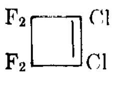
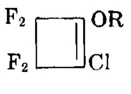
with either methoxide or ethoxide ion to form the monoether, IIa or IIb. Further reaction with alkoxide ion gives a triether, IIIa or IIIb, whose structure had been demonstrated.[2]

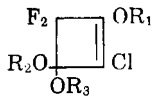


I



II

a. R = Me
b. R = Et

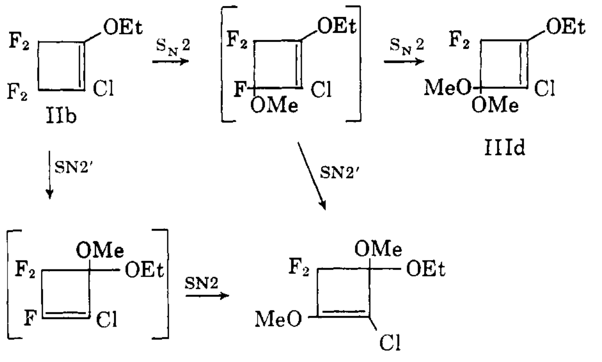


III

a. $R_1 = R_2 = R_3 =$ Me
b. $R_1 = R_2 = R_3 =$ Et
c. $R_1 = R_2 =$ Me
$R_3 =$ Et
d. $R_1 =$ Et
$R_2 = R_3 =$ Me

Until now it was not known whether the reaction of the monoether with alkoxide ion proceeded *via* two S_N2 processes, or a combination of one S_N2 and one S_N2' step,[3] as either path would give the same product if the same alkoxide were used throughout.

We have now shown that this reaction involves one S_N2' step, by reaction of the monoether with an alkoxide ion different from that used to form the monoether. Thus, reaction of IIb with methoxide ion should give IIIc if an S_N2' step is involved, but IIId if only S_N2 steps are involved. We have found that IIIc is the only product obtained, as shown by gas chromatography and n.m.r. analysis.[4]



IIb IIId IIIc

That the correct structure of this triether is IIIc rather than IIId was determined from its n.m.r. spectrogram.[5] Clearly, with IIId both groups of methyl protons would be equivalent, whereas with IIIc the methyl groups would not be equivalent. Furthermore, in the spectrum of IIIb there are two distinct resonance positions of the methylene and methyl protons with relative intensities of 1 to 2. The high intensity methylene quartet is centered at 6.23 τ and is obviously the resonance of the ketal ethyl group. The presence of *two* methyl peaks at 6.00 τ and 6.53 τ and a methylene quartet centered at 6.23 τ in the spectrogram of this product thus conclusively demonstrates the correctness of structure IIIc.

Experimental

1-Ethoxy-2-chloro-3,3,4,4-tetrafluorocyclobutene.—To a stirred solution of 24.0 g. (0.123 mole) of 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene in 55 ml. of 95% ethanol was added dropwise a solution of 6.9 g. (0.12 mole) of potassium hydroxide in 120 ml. of ethanol, over a period of 1 hr. The reaction mixture was poured into cold water, extracted with methylene chloride, and the methylene chloride extract washed five times with water. The methylene chloride solution was dried twice over sodium sulfate, followed by magnesium sulfate, and rectified through a 20-in. Fenske column. There was obtained 12.4 g. (0.061 mole) of the monoether, b.p. 73.5–75.5°(100 mm.), n^{25}_{D} 1.3813, (lit.,[2] b.p. 129°, n^{25}_{D} 1.3818)

1,3-Dimethoxy-3-ethoxy-2-chloro-4,4-difluorocyclobutene.—To a stirred solution of 11.4 g. (0.056 mole) of the monoether in 50 ml. of anhydrous methanol was added a solution of 6.3 g. (0.11 mole) of potassium hydroxide in 75 ml. of methanol. After refluxing for 2 hr., the solution was only slightly alkaline. The reaction mixture was poured into cold water, extracted with methylene chloride, and the methylene chloride extract washed five times with water. The solution was dried twice over sodium sulfate, followed by magnesium sulfate, and the solvent stripped on a Rotovac under vacuum. Vacuum distillation of the residue yielded 8.2 g. (0.038 mole) of triether, IIIc, b.p. 107–108° (22 mm.), n^{25}_{D} 1.4272, d^{25}_{4} 1.277. Molar refraction: calcd. 46.62; obsd. 46.00.

Anal. Calcd. for $C_8H_{11}F_2ClO_3$: C, 42.15; H, 4.86; F, 16.63; Cl, 15.48. Found: C, 42.24; H, 4.85; F, 16.80; Cl, 15.42.

