

SHORT
COMMUNICATIONS

Cyclization of 7-Methylene-3-[2-(4-nitrobenzoyloxy)ethoxy]-bicyclo[3.3.1]non-2-ene in the Presence of Acids

M. Yu. Skomorokhov and Yu. N. Klimochkin

Samara State Technical University, ul. Galaktionovskaya 141, Samara, 443010 Russia
e-mail: orgchem@sstu.samara.ru

Received November 23, 2000

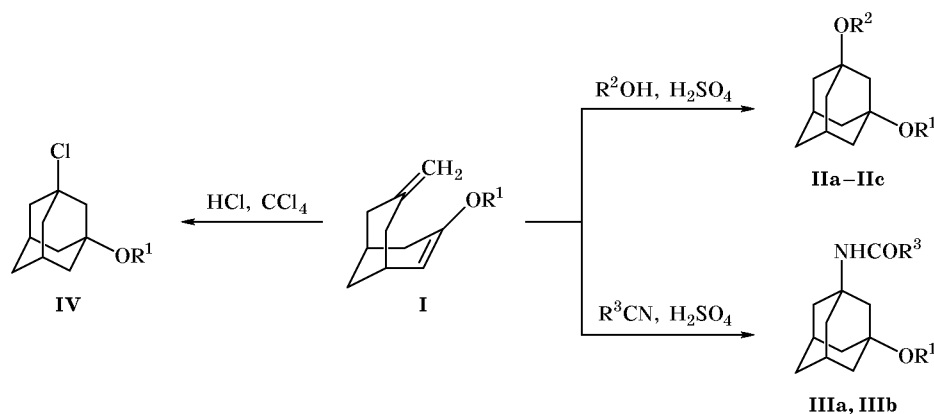
It is well known that transannular cyclization of carbonyl bicyclo[3.3.1]nonane derivatives by the action of weak and strong acids [1, 2] leads to formation of 1,3-disubstituted adamantanes. We have found that 7-methylene-3-[2-(4-nitrobenzoyloxy)ethoxy]bicyclo[3.3.1]non-2-ene (**I**) is extremely unstable in the presence of traces of acids. It is rapidly converted into adamantane derivatives **IIa–IIc**, **IIIa**, and **IIIb** in nucleophilic solvents in the presence of sulfuric acid. Vinyl ether **I** is also capable of reacting with hydrogen chloride in carbon tetrachloride to afford 1-chloro-3-[2-(4-nitrobenzoyloxy)ethoxy]adamantane (**IV**) (Scheme 1).

7-Methylene-3-[2-(4-nitrobenzoyloxy)ethoxy]bicyclo[3.3.1]non-2-ene (I) was synthesized by the procedure reported in [3]. mp 114–116 (from MeOH). IR spectrum, ν , cm^{-1} : 1735, 1660, 1600, 1520, 1240, 1050, 895. ^1H NMR spectrum (DMSO- d_6), δ , ppm: 1.51–2.55 m (10H), 4.03 t (2H, COCH_2 , $J = 4$ Hz), 4.53 d (H, $\text{HC}=\text{CO}$, $J = 6$ Hz), 4.61 t (2H, CH_2OCO ,

$J = 4$ Hz), 4.64 s (1H, $=\text{CH}_2$), 4.72 s (1H, $=\text{CH}_2$), 8.19 d (2H, H_{arom} , $J = 9$ Hz), 8.36 d (2H, H_{arom} , $J = 9$ Hz). Mass spectrum, m/z (I_{rel} , %): 343 [M]⁺ (15.4), 288 (14.4), 194 (100), 150 (70.6), 104 (54). Found, %: C 66.43; H 6.21; N 4.01. $\text{C}_{19}\text{H}_{21}\text{NO}_5$. Calculated, %: C 66.46; H 6.16; N 4.08.

1-Hydroxy-3-[2-(4-nitrobenzoyloxy)ethoxy]adamantane (IIa). Concentrated sulfuric acid, 0.01 ml, was added at 10°C to a mixture of 0.5 g (1.5 mmol) of ether **I** and 30 ml of 80% dioxane. The mixture was kept for 10 min, poured into water, and extracted with chloroform. The extract was washed with a solution of sodium carbonate, dried over anhydrous Na_2SO_4 , and evaporated, and the residue was recrystallized from benzene–cyclohexane. Yield 0.27 g (50%), mp 130–132°C. IR spectrum, ν , cm^{-1} : 3720, 1735, 1600, 1520, 1240, 1050. ^1H NMR spectrum (CDCl_3), δ , ppm: 1.03 s (1H, OH), 1.31–2.31 m (14H, Ad), 3.71 t (2H, AdOCH_2 , $J = 4$ Hz), 4.41 t (2H, CH_2OCO , $J = 4$ Hz), 8.19 d (2H, H_{arom} ,

Scheme 1.



I–IV, $\text{R}^1 = (\text{CH}_2)_2\text{OC}(\text{O})\text{C}_6\text{H}_4\text{NO}_2-4$; **II**, $\text{R}^2 = \text{H}$ (a), Me (b), Ac (c); **III**, $\text{R}^3 = \text{Me}$ (a), Ph (b).

$J = 9$ Hz), 8.36 d (2H, H_{arom} , $J = 9$ Hz). Mass spectrum, m/z (I_{rel} , %): 361 [M]⁺ (3.5), 194 (31.5), 151 (100), 93 (30). Found, %: C 63.10; H 6.35; N 3.95. $C_{19}H_{23}NO_6$. Calculated, %: C 63.15; H 6.41; N 3.88.

