PREPARATION OF DICYCLOBUTYLIDENE BY THE DISPROPORTIONATION OF METHYLENECYCLOBUTANE

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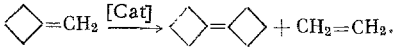
UDC 541.124:542.91:547.513

The disproportionation reaction has been widely studied for open chain olefins, and also cyclic olefins and dienes [1]. On the example of methylenecyclobutane (MCB) we were the first to show that carbocycles containing a semicyclic double bond can undergo disproportionation:



This opens up a new path for the synthesis of various bi- and polycyclic hydrocarbon systems. As catalysts we tested the oxides of Mo, W and Re. A very effective catalyst for the disproportionation of MCB proved to be Re_2O_7/Al_2O_3. The reaction was run in the liquid phase at 30-35°C, with a continuous removal of the ethylene, in a static system that had been previously purged with argon. In 20 h the yield of dicyclobutylidene (I) reached 60% (isolated in a purity of 97% by fractional distillation); bp 41° (12 mm); n_D^{20} 1.4835; d_4^{20} 0.8704. Found: C 88.36; H 11.34%; mol. wt. 107.5 (cryoscopically in benzene); bromine number 149; MR 35.24. C_8H_{12}. Calculated: C 88.88; H 11.12%; mol. wt. 108; bromine number 148; MR 35.46.

The NMR spectrum (60 MHz) of compound (I) contained a triplet with δ 2.5 ppm, which corresponds to the α-protons, and a multiplet with δ 1.9 ppm, which corresponds to the β-protons; the ratio of the intensities of these signals was 2 : 1.

The hydrogenation of (I) in pentane over solution Pt/C (25°, 4 h) gave dicyclobutyl in 97% yield; bp 136-139°; n_D^{20} 1.4512. NMR spectrum: multiplet at 1-2.5 ppm, which corresponds to the protons of the CH and CH_2 groups of 4-membered rings.

LITERATURE CITED

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A. V. Topchiev Institute of Petrochemical Synthesis, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1429, June, 1973. Original article submitted February 19, 1973.