LETTERS
TO THE EDITORSynthesis of Di(1,1,3-trihydroperfluoropropoxy)methane
and Di(1,1,3-trihydroperfluoropropoxy)ethane

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The simplest fluorine-containing acetals like di(2-fluoroethoxy)methane and di(2-fluoroethoxy)ethane possess zoocidal and insecticidal activities [1]. They are less toxic as distinct from the chloroderivative analogs. In this connection the development of the synthesis methods of fluorine-containing acetals remains actual.

We considered synthesis of such acetals as di(1,1,3-trihydroperfluoropropoxy)methane **I** and di(1,1,3-trihydroperfluoropropoxy)ethane **II**.

The synthesis of acetal **I** was accomplished by the reaction of 1,1,3-trihydroperfluoropropanol **III** with paraformaldehyde in the presence of 96% sulfuric acid at room temperature in 20–24 h. Yield of acetal **I** was 27%. At the use of dry hydrogen chloride the yield of **I** increases to 43%. The notable increase in the yield of acetal **I** is probably due to α -chloroether formation as an intermediate compound followed by its reaction with the next molecule of polyfluorinated alcohol.

To test this assumption we carried out the synthesis of acetal **II** by the reaction of 1-chloro-1-(1,1,3-trihydroperfluoropropoxy)ethane **IV** with polyfluorinated alcohol **III**.

The yield of acetal **II** obtained by various methods varied as follows:

- acetic aldehyde + alcohol **III**, sulfuric acid, 14.1%;
- acetic aldehyde + alcohol **III**,
- dry hydrogen chloride, 37.5%;
- α -chloroether **IV** + alcohol **III**, 60.7%.

Therefore, the most effective approach to polyfluorinated acetals is the reaction of α -chloroethers with polyfluorinated alcohols. Evidently the optimum conditions of α -chloroethers formation may be selected (without isolation of the α -chloroethers) varying the amount of added HCl.

1,1-Di(1',1',3-trihydroperfluoropropoxy)methane (I). To a solution of 13.2 (0.01 mol) g of 1,1,3-trihydroperfluoropropanol **III** in 30 ml of chloroform was added 1.5 g (0.05 mol) of paraformaldehyde at room temperature. The dry hydrogen chloride was bubbled through this mixture till the dissolution of the paraformaldehyde. After the reaction mixture separated in two layers the water layer was rejected. The organic layer was dried with calcium chloride. Hydrogen chloride was removed by flushing with dry nitrogen. Then the solvent was removed and the residue was distilled in a vacuum. Yield 6.0 g (43.0%), bp 58–59°C (5 mm Hg), n_D^{20} 1.3370, d_4^{20} 1.486. Found, %: C 30.75; H 2.51; F 55.16. $\text{C}_7\text{H}_8\text{O}_2\text{F}_8$. Calculated, %: 30.43; 2.54; 55.07.

1,1-Di(1',1',3-trihydroperfluoropropoxy)ethane (II). To a solution of 9.7 (0.05 mol) g of 1-chloro-1-(1',1',3-trihydroperfluoropropoxy)ethane in 50 ml of dry hexane cooled to 0°C was added 6.6 g (0.05 mol) of trihydroperfluoropropanol in 20 ml of dry hexane. To remove the liberating hydrogen chloride we passed dry nitrogen gradually increasing the temperature to 30°C under stirring for 3 h. After the removal of the solvent in a vacuum the residue was distilled. Yield 8.8%, bp 61–62°C (5 mm Hg), n_D^{20} 1.3420, d_4^{20} 1.4058. Found, %: C 33.06; H 3.43; F 52.21. $\text{C}_8\text{H}_{10}\text{O}_2\text{F}_8$. Calculated, %: C 33.10; H 3.45; F 52.41.

REFERENCES

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