SYNTHESIS OF 4-CHLOROTETRAHYDROPYRANS BY THE REACTION OF DI(CHLOROMETHYL) ETHER WITH ALKYL HALIDES

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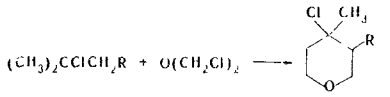
We have found that the reaction of tertiary alkyl chlorides with di(chloromethyl) ether leads to 4-chlorotetrahydropyrans. The reaction takes place readily both in the presence of a solvent and without one under the influence of Friedel–Crafts catalysts (0.5-1% of $ZnCl_2$, $FeCl_3$, $SnCl_4$, etc.). To prevent the formation of telomeric products, the reaction is best performed in ether at 30-40°C. The structure of the compounds obtained was shown by IR spectroscopy (absence of the absorption of a C=C bond), by elementary analysis, and by independent synthesis.



4-Chloro-4-methyltetrahydropyran, yield 53%, bp 43°C (9 mm), d_4^{20} 1.0742, n_D^{20} 1.4580. Found, %: Cl 26.4. MR_D 34.17. $C_6H_{11}ClO$. Calculated, %: Cl 26.6. MR_D 34.22. The same compound [bp 45°C (10 mm), n_D^{20} 1.4590] was obtained by the chloromethylation of methallyl carbinol. According to GLC (column 420 cm long, 7% of PEG-1500 on Chromaton, temperature 130 and 150°C, rate of flow of the carrier gas, nitrogen, 40-60 ml min) the two samples were identical.

4-Chloro-3,4-dimethyltetrahydropyran, yield 40%, bp 76-77°C (22 mm), d_4^{20} 1.040, n_D^{20} 1.4590. Found, %: Cl 23.9. MR_D 39.04. $C_7H_{11}ClO$. Calculated, %: Cl 23.9. MR_D 38.79.

Under the conditions described, primary and secondary alkyl halides give mainly high-boiling telomeric products.

LITERATURE CITED

1. E. Hahschke, Chem. Ber., 88, 1053 (1955).

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