

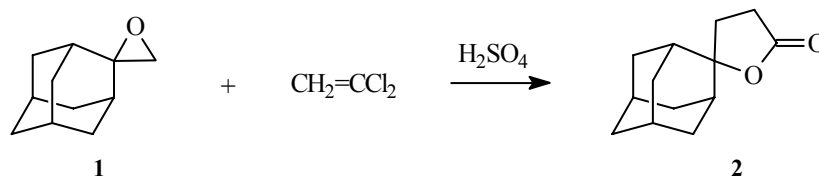
LETTERS TO THE EDITOR

SYNTHESIS OF LACTONE FROM ADAMANTANE-2-SPIRO-2'-OXIRANE

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In the Bott reaction [1], alcohols, their esters and olefins are used as the sources of the carbenium ions reacting with 1,1-dichloroethylene. With the aim of determining the ability of compounds of other classes to react with 1,1-dichloroethylene, we have studied the reaction of the latter with adamantane-2-spiro-2'-oxirane (**1**) in concentrated sulfuric acid, as a result of which we obtained adamantane-2-spiro-2-tetrahydro-5'-furanone (**2**). Under the reaction conditions, obviously oxirane **1** cannot be rearranged to aldehyde, and alkene is added to the least substituted carbon atom of the heterocycle, which is probably connected with steric hindrances and participation of the protonated form of oxirane in the reaction. Steric hindrances can also explain the fact that lactone **2** formed does not react further with olefin. Along with lactone **2**, a mixture is also formed of chlorinated derivatives of adamantane that is difficult to separate. In the ^1H NMR spectrum of compound **2**, we observe nonequivalence of the methylene groups of the heterocycle. This is probably connected with deviation of the methylene group adjacent to the adamantane moiety from the plane formed by the remaining four atoms of the heterocycle, which is typical of five-membered lactones and allows us to study, for example, their enantiomerism [2].



Adamantane-2-spiro-2'-tetrahydro-5'-furanone. 1,1-Dichloroethylene (1 ml, 12 mmol) and then solution of adamantane-2-spiro-2'-oxirane [3] (2 g, 12 mmol) in 1,1-dichloroethylene (9 ml, 110 mmol), at a temperature no higher than 5°C , were added dropwise with stirring to concentrated sulfuric acid (30 ml, 580 mmol) cooled down to 0°C . The mixture was held with cooling for 1 h, poured onto ice, and neutralized with 20% solution of sodium hydroxide up to pH 5; then the products were extracted with hexane. After chromatographing on silica gel (hexane as the eluent) and crystallization from hexane, 0.71 g (28%) of product were isolated; mp $111\text{--}112^\circ\text{C}$. IR spectrum (Shimadzu FTIR-8400S, KBr), ν , cm^{-1} : 1761 (C=O), 1245 (C–O),

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1206 (C–O). ¹H NMR spectrum (Tesla BS-567A, 100 MHz, CDCl₃), δ, ppm (*J*, Hz): 1.6-2.0 (14H, m); 2.20 (1H, dd, *J* = 7.3 and *J* = 1.8); 2.29 (1H, dd, *J* = 9.2 and *J* = 3.0); 2.60 (1H, dd, *J* = 9.2 and *J* = 3.0); 2.69 (1H, dd, *J* = 7.3 and *J* = 1.8). Found, %: C 75.57; H 8.86. C₁₃H₁₈O₂. Calculated, %: C 75.69; H 8.80.

REFERENCES

1. K. Bott, *Angew. Chem.*, **77**, 967 (1965).
2. A. F. Beecham, *Tetrahedron Lett.*, **32**, 3591 (1968).
3. A. K. Shiryayev and I. K. Moiseev, *Zh. Obshch. Khim.*, **58**, 1680 (1988).