SYNTHESIS OF 1-METHYL-1-METHOXY-2,2-DICHLOROCYCLOPROPANE

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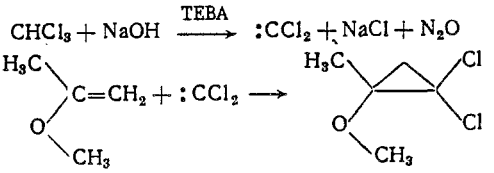
gem-Dichlorocyclopropane derivatives are of great interest as promising biologically active compounds and intermediates in organic synthesis [3]. In the present work we examined the possibility of preparing a gem-dichloropropane compound from 2-methoxypropene (2-MTP), one of the large tonnage products of the chemical pharmaceutical industry. This type of derivative has not been described previously in the literature; based on general expectations it can be assumed that their use for the pharmaceutical industry requirements is promising [5, 6]. The preparation of 1-methyl-1-methoxy-2,2-dichlorocyclopropane (MMCP) was based on the generation of carbenes in a two-phase system [4, 7]; the reaction can be described by the following scheme.



EXPERIMENTAL

The synthesis was carried out in a four-necked flask, fitted with stirring device, reflux condenser, a dropping funnel and a thermometer. The cyclopropanylation reaction was carried out by a method proposed previously in [7], whereby first methylene chloride, 2-MTP, an aqueous solution of sodium hydroxide, triethylbenzylammonium chloride (TEBA) and ethanol were charged into the reactor. The mixture was then brought with stirring up to 40°C. Chloroform was added dropwise at this temperature in the course of 30 min, and the reaction was carried out.

At the end of the reaction, the mixture was treated with diethyl ether. The extract was separated and dried over calcium chloride, and the organic layer was then fractionated at reduced pressure in a nitrogen atmosphere.

The course of the reaction was followed using the GLC method, both from the loss of the initial 2-MTP and from the accumulation of its cyclopropane derivative MMCP. The conversion of 2-MTP was monitored by a method described previously in [1, 2]. The end product, MMCP was determined on a LKhM-8 MD apparatus with a flame-ionization detector, equipped with a 3 m × 3 mm steel capillary column. The carrier was chromaton NAW-HMDS, 0.125 mesh, and the stationary phase was SF-30 (5%).

It was shown experimentally that MMCP is formed in the course of the first 3 h from the moment of the introduction of chloroform into the reactor. A further extension of the duration of the process does not lead to increase in the yield of MMCP. The maximal yield of the cyclopropane derivative is 89.6%.

1-Methyl-1-methoxy-2,2-dichlorocyclopropane (MMCP) is a transparent liquid, bp 58°C/95 mm Hg. Its structure was confirmed by $^1H_1$ NMR spectroscopy. The spectrum was run at 27°C on a "Varian XL-100A" spectrometer with a working frequency of 100 MHz at 27°C, using TMS as internal standard. PMR spectrum (CCl_4), δ, ppm: 1.32 (3H, s), 2.12 (2H, s), 3.48 (3H, s).

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