1-Methoxy-3-[2-(4-nitrobenzoyloxy)ethoxy]adamantane (IIb) was synthesized by a similar procedure using methanol as solvent. Yield 0.4 g (74%), n_D^{20} 1.5448. IR spectrum, ν , cm^{-1} : 1735, 1600, 1520, 1240, 1100, 1050. ^1H NMR spectrum (CDCl_3), δ , ppm: 1.30–2.33 m (14H, Ad), 3.18 s (3H, CH_3), 3.71 t (2H, AdOCH_2 , $J = 4$ Hz), 4.41 t (2H, CH_2OCO , $J = 4$ Hz), 8.19 d (2H, H_{arom} , $J = 9$ Hz), 8.36 d (2H, H_{arom} , $J = 9$ Hz). Found, %: C 63.90; H 6.73; N 3.70. $C_{20}H_{25}NO_6$. Calculated, %: C 63.99; H 6.71; N 3.73.

1-Acetoxy-3-[2-(4-nitrobenzoyloxy)ethoxy]adamantane (IIc) was synthesized in a similar way using acetic acid as solvent. Yield 0.46 g (78%), n_D^{20} 1.5417. IR spectrum, ν , cm^{-1} : 1750, 1735, 1600, 1520, 1240, 1050. ^1H NMR spectrum (CDCl_3), δ , ppm: 1.30–2.3 m (14H, Ad), 1.89 s (3H, COCH_3), 3.67 t (2H, AdOCH_2 , $J = 4$ Hz), 4.36 t (2H, CH_2OCO , $J = 4$ Hz), 8.19 d (2H, H_{arom} , $J = 9$ Hz), 8.36 d (2H, H_{arom} , $J = 9$ Hz). Found, %: C 62.60; H 6.21; N 3.50. $C_{21}H_{25}NO_7$. Calculated, %: C 62.52; H 6.25; N 3.47.

1-Acetamido-3-[2-(4-nitrobenzoyloxy)ethoxy]adamantane (IIIa) was obtained in a similar way using acetonitrile as solvent. Yield 0.36 g (62%), mp 160–161°C (from benzene). IR spectrum, ν , cm^{-1} : 3320, 1735, 1680, 1520, 1240, 1050. ^1H NMR spectrum ($\text{DMSO}-d_6$), δ , ppm: 1.75 s (3H, COCH_3), 1.45–2.31 m (14H, Ad), 3.71 t (2H, AdOCH_2 , $J = 4$ Hz), 4.41 t (2H, CH_2OCO , $J = 4$ Hz), 7.36 s (1H, NH), 8.19 d (2H, H_{arom} , $J = 9$ Hz), 8.36 d (2H, H_{arom} , $J = 9$ Hz). Found, %: C 62.63; H 6.48; N 6.90. $C_{21}H_{26}N_2O_6$. Calculated, %: C 62.67; H 6.51; N 6.96.

1-Benzamido-3-[2-(4-nitrobenzoyloxy)ethoxy]adamantane (IIIb) was synthesized by the same procedure using benzonitrile as solvent. Yield 0.32 g (47%), mp 164–166°C (from benzene). IR spectrum,

ν , cm^{-1} : 3350, 1735, 1675, 1600, 1520, 1240, 1050. ^1H NMR spectrum ($\text{DMSO}-d_6$), δ , ppm: 1.45–2.31 m (14H, Ad), 3.71 t (2H, AdOCH_2 , $J = 4$ Hz), 4.41 t (2H, CH_2OCO , $J = 4$ Hz), 7.64 s (1H, NH), 7.35–7.78 m (5H, H_{arom}), 8.19 d (2H, H_{arom} , $J = 9$ Hz), 8.36 d (2H, H_{arom} , $J = 9$ Hz). Found, %: C 67.33; H 6.11; N 6.08. $C_{26}H_{28}N_2O_6$. Calculated, %: C 67.23; H 6.08; N 6.03.

1-Chloro-3-[2-(4-nitrobenzoyloxy)ethoxy]adamantane (IV). Dry hydrogen chloride was passed over a period of 10 min through a solution of 0.5 g (1.5 mmol) of ether **I** in 20 ml of carbon tetrachloride, maintained at 25°C. The mixture was kept for 0.5 h and poured into water, and the product was extracted into benzene. The extract was washed with a solution of sodium carbonate, dried over anhydrous sodium sulfate, and evaporated, and the residue was recrystallized from methanol. Yield 0.31 g (56%), mp 78–80°C. IR spectrum, ν , cm^{-1} : 1735, 1600, 1520, 1240, 1050, 720. ^1H NMR spectrum ($\text{DMSO}-d_6$), δ , ppm: 1.31–2.30 m (14H, Ad), 3.72 t (2H, AdOCH_2 , $J = 4$ Hz), 4.48 t (2H, CH_2OCO , $J = 4$ Hz), 8.19 d (2H, H_{arom} , $J = 9$ Hz), 8.36 d (2H, H_{arom} , $J = 9$ Hz). Found, %: C 60.15; H 5.89; N 3.68. $C_{19}H_{23}ClNO_5$. Calculated, %: C 60.08; H 5.84; N 3.69.

The IR spectra were obtained on an IKS-22 spectrometer. The ^1H NMR spectra were measured on a Bruker WM-300 instrument (300 MHz) using HMDS as internal reference. The mass spectra (70 eV) were run on a Finnigan MAN JNCOS50 spectrometer.

REFERENCES

1. Stetter, H., Tacke, P., and Gartner, J., *Angew. Chem.*, 1965, vol. 77, no. 4, p. 171.
2. Gubernatorov, V., Kogai, B., and Sokolenko, V., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, no. 5, pp. 1203–1204.
3. Skomorokhov, M.Yu. and Klimochkin, Yu.N., *Russ. J. Org. Chem.*, 2001, vol. 37, no. 7, pp. 1050–1051.