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SHORT COMMUNICATIONS

Halogen Addition to Esters of 7-Methylenebicyclo[3.3.1]non-2-en-3-ol

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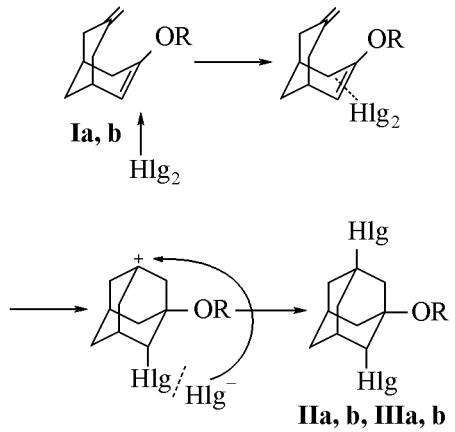
Electrophilic addition of halogens to pseudo-conjugated π–π-systems is sufficiently well studied by the example of bicyclo[3.3.1]nonane derivatives that via transannular cyclization afford 1,3-disubstituted adamantanes [1, 2].

We found that esters of 7-methylenebicyclo[3.3.1]-non-2-en-3-ol **Ia, b** rapidly reacted with halogens (Br_2, I_2) in tetrachloromethane yielding 1,4-dihalo-3-substituted adamantanes **II–IIIa, b**. The analysis of ^{1}H NMR spectra of compounds obtained revealed that the halogens added to esters **Ia, b** to afford exclusively 1,4-dihalides **IIa, b, IIIa, b** in Z-configuration.



IIa, b, IIIa, b

R = $(CH_2)_2OAc$ (**a**), $(CH_2)_2OC(O)PhNO_2$-*p* (**b**); Hlg = I (**II**), Br (**III**).

(*Z*)-1-(2-Acetoxyethoxy)-2,5-diiodoadamantane (IIa). To 0.7 g (3 mmol) of compound **Ia** in 15 ml of tetrachloromethane at 20°C was added 0.79 g (3.1 mmol) of iodine, the mixture was stirred for 40 min, treated with water solution of Na_2SO_3, the organic layer was washed with water, dried on anhydrous Na_2SO_4, the solvent was distilled off. We obtained 1 g (70%) of compound **IIa**, n_D^{20} 1.6752. IR spectrum, cm^{-1}: 1750, 1240, 1050. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.62–2.71 m (12H, Ad), 2.08 s (3H, $COCH_3$), 3.73 m (2H, $COCH_2$), 4.17 m (2H, CH_2OAc), 4.61 s (1H, ICH). Mass spectrum, *m/z* (I_{rel}, %): 363 [*M*–127]$^+$ (2.4), 91 (11.5), 87 (100), 43 (31.2). Found, %: C 34.19; H 4.06. $C_{14}H_{20}I_2O_3$. Calculated, %: C 34.31; H 4.11.

(*Z*)-2,5-Diiodo-1-[2-(4-nitrobenzoyloxy)ethoxy]-adamantane (IIb) was obtained by a similar procedure. Yield 60%, mp 141–142°C (hexane). IR spectrum, cm^{-1}: 1735, 1600, 1520, 1240, 1050. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.61–2.83 m (12H, Ad), 3.79 m (2H, $COCH_2$), 4.43 m [2H, $CH_2OC(O)$], 5.02 s (1H, ICH), 8.2–8.4 m (4H). Mass spectrum, *m/z* (I_{rel}, %): 470 [*M*–127]$^+$ (3.2), 195 (54.3), 194 (100), 149 (63.2), 104 (41.6). Found, %: C 38.09; H 3.56; N 2.31. $C_{19}H_{21}I_2NO_5$. Calculated, %: C 38.21; H 3.56; N 2.35.

(*Z*)-3-(2-Acetoxyethoxy)-1,4-dibromoadamantane (IIIa) was obtained by reaction of compound **Ia** with bromine (–5°C, 10 min). The reaction product was isolated by chromatography on silica gel. Yield 35%, n_D^{20} 1.6332. IR spectrum, cm^{-1}: 1750, 1240, 1050. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.62–2.54 m (12H, Ad), 2.07 s (3H, $COCH_3$), 3.63 m (2H, $COCH_2$), 4.19 m (2H, CH_2OAc), 4.39 d (1H, BrCH, *J* 17 Hz). Mass spectrum, *m/z* (I_{rel}, %): 396 [*M*]$^+$ (1.2), 107 (91.1), 84 (100), 43 (60.0). Found, %: C 42.29; H 5.16. $C_{14}H_{20}Br_2O_3$. Calculated, %: C 42.45; H 5.09.

(*z*)-1,4-Dibromo-3-[2-(4-nitrobenzoyloxyethoxy]-adamantane (IIIb) was obtained in a similar way. Yield 23%, mp 149–152°C (hexane). IR spectrum, cm^{-1}: 1735, 1600, 1520, 1240, 1050. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.61–2.53 m (12H, Ad), 3.71 m (2H, $COCH_2$), 4.46 m [2H, $CH_2OC(O)$], 4.83 d (1H, BrCH, *J* 17 Hz). Mass spectrum, *m/z* (I_{rel}, %): 503 [*M*]$^+$ (0.5), 195 (50.2), 194 (100), 149 (62.0), 104 (35.7). Found, %: C 45.26; H 4.17; N

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2.73. $C_{19}H_{21}Br_2NO_5$. Calculated, %: C 45.35; H 4.21; N 2.78.

IR spectra were recorded on spectrophotometer IKS-22, ^1H NMR spectra were registered on spectrometer Bruker AC-200 (200 MHz, internal reference HMDS). Mass spectra were measured on Finnigan MAN JNCOS 50 instrument, ionizing electrons energy 70 eV.

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