) formed depends upon the relative rates of formation of (II) and (III). This point is being investigated further.

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References

[1] Aromatic Substitution. Part VI. Part V. Abramovitch, R. A. & Giam, C.-S., *Canad. J. Chem.*, 1963, 41, 3127
[2] Levitt, L. S. & Levitt, B. W., *Chem. & Ind.*, 1963, 1621
[3] Barrett, G. C. & Schofield, K., *ibid.*, 1963, 1980
[4] Roberts, J. D., Semenow, D. A., Simmons, H. E., Jr. & Carlsmith, L. A., *J. Amer. chem. Soc.*, 1956, 78, 601; Roberts, J. D., Vaughan, C. W., Carlsmith, L. A. & Semenow, D. A., *J. Amer. chem. Soc.*, 1956, 78, 611
[5] We thank Dr. E. L. Eliel for the mass-spectroscopic analyses

Chloroethylene Oxide

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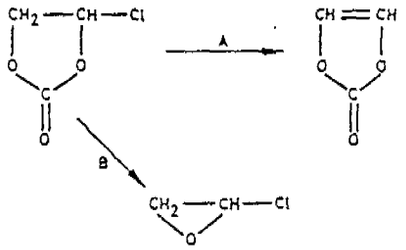
Sábanejeff[1] reported fragmentary data on the preparation of chloroethylene oxide by heating 1-iodo-2-chloroethylene with water at 150° in a sealed tube. Recently Walling and Fredericks[2] reported the isolation of chloroethylene oxide from the reaction of t-butyl hypochlorite with ethylene oxide but no physical constants were given. We first isolated chloroethylene oxide as a by-product in the preparation of vinylene carbonate[3] according to reaction (A) in the presence of triethylamine.



In order to produce chloroethylene oxide in improved yield according to reaction (B), triethylamine was replaced by acidic reagents, since bases favour elimination of hydrogen chloride or complete hydrolysis of the carbonate group. We first tried to adopt the synthesis reported for the analogue, bromoethylene oxide[4] prepared in very low yield by treating β,β-dibromoethanol with methyl alcoholic potassium hydroxide. In our hands chloroethylene oxide could not be prepared conveniently by dehydrohalogenation of β,β-dichloroethanol with sodium hydroxide in methylene chloride, an excellent method for routine preparation of epoxides.

It has been shown that acidic reagents, such as aluminum chloride, zinc chloride or sulphuric acid at high temperature will decompose ethylene carbonate into ethylene oxide and carbon dioxide.[5] Polyhalogenated hydrocarbons, such as hexachloroethane, also accomplish this decomposition.[6] Upon heating monochloroethylene carbonate with acidic reagents, we obtained chloroethylene oxide. Our best yields (34%) were obtained by heating a mixture of 24·5 g. monochloroethylene carbonate and 12 drops of concentrated sulphuric acid to 230°C. The crude distillate upon careful fractionation afforded 5·2 g. of colourless oil boiling at 78–79° (Found: C, 30·40; H, 4·10; Cl, 44·87. Calc. for C_2H_3ClO: C, 30·57; H, 3·82; Cl, 45·22%). The infrared curve (taken immediately after distillation) shows that hydroxyl and carbonyl groups are absent, thus contamination with isomeric chloroacetaldehyde was ruled out. Upon standing, however, carbonyl absorption develops; chloroethylene oxide is readily transformed to chloroacetaldehyde.

Chloroethylene oxide, therefore, would be expected to give reactions characteristic of chloroacetaldehyde.

Chloroethylene oxide gives off strongly acidic fumes upon exposure to the atmosphere; it is a strong lachrymator which irritates the mucous membranes. It is soluble in ethanol and ether, insoluble in water (chloroacetaldehyde is soluble in water). Upon standing at room temperature the product deposits a solid which is insoluble in water, ethanol, ether and

0·5N hydrochloric acid; the solid vaporises at 112–115° and upon distillation yields chloroacetaldehyde, boiling at 85·5°. The solid proved to be the amorphous trimer of chloroacetaldehyde analogous to that of acetaldehyde. Natterer[7] has reported that the purest samples of chloroacetaldehyde are obtained by heating the solid polymer of chloroacetaldehyde. Natterer's polymer had no definite melting point; it disappeared upon heating at about 100°. Our purified polymer vaporised at 162–164° (Maquenne-block) (Found: Cl, 45·14; Calc. for $(C_2H_3ClO)_3$: Cl, 45·22%). Infrared analysis showed a major peak at 9μ (ether linkage); C = O absorption was absent.

