

LETTERS  
TO THE EDITOR

## Reductive Dehalogenation of 1,3-Dibromoadamantane by Sodium Methoxide in Methanol

M. Yu. Skomorokhov and Yu. N. Klimochkin

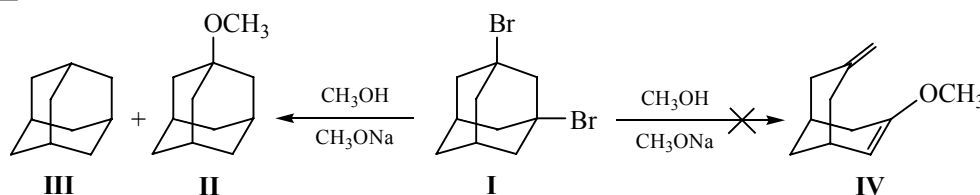
Samara State Technical University, ul. Molodogvardeiskaya 244, Samara, 443010 Russia  
e-mail: orgchem@samgtu.ru

Received April 18, 2011

DOI: 10.1134/S1070363211090325

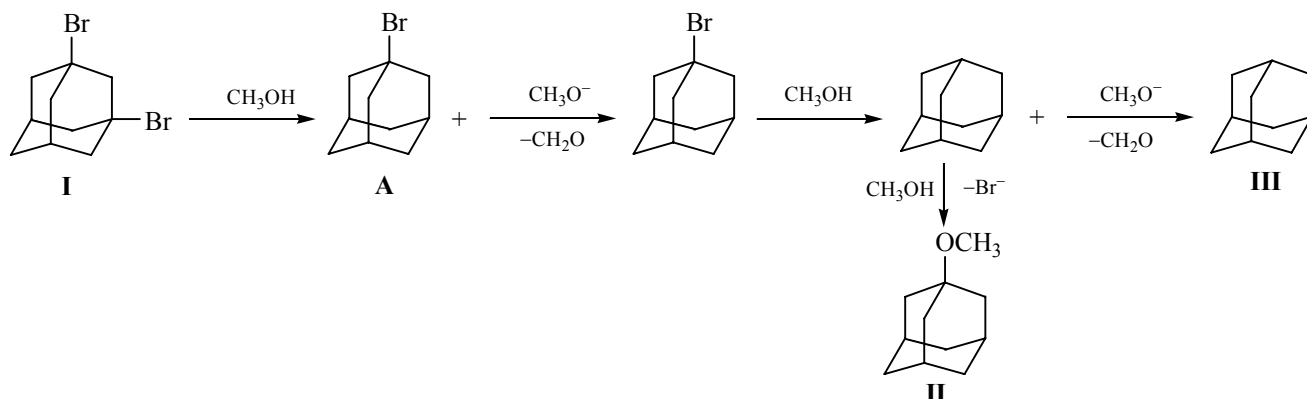
The reaction of 1,3-dihaloadamantanes with glycols in the presence of a strong base have been found to give vinyl ethers and spirodioxolanes of bicycle-[3.3.1]nonane series [1]. Aiming to synthesize new 3-alkoxy-7-methylenebicyclo[3.3.1]non-2-ene, we studied the reaction of 1,3-dibromadamantane **I** with the primary alcohols in the presence of a strong base.

The reaction of 1,3-dibromadamantane with 30% solution of sodium methoxide in methanol at 175°C affords a mixture of 1-methoxyadamantane **II** and adamantane **III** (88 and 12%, respectively, according to GLC). The target 3-methoxy-7-methylenebicyclo[3.3.1]non-2-ene **IV** was not found in the reaction products.



The formation of 1-methoxyadamantane proceeds probably via the stage of 3-bromoadamant-1-ylcarbenium ion **A** formation. This ion is highly reactive due to the negative inductive effect of the bromine atom and is able to detach a hydride ion from the methoxy anion to form the 1-bromoadamantane. The latter is converted into the methoxyadamantane **II** by the  $\text{S}_{\text{N}}1$  reaction. Adamantane **III** formation is probably due to the elimination of the hydride ion from

the methoxide anion formed at the solvolysis of 1-bromoadamantane with adamant-1-ylcarbenium ion. The relative ease of the elimination of the hydride ion from the methoxide anion may be due to the fact that the latter forms a stable neutral molecule of formaldehyde. The intermolecular hydride transfer in a basic media is very rare. Only one example of such transformation of adamantane derivatives was reported [2].



Dibromide **I** does not react with ethanol, 1-butanol, and benzyl alcohol at 175°C in the presence of sodium alkoxide.

To a solution of 28 g (1.22 mol) of sodium in 200 ml of methanol was added 84 g (0.28 mol) of 1,3-dibromoadamantane **I**. The mixture was heated in a pressure reactor at 175°C for 24 h, poured into water, and extracted with chloroform. The organic layer was washed with water, dried over anhydrous sodium sulfate, and concentrated. The residue was purified by the column chromatography on silica gel eluting with petroleum ether to give compounds **II** and **III**.

**Adamantane (III)**. Yield 3.6 g (9%), mp 265–267°C (mp 266–268°C [3]).

**1-Methoxyadamantane (II)**. Yield 5.28 g (61%), bp 90–92°C (5 mm Hg),  $n_D^{20}$  1.4990 ( $n_D^{20}$  1.4971 [4]).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.62 s (6H, Ad), 1.73 s (6H, Ad), 2.13 s (3H, Ad), 3.32 s (3H, OCH<sub>3</sub>). Mass

spectrum,  $m/z$  ( $I_{\text{rel}}$ , %): 166 [ $M^+$ ] (24), 135 (10), 109 (100), 40 (20).

The NMR spectra were recorded on a Bruker AC-200 spectrometer operating at 200 MHz (CDCl<sub>3</sub>). The mass spectra (EI, 70 eV) were registered on a Finnigan MAN JNCOS50 spectrometer. The GLC analysis was carried out on a Tsvet-100 chromatograph with a flame ionization detector and 25 m quartz capillary column using a stationary phase SE-30, carrier gas – helium.

#### REFERENCES

1. Skomorokhov, M.Yu. and Klimochkin, Yu.N., *Zh. Org. Khim.*, 2001, vol. 37, p. 1096.
2. Yurchenko, A.G., Isaev, S.D., Murzinova, Z.R., and Chernyakhovskaya, E.E., *Zh. Org. Khim.*, 1972, vol. 8, p. 2617.
3. Alper, P., *J. Org. Chem.*, 1977, no. 42, p. 3522.
4. Baklan, V.F., Hil'chevskii, A.N., and Kukhar', V.P., *Zh. Org. Khim.*, 1984, vol. 20, p. 2238.