

SHORT
COMMUNICATIONS

Uncommon Reaction of 1,3-Dehydroadamantane with 3-Bromo-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one

G. M. Butov^a, V. M. Mokhov^b, G. Yu. Parshin^a, and R. U. Kunaev^a

^aVolzhskii Polytechnical Institute (Branch of the Volgograd State Technical University), Volzhskii, 404121 Russia
e-mail: vht@volpi.ru

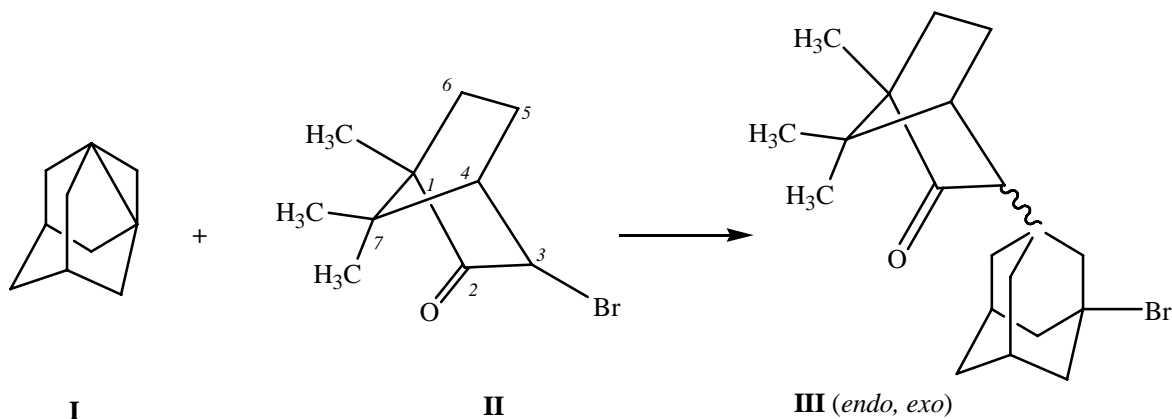
^bVolgograd State Technical University, Volgograd, Russia

Received January 26, 2007

DOI: 10.1134/S1070428007080301

We formerly established that 1,3-dehydroadamantane (**I**) reacted with compounds containing labile hydrogen atoms, in particular, attacking the α -carbon of ketones and aldehydes [1, 2]. The presence of a halogen enhanced the lability of the hydrogen attached to the carbon atom linked to the halogen, and this circumstance should facilitate the reaction at the C–H bond. However it was

established by GC-MS method that compound **I** reacted with a haloderivative of a bicyclic ketone, 3-bromo-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one (bromocamphor) (**II**), with the rupture not of the C³–H bond, but of the C³–Br bond to provide two addition products **III** at the α -carbon C³ (in a ratio \approx 1:1), m/z 364 [M]⁺. The products are presumably *endo,exo*-isomers.



The composition and structure of addition products **III** were confirmed by ¹H NMR spectra and by GC-MS method. The formation of stereoisomeric compounds **III** was proved by an appearance on a chromatogram of the corresponding peaks with close values of retention time (16.61 and 16.75 min) and by identical mass spectra of both substances. The mass spectrum lacked the ion with m/z 135 corresponding to a monosubstituted adamantyl moiety, but contained an ion with m/z 133 characteristic

of 1,3-disubstituted adamantane; ions with m/z 364, 285, and 215 testify to the presence of bromine atom in the position 3 of adamantane.

endo,exo-1,7,7-Trimethyl-3-(3-bromoadamant-1-yl)-bicyclo[2.2.1]heptan-2-one (**III**). To 2.31 g (0.01 mol) of ketone **II** under an atmosphere of dry argon was added dropwise at room temperature a solution of 1.34 g (0.01 mol) of freshly sublimed 1,3-dehydroadamantane (**I**) in 20 ml of anhydrous ethyl ether. The

solvent was distilled off, and the reaction mixture was heated at 100°C without stirring for 5 h. On completion of the process the unreacted initial compounds were removed in a vacuum, the residue was extracted with hot ethanol, and on cooling the precipitated crystals were filtered off. Yield 2.91 g (0.008 mol, 80%), colorless crystals, mp 155–157°C (EtOH). ¹H NMR spectrum (DMSO-*d*₆), δ, ppm: 0.8 s (6H, 2CH₃), 0.93 s (3H, CH₃), 1.19–1.25 m, 1.6–1.9 m, 2.1–2.3 m (20H). Mass spectrum, *m/z* (*I*_{rel}, %): 364 (17.5) [*M*]⁺, 338 (1), 285 (100) [*M*–Br]⁺, 215 (20), 133 (17.5). ¹H NMR spectrum was registered on a spectrometer Bruker DRX-500, operating frequency 500 MHz Chromato mass spectra

were obtained on a GC-MS instrument Hewlett Packard GC 5890 Series II/MSD 5972 Series.

The study was carried out under a financial support of the Federal Agency on Education of the Russian Federation, program “Development of the Research Potential of the High School”, 2005. (subprogram 3, part 3, project cod 4507).

REFERENCES

1. No, B.I., Butov, G.M., Mokhov, V.M., and Parshin, G.Yu., *Zh. Org. Khim.*, 2002, vol. 38, p. 316.
2. No, B.I., Butov, G.M., Mokhov, V.M., and Parshin, G.Yu., *Zh. Org. Khim.*, 2002, vol. 38, p. 1428.