In one experiment a sample of chloroethylene oxide which had deposited polymer was diluted with ethyl ether. After the polymer was removed by filtration, the filtrate was fractionated. Fractions boiling from 82–85·5°c. deposited crystals soluble in water, absolute ethanol and ether. After washing with chloroform and drying *in vacuo*, the crystals melted at 87°c. (Found: Cl, 40.8; Calc. for

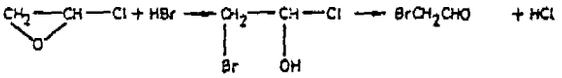
$$ClCH_2CH(OH)\text{-}O\text{-}CH(OH)CH_2Cl:\ Cl,\ 40.6\%).$$

Wet ether or exposure to atmosphere converted chloroethylene oxide into 1,1'-dihydroxy-2,2'-dichloroethyl ether, the "chloroacetaldehyde hydrate" of the early literature.[7]

Chloroethylene oxide gives an immediate precipitate with 1% aqueous silver nitrate and a positive Tollen's test at room temperature. With concentrated sulphuric acid it gives a red colour and with 10% sodium hydroxide solution a yellow colour. With 2,4-dinitrophenylhydrazine, chloroethylene oxide gives chloroacetaldehyde 2,4-dinitrophenylhydrazone (m.p. and mixed m.p. with an authentic specimen, 154–156°).

Upon heating chloroethylene oxide under reflux with absolute ethanol a colourless oil boiling at 152–153° was obtained. This product was chloroacetaldehyde diethyl acetal, reported b.p. 155°.[3]

Chloroethylene oxide shows no oxirane ring by conventional addition of HBr solution and titration of excess of HBr. The following reaction explains the failure of the analysis:



The addition compound loses one mole of HCl for every mole of HBr added, thus giving a negative test for the oxirane group. Infrared analysis shows absorption bands at 7·8, 8·7 and 11·6μ characteristic of the epoxy group.[9]

We have not determined the molecular weight, but the boiling point approximates to that for the postulated monomer as will be clear from the following consideration. Epichlorohydrin boils 37° higher than chloroethylene oxide; propyl chloride boils 35° higher than ethyl chloride. In both cases the methylene group raises the boiling point about 35°c.

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References

1 Sabanejeff, A., *Liebigs Ann.*, 1883, 216, 268
2 Walling, C. & Fredericks, P. S., *J. Amer. chem. Soc.*, 1962, 84, 3326
3 Newman, M. S. & Addor, R. W., *ibid.*, 1953, 75, 1263
4 Demole, E., *Ber. dtsch. chem. Ges.*, 1876, 9, 45
5 Ethylene Carbonate, Technical Bulletin, Jefferson Chem. Co., 1959
6 French Patent, 1,100,845, September 26, 1955
7 Natterer, K., *Monats.*, 1882, 3, 442
8 Fritsch, P. & Schumacher, W., *Liebigs Ann.*, 1894, 279, 307
9 Bellamy, L. J., Infrared Spectra of Complex Molecules, 2nd Edition *p.* 118 (J. Wiley & Sons, Inc.)

R&S 136105

Optically Active *O*-Ethyl Ethylphosphonochloridothionates: A New Route to Optically Active Organophosphorus Compounds

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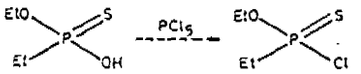
Optically active phosphinyl chlorides, $R^1R^2P(O)Cl$ (R^1, R^2=alkyl or alkoxyl),[1] have recently been used to study the stereochemistry at an asymmetric phosphorus atom. Their usefulness is limited however by the fast racemisation and low optical rotation values.

We report now a synthetic route to a wide range of optically active organophosphorus compounds containing the *P(S)* group with optically active *O*-ethyl ethylphosphonochloridothionates (II) as the key intermediates. The readily-available *O*-ethyl ethylphosphonothioic acids (I), resolved according to Arton *et al.*,[2] have been converted into optically active phosphonochloridothionates (II) with phosphorus pentachloride. The analogous reaction on symmetrical phosphinothioic acids has been described previously.[3]



(I) (II)

$[\alpha]_D^{20}$ −14·75° $[\alpha]_D^{20}$ −73·80°
$[\alpha]_D^{20}$ +8·25° $[\alpha]_D^{20}$ +41·50°

The reaction of the (−)-and (+)-acid (I) with a molar ratio of phosphorus pentachloride was carried out at −15° to −10° in carbon tetrachloride solution. The crude (−) and (+) chlorides (II) were purified by distillation (b.p. 21°/0·1 mm., n_D^{20} 1·4930, yield 75–85%). The phosphonochloridothionates (II) were shown by thin-layer chromatography to be free of any traces of ethyl ethylphosphonochloridate, Et(EtO)P(O)Cl, as impurities.