Analysis by gas–liquid chromatography showed this material to be greater than 99.5% pure, with less than 0.5% of the monoether present.

Acknowledgment.—The authors wish to express their appreciation to Professor Melvin Hanna of this Chemistry Department for assistance in the interpretation of the n.m.r. spectra.

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[2] J. D. Park, S. Cohen, and J. R. Lacher, *ibid.*, **84**, 2919 (1962).

[3] For evidence supporting the S_N2' mechanism for the reaction of nucleophiles with fluoroolefins, see: (a) W. T. Miller, Jr., J. H. Fried, and N. Goldwhite, *ibid.*, **82**, 3091 (1960); (b) John H. Fried and William T. Miller, Jr., **81**, 2078 (1959).

[4] It seems more likely to us that the first step in the mechanism is S_N2, followed by an S_N2 displacement of the vinyl fluoride, but as we have been unable so far to isolate either of the compounds shown in brackets, we cannot say with certainty that this assumption is correct. Further work on these reactions is continuing in this laboratory, and will be reported in the near future.

[5] N.m.r. spectra were taken using a Varian A-60 analytical spectrometer. Pure liquid samples were used with tetramethylsilane as an internal reference

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A Novel Preparation of Tetraethylpyrophosphite

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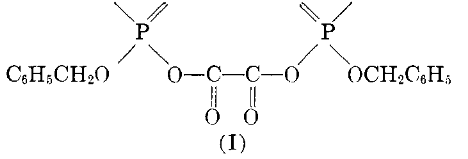
Received November 2, 1962

Mason and Todd[1] have described a preparation of tetrabenzyl pyrophosphate based on the reaction of oxalyl chloride and dibenzyl phosphate to give the comparatively stable intermediate (I)



(I)

which subsequently rearranges losing carbon dioxide and carbon monoxide. We wish to report the preparation of tetraethyl pyrophosphite (III) by a closely related method, from diethyl phosphorochloridite and silver carbonate in an inert solvent.

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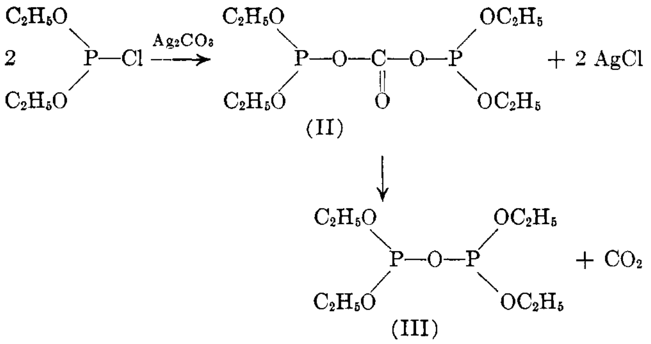
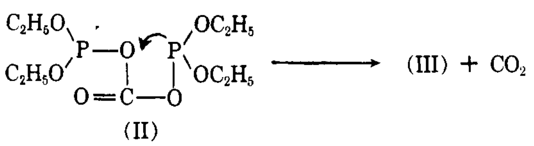
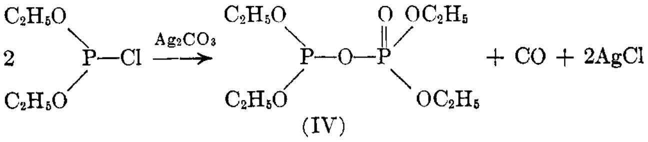
[1] H. S. Mason and A. R. Todd, *J. Chem. Soc.*, 2267 (1951).



The reaction appears to proceed via the formation of a phosphorous carbonic anhydride (II). Whereas intermediate I is sufficiently stable to isolate and requires heating to effect decomposition, intermediate II is very unstable, as evidenced by the immediate evolution of gas (mainly CO_2) on mixing the reagents. This instability is probably a consequence of the ease with which a four centre cyclic mechanism may occur, such as is commonly found[2] in organophosphorus compounds.



This simple preparation (from two commercially available chemicals) appears to provide one of the easiest syntheses of the tetralkyl pyrophosphites, which are of importance in peptide synthesis[3] and the preparation of pyrophosphates specifically positionally labeled[4] with oxygen-18. Tetra-*n*-propyl pyrophosphite was prepared in the same way in both cases a yield of over 60% being obtained. The main side product accounting for *ca.* 15% of the yield based on phosphorochloridite is tetraethyl phosphorous phosphoric anhydride (IV).



The formation of this molecule from intermediate II implies the formation of carbon monoxide which in fact forms about 10% of the evolved gases.

