

SYNTHESIS OF 2-CHLORO-1,3-BENZODIOXOLE

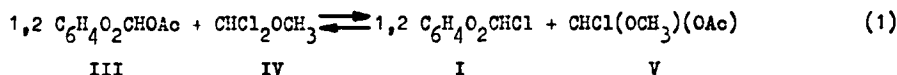
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The stability of 2-chloro-1,3-dioxolanes and of the analogous dialkoxyalkyl chlorides has been given considerable attention during the last decade¹⁻¹³. Following the considerations given by J.W. Scheeren⁹ one should expect 2-chloro-1,3-benzodioxole (I) to be a reasonable stable compound in contrast with the recent statement of H. Gross and B. Costisella¹⁰. 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-benzodioxoles¹⁰⁻¹¹. 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 PCl₅ in an earlier attempt¹², they concluded compound I to be "nicht existenzfähig". (Instead of the monochloro compound the dichloro compound 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 PCl₅.



Reaction (1) is made irreversible by the decomposition of the highly unstable V¹⁶.



Since it was presumed that radical substitutions were responsible for the disagreement between the considerations of Scheeren⁹ and the experiments of Gross and Costisella¹⁰, 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 (N₂ 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 CCl₄ 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.

References

1. H.W. Post and E.R. Erickson, J.Org.Chem. **1**, 231 (1936)
2. A. Magnani and S.M. Elvain, J.Am.Chem.Soc. **60**, 2210 (1938)
3. H. Baganz and L. Domaschke, Chem.Ber. **91**, 653 (1958)
4. S. Hünig, Angew.Chem. **76**, 400 (1964)
5. H. Gross and E. Hßft, Z.Chem. **4**, 417 (1964)
6. H. Gross and J. Freiberg, Chem.Ber. **100**, 3777 (1967)
7. J. Jonas, T.P. Forrest, M. Kratochvil and H. Gross, J.Org.Chem. **33**, 2126 (1968)
8. H. Gross, J. Freiberg and B. Costisella, Chem.Ber. **101**, 1250 (1968)
9. J.W. Scheeren, Tetrahedron Letters **54**, 5613 (1968)
10. H. Gross and B. Costisella, Liebigs Ann.Chem. **720**, 146 (1968)
11. Mannosuke Arai, Bull.Chem.Soc. Japan **35**, 1272 (1962)
12. H. Gross, A. Rieche and E. Hßft, Chem.Ber. **94**, 544 (1961)
13. H. Gross and J. Rusche, Chem.Ber. **99**, 2625 (1966)
14. J.W. Scheeren, A.P.M. van der Veek and W. Stevens, Rec.Trav.Chim. **88**, 195 (1969)
15. A.P.M. van der Veek, forthcoming Thesis, Leiden
16. A. Rieche and H. Gross, Chem.Ber. **92**, 83 (1959)
17. A. Rieche, H. Gross and E. Hßft, Chem.Ber. **93**, 88 (1960)
18. H. Laato, Suomen Kemistilehti B **32**, 66 (1959)