Tetrahedron Letters No. 29, pp 2603 - 2604. 0040-4039/78/0715-2603$02.00/0

THE CLEAVAGE OF 2,3-DI(*sec* or *tert*)ALKOXY-1,4-DIOXANES BY PHOSPHORUS PENTACHLORIDE. AN ALTERNATIVE ROUTE TO ACETYLENE DIETHERS.

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(Received in UK 24 April 1978; accepted for publication 19 May 1978)

We have recently described the synthesis of diisopropoxy- and di-*tert*-butoxyethyne, which are fairly stable acetylene diethers[1]. Di-*tert*-butoxyethyne, in particular, is a valuable intermediate which has allowed the synthesis of deltic and squaric acid by a 2 + 1 and a 2 + 2 cycloaddition, respectively[2].

1,2-Dialkoxy-1,2-dichloroethanes are the actual key intermediates for the synthesis of acetylene diethers, either by a direct double dehydrochlorination or, preferably, through the 1,2-dialkoxyethenes followed by a bromination-dehydrobromination sequence[1].

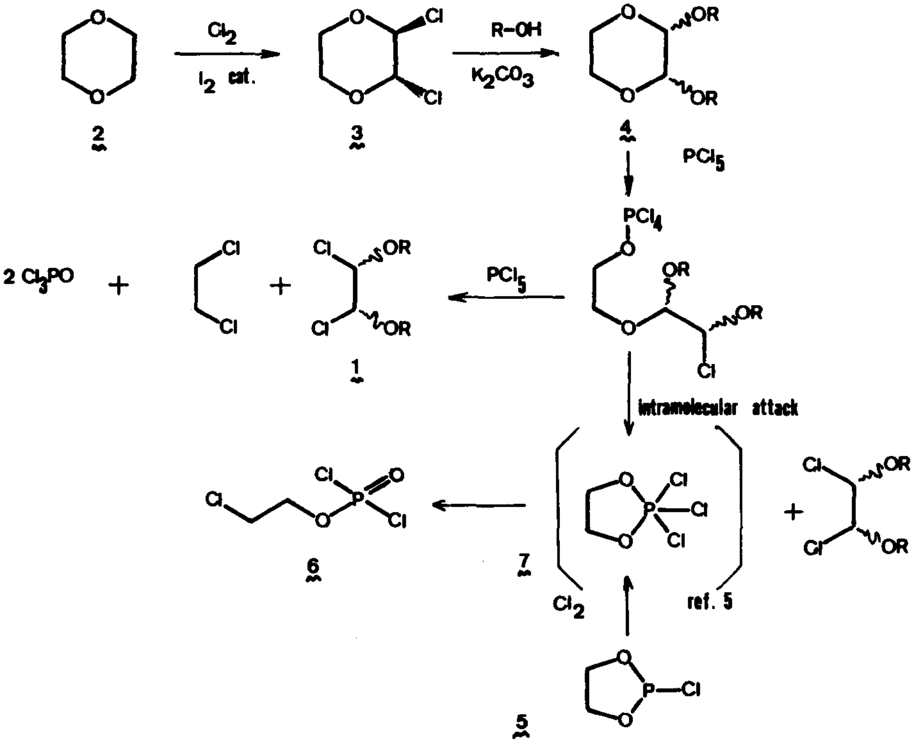
In the present communication we wish to describe an alternative procedure for the synthesis of 1,2-di(*sec* or *tert*)alkoxy-1,2-dichloroethanes (**1**, R =iso-C_3H_7 or *tert*-C_4H_9) starting from dioxane (Scheme 1).

Iodine-catalyzed chlorination of dioxane (**2**), at 90º, gives 96% yield of *trans*-2,3-dichloro-1,4-dioxane[3] (**3**), which reacts with excess of boiling isopropyl alcohol, in the presence of potassium carbonate, to afford a 60:40 mixture of *cis*- and *trans*-2,3-diisopropoxy-1,4-dioxane (**4**, R = iso-C_3H_7), b.p. 49-50º/0.2 torr, in 91% yield[4]. The cleavage of the cyclic acetals with PCl_5, in CH_2Cl_2 solution, occurs according to two different pathways: i) by a double intermolecular attack to give Cl_3PO, 1,2-dichloroethane and a mixture of *rac*- and *meso*-1,2-dichloro-1,2-diisopropoxyethane (**1**, R = iso-C_3H_7), and ii) by an intermolecular attack followed by an intramolecular one to afford the mixture of bis-chloroacetals **1** (R = iso-C_3H_7) and 2-chloroethyl dichlorophosphate (**6**). In both cases, the *primary alcohol* is, however, selectively displaced by the chloride ion, as previously observed in the reaction of PCl_5 with related acyclic mixed acetals[1].

2-Chloroethyl dichlorophosphate (**6**) is probably formed *via* 2,2,2-trichloro-1,3,2-dioxaphosphole (**7**)[5]. NMR spectroscopy analyses of the crude reaction mixture allowed to conclude that the intramolecular attack accounts for nearly 75% of the observed reaction. The mixture of *rac*- and *meso*-1,2-dichloro-1,2-diisopropoxyethanes (**1**, R = iso-C_3H_7) could be separated from the reaction mixture by fractional distillation (b.p. 97-8º/18 torr)[1], in 88% yield.

In a similar way, *trans*-2,3-dichloro-1,4-dioxane (**3**) reacts with excess of boiling *tert*-butyl alcohol, in the presence of dry potassium carbonate, to give a 25:75 mixture of *cis*- and *trans*-2,3-di-*tert*-butoxy-1,4-dioxane (**4**, R = *tert*-C_4H_9) in 85% yield (b.p. 55-6º/0.2 torr; *trans* isomer, m.p. 64-5º). The cleavage with PCl_5 occurs exclusively by the intramolecular attack and affords a mixture of 1,2-dichloro-1,2-

di-*tert*-butoxyethane (**1**, R = *tert*-C_4H_9) and 2-chloroethyl dichlorophosphate (**6**). In order to destroy the dichlorophosphate **6**, the crude reaction mixture was dissolved in hexane and treated with powdered NaOH. After filtration and evaporation of the solvent *in vacuo*, 1,2-dichloro-1,2-di-*tert*-butoxyethane (only one isomer!) was isolated in 81% yield, as colorless crystals, m.p. 77-8º (dec), identical to those previously obtained from glyoxal[1].



Scheme 1

NOTES AND REFERENCES

1. M.A. Pericás and F. Serratosa, *Tetrahedron Letters*, 4433 (1977).
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3. J.J. Kucera and D.C. Carpenter, *J. Am. Chem. Soc.*, *57*, 2346 (1935).
4. B. Duval, R.H. Hall, and B.K. Howe, *J. appl. Chem.*, 546 (1952), have claimed that some 2,3-diisopropoxy-1,4-dioxane was formed in the acid catalyzed reaction of aqueous glyoxal with isopropyl alcohol; however, yields were not reported.
5. P.A. Rossiikaya and M.I. Kabatschnik, *Izvest. Akad. Nauk SSSR, Ser. khim*, 509 (1947)(C.A., *42*, 2924 (1948)), have reported that chlorination of 2-chloro-1,3,2-dioxaphosphole (**5**), at -15º, gives 2-chloroethyl dichlorophosphate (**6**).