

SHORT  
COMMUNICATIONS

## New Fragmentation of 1,3-Dibromoadamantane

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Received May 5, 2000

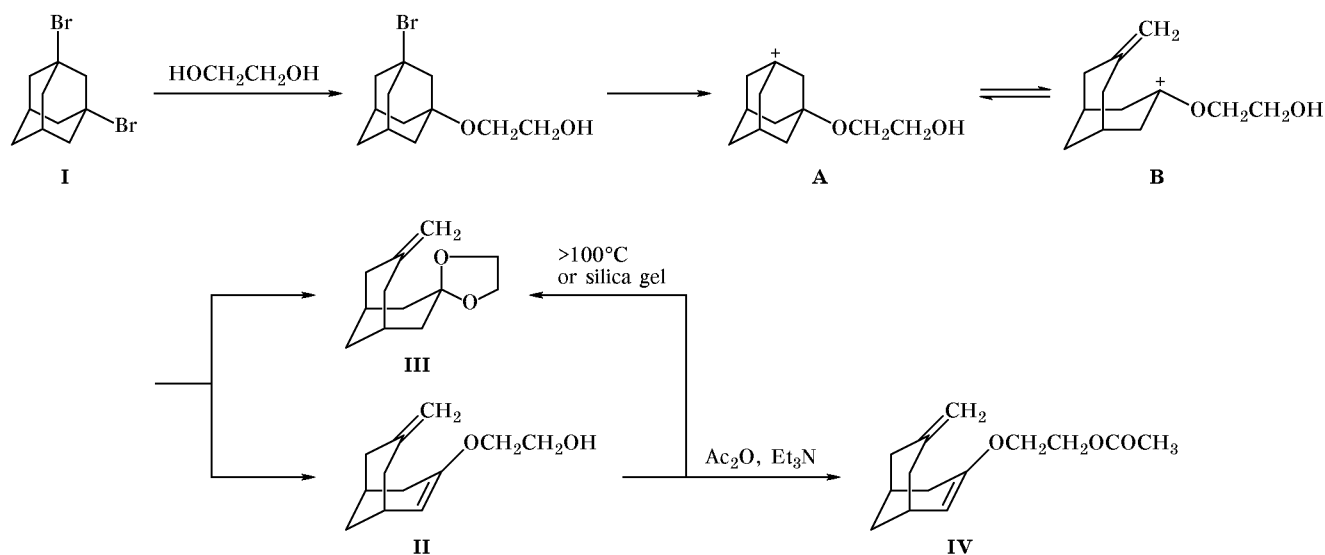
It is known that tricyclic 1,3-dibromoadamantane (**I**) can be converted into 7-methylenebicyclo[3.3.1]nonan-3-one [1]. We have found that in the presence of a strong base in ethylene glycol at 200°C dibromoadamantane (**I**) gives rise to a mixture of 3-(2-hydroxyethoxy)-7-methylenebicyclo[3.3.1]non-2-ene (**II**) and 3,3-ethylenedioxy-7-methylenebicyclo[3.3.1]nonane (**III**). The reaction is likely to involve intermediate formation of adamantylcarbenium ion **A** which undergoes isomerization according to Grob [2], yielding cation **B**. The latter is stabilized through formation of compounds **II** and **III** (Scheme 1). As might be expected [3], vinyl ether **II** is converted into 1,3-dioxolane derivative **III** on distillation or during chromatography on silica gel. We succeeded in isolating only 3-(2-acetoxyethoxy)-7-methylenebicyclo[3.3.1]non-2-ene (**IV**).

**Ring opening in 1,3-dibromoadamantane.** To a solution of 25 g (1.09 mol) of sodium in 500 ml

of ethylene glycol we added 70 g (0.238 mol) of dibromoadamantane **I**. The mixture was refluxed for 3 h, poured into water, and extracted with chloroform. The extract was washed with water, dried over anhydrous sodium sulfate, and evaporated. The residue was dissolved in 100 ml of toluene, 22 ml (0.165 mol) of triethylamine and 14 ml (0.137 mol) of acetic anhydride were added, and the mixture was refluxed for 1 h and washed with a 5% solution of sodium carbonate and water. The solvent was distilled off, and the residue was distilled under reduced pressure.

**3,3-Ethylenedioxy-7-methylenebicyclo[3.3.1]nonane (**III**)** (first fraction). Yield 5 g (11%), bp 99–100°C (1 mm),  $n_D^{20}$  1.5071. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1660, 1110, 890.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.25–2.35 m (12H), 3.77 m (4H,  $\text{OCH}_2\text{CH}_2\text{O}$ ), 4.66 s (2H,  $=\text{CH}_2$ ). Mass spectrum,  $m/z$  ( $I_{\text{rel}}$ , %): 194 [ $M$ ] $^+$  (17), 139 (100), 106 (41), 92 (33). Found, %: C 79.11; H 9.40.  $\text{C}_{12}\text{H}_{18}\text{O}_2$ . Calculated, %: C 79.19; H 9.34.

Scheme 1.



**3-(2-Acetoxyethoxy)-7-methylenebicyclo[3.3.1]-non-2-ene (IV)** (second fraction). Yield 7.5 g (14%), bp 135–136°C (1 mm),  $n_D^{20}$  1.5028. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1750, 1660, 1050, 895.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.6–2.5 m (10H), 1.98 s (3H,  $\text{COCH}_3$ ), 3.73 t (2H,  $\text{OCH}_2$ ,  $J = 4.5$  Hz), 4.17 t (2H,  $\text{CH}_2\text{OAc}$ ), 4.43 s (1H, =CH), 4.62 s (1H, =CH), 4.46 d (1H,  $\text{HC}=\text{CO}$ ,  $J = 6$  Hz). Mass spectrum,  $m/z$  ( $I_{\text{rel}}$ , %): 236 [ $M$ ] $^+$  (3), 87 (100), 43 (47). Found, %: C 71.10; H 8.47.  $\text{C}_{14}\text{H}_{20}\text{O}_3$ . Calculated, %: C 71.16; H 8.53.

In a similar way, 1,3-dibromoadamantane (**I**) reacted with 1,4-butanediol in the presence of sodium alkoxide. Acetylation followed by vacuum distillation gave 10.1 g (16%) of 3-(4-acetoxybutoxy)-7-methylenebicyclo[3.3.1]non-2-ene, bp 148–149°C (1 mm),  $n_D^{20}$  1.4933. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1750, 1660, 1050, 895.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.6–2.5 m (14H), 1.98 s (3H,  $\text{COCH}_3$ ), 3.61 m (2H,  $\text{OCH}_2$ ), 4.05 m (2H,  $\text{CH}_2\text{OAc}$ ), 4.46 s (1H, =CH), 4.67 s (1H, =CH),

4.46 d (1H,  $\text{HC}=\text{CO}$ ,  $J = 6$  Hz). Mass spectrum,  $m/z$  ( $I_{\text{rel}}$ , %): 264 [ $M$ ] $^+$  (7), 149 (76), 107 (58), 43 (100). Found, %: C 72.71; H 9.20.  $\text{C}_{16}\text{H}_{24}\text{O}_3$ . Calculated, %: C 72.69; H 9.15.

The IR spectra were recorded on an IKS-22 spectrometer from samples prepared as thin films. The  $^1\text{H}$  NMR spectra were obtained on a Bruker AC-200 instrument (200 MHz) in  $\text{CDCl}_3$  with HMDS as internal reference. The mass spectra (70 eV) were run on a Finnigan MAN JNCOS50 spectrometer.

#### REFERENCES

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