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SYNTHESIS OF 2-CHLORO-1,3-BENZODIOXOLE

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The stability of 2-chloro-1,3-dioxolanes and of the analogous dialkoxyalkyl chlorides has been given considerable attention during the last decade[1-13]. Following the considerations given by J.W. Scheeren[9] one should expect 2-chloro-1,3-benzodioxole (I) to be a reasonable stable compound in contrast with the recent statement of H. Gross and B. Costisella [10]. These authors described the synthesis of some 2-chloro-1,3-benzodioxoles substituted in the aromatic ring by electron withdrawing substituents. They performed this synthesis by the action of sulfurylchloride on the corresponding 1,3-benzodioxoles[10-11]. Because of the inapplicability of this method to 1,3-benzodioxole itself and having failed to prepare I from 2-ethoxy-1,3-benzodioxole (II) and PCl_5 in an earlier attempt[12], they concluded compound I to be "nicht existenzfähig". (Instead of the monochlorocompound the dichlorocompound 2,2-dichloro-1,3-benzodioxole was isolated from both reactions).

We succeeded in preparing I starting from 2-acetoxy-1,3-benzodioxole (III)[14,15] being a more polar and more reactive compound compared to II, and asym. dichlorodimethyl ether (IV)[12,16,17,18] in refluxing benzene. IV seemed to be a more gentle reagent for "ionic" chlorination as compared to PCl_5.

$$\underset{\text{III}}{1{,}2\ C_6H_4O_2CHOAc} + \underset{\text{IV}}{CHCl_2OCH_3} \rightleftharpoons \underset{\text{I}}{1{,}2\ C_6H_4O_2CHCl} + \underset{\text{V}}{CHCl(OCH_3)(OAc)} \qquad (1)$$

Reaction (1) is made irreversible by the decomposition of the highly unstable V[16].

$$\underset{\text{V}}{CHCl(OCH_3)(OAc)} \longrightarrow HCO(OCH_3) + AcCl \qquad (2)$$

Since it was presumed that radical substitutions were responsible for the disagreement between the considerations of Scheeren[9] and the experiments of Gross and Costisella[10], radical sources were excluded by using 2,6-di-t.-butyl p-cresol as scavenger; the experiments were carried out in a nitrogen atmosphere throughout.

Compound I was obtained in about 50% yield by distilling off methyl formate and AcCl (N_2 atmosphere, exclusion of moisture) as they were formed from reaction mixtures of compounds III and IV in benzene (molar ratio 1:1.1:3). After ~ one eq. of methyl formate and of AcCl had been removed the reaction mixture was fractionated under reduced pressure. A fraction boiling at 62-63 °C/0.5 mm was isolated and identified as I by its P.M.R.-spectrum in CCl_4 solution: 7.05 p.p.m. (S), relative integral 4 and 7.98 p.p.m. (S) relative integral 1.

Compound I was further identified by its reaction with ethanol and triethylamine which provides II in 90% yield and by its reaction with NaAc in acetonitrile giving NaCl and III in 90% yield.

The title compound is being subjected to further experiments.

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