Experimental

Tetraethyl pyrophosphite was prepared by the slow addition of diethyl phosphorochloridite (5 g.) to a stirred suspension of silver carbonate (3.5 g.) in dry benzene. An intermediate exothermic reaction occurs with the evolution of gas. The product is then fractionally distilled without separating the solid to give: (i) tetraethyl pyrophosphite (II), b.p. 87–89° (1 mm.) [lit.[5] b.p. 82–83° (2–3 mm.)] in about 60% yield; and (ii) tetraethyl phosphorous phosphoric anhydride (IV) b.p. 110–114° (1 mm.) [lit.[5] b.p. 116–117° (2 mm.)] in about 15% yield.

The gas was shown by mass spectrometry to be a mixture of carbon dioxide (about 90%) and carbon monoxide (about 10%). The identity of tetraethyl pyrophosphite (II) and tetraethylphosphorous phosphoric anhydride (IV) was confirmed by the oxidation equivalent of the hydrolyzed products (126 and 253, respectively) and by the infrared spectra in chloroform solution, maxima being observed at 1035 cm.$^{-1}$ (P—O—Et) and 945, 985 cm.$^{-1}$ (P—O—P) for both compounds with an additional peak at 1280 cm.$^{-1}$ (P—O) for the phosphoric phosphorous anhydride. An analogous reaction occurs with di-*n*-propyl phosphorochloridite.

The reaction mixture was distilled directly without filtering in order not to lose some of the product as the stable complex known to be formed between silver chloride and esters of phosphorous anhydride.[5]

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(2) M. Scholkoof, *Angew Chem.*, **71**, 260 (1959); A. Lapidot and D. Samuel, *J. Chem. Soc.*, 2110 (1962).

(3) G. W. Anderson, J. Blodinger, and A. D. Welcher, *J. Am. Chem. Soc.*, **74**, 5309 (1952).

(4) D. Samuel and B. L. Silver, *Chem. Ind.* (London), 556 (1961).

(5) A. E. Arbuzov and B. A. Arbuzov, *Zh. Obschch. Khim.*, **2**, 348 (1932).

Levopimaramide and the Hofmann Reaction

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Received November 7, 1962

Isocyanates have been prepared from rosin by reaction of the amide with hypohalite by the Hofmann reaction.[3,4] The product from the reaction was the isocyanate rather than the amine or urea described by Wallis, *et al.*,[5] because of its unusual resistance to hydrolysis. In previous work the resin acid moiety was modified by either hydrogenation, dehydrogenation, disproportionation or aromatization which obviated reaction of the olefinic system with hypohalite as described by other workers. For example, Uraneck, *et al.*,[6] used hypohalite to modify rosin for use as soaps for emulsion polymerizations and Lombard, *et al.*,[7] reported the reaction of hypohalite on abietic acid. It was the purpose of the present investigation to determine if isocyanates containing the reactive conjugated diene system of levopimaric acid could be prepared.

The most reactive (and least thermodynamically stable) resin acid, levopimaric acid, is extremely sensitive to acidic conditions. Rapid rearrangement to abietic acid in the presence of 0.1 *N* ethanolic hydrochloric acid has been noted.[8,9] This sensitivity to acidic conditions precluded the preparation of the free acid chloride; however, in the presence of pyridine, the acid chloride, formed with phosphorus trichloride, was stable and pure levopimaramide was prepared without difficulty. Good yields of an isocyanate mixture were obtained by reaction of potassium hypobromite with pure levopimaramide in ether solution. Deviations from the preparative procedure resulted in large amounts of apparently isomeric and nondistillable compounds.

The crude product usually contained 10–30% of nonvolatile material which was conveniently removed by

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(2) One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

(3) V. N. Belov and S. D. Kustova, *J. Gen. Chem., USSR*, **24**, 1083 (1954) (Engl. translation).

(4) S. T. Putman (to Hercules Powder Co.), U. S. Patent 2,491,580 (1949).

(5) E. S. Wallis and J. F. Lane, *Org. Reactions*, **3**, 273 (1946).

(6) C. A. Uraneck and S. H. Landes (to Phillips Petroleum Co.), U. S. Patent 2,679,497 (1954).

(7) R. Lombard and G. Gremmeimaier, *Bull. soc. chim. France*, 1490 (1961).

(8) D. E. Baldwin, V. M. Loeblich, and R. V. Lawrence, *J. Am. Chem. Soc.*, **78**, 2015 (1956).

(9) W. H. Schuller and R. V. Lawrence, American Chemical Society, Florida Section, Meeting-in-Miniature, May 11–12, 1962; *FLACS*, **15**, No. 8, 23 (1962).