*Russian Journal of Organic Chemistry, Vol. 37, No. 4, 2001, pp. 601–602. Translated from Zhurnal Organicheskoi Khimii, Vol. 37, No. 4, 2001, pp. 635–636.*


## SHORT COMMUNICATIONS

# Xylenes Alkylation with 2-(1-Adamantylimino)-5-methyl-1,3-oxathiolane

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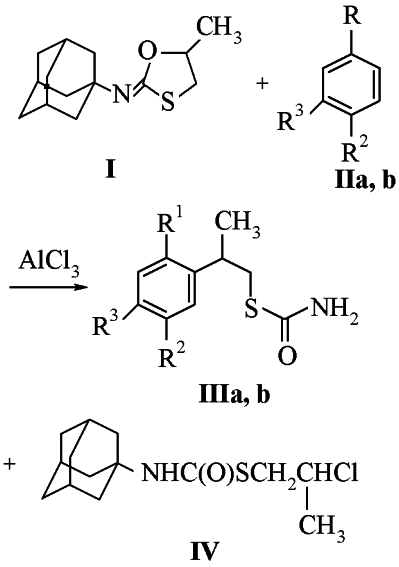
Received December 1, 2000

The 2-alkylimino-1,3-oxathiolanes are known to readily undergo methylation at imine nitrogen [1]; however they are not regarded as alkylating agents. We found that 2-(1-adamantylimino)-5-methyl-1,3-oxathiolane (**I**) could be applied to alkylation of aromatic compounds. The reaction of oxathiolane **I** with *p*- and *m*-xylene (**IIa, b**) in the presence of aluminum chloride gave rise to 2-arylpropyl thiocarbamates **IIIa, b**. The splitting of the adamantyl moiety may be ascribed to the high stability of the corresponding carbocation that alkylates the xylene present in excess. The formation of a mixture of isomeric hydrocarbons is due to probable isomerization on the aluminum chloride both of the original xylenes [2] and the adamantylxylenes. Reaction products **IIIa, b** do not suffer isomerization presumably because of complex formation at the functional group with aluminum chloride. Unlike *p*- and *m*-xylene *o*-xylene and toluene give rise to inseparable isomers mixtures (as show the corresponding $^{13}C$ NMR spectra).




$R^1 = R^2 = CH_3$, $R^3 = H$ (**a**); $R^1 = R^3 = CH_3$, $R^2 = H$ (**b**).

Iminooxathiolane **I** apparently first reacts with the hydrogen chloride present in the mixture to afford *N*-(1-adamantyl)-2-chloropropyl thiocarbamate (**IV**) which further alkylates arene with the 2-chloropropyl moiety. This assumption is confirmed by reaction of thiocarbamate **IV** with xylene giving the same reaction products as iminooxathiolane **I**; in reaction at 0°C formed only thiocarbamate **IV**.

2-(1-Adamantylimino)-5-methyl-1,3-oxathiolane (I) was obtained by procedure [3].

**2-(2,5-Dimethylphenyl)propyl thiocarbamate (IIIa).** To 10 ml (81 mmol) of p-xylene at 0–5°C was added 1.6 g (12 mmol) of aluminum chloride, and after standing for 0.5 h was added 1 g (4 mmol) of 2-(1-adamantylimino)-5-methyl-1,3-oxathiolane. Within 1 h the temperature was raised to 40°C. The reaction mixture was maintained at 40°C for 1 h, and then poured on ice. The organic layer was separated, dried with sodium sulfate, the xylene was distilled off in a vacuum, and the residue was subjected to column chromatography on silica gel (eluent cyclohexane). Yield of compound **IIIa** 0.5 g (56%), mp 98–100°C. IR spectrum (KBr, ν, $cm^{-1}$): 3330, 1640, 1605. $^1H$ NMR spectrum ($CDCl_3$, δ, ppm): 1.59 d (3H, $CH_3$, *J* 6.4 Hz), 2.60 s (6H, $2CH_3$), 3.44 m (1H, CH), 5.88 s (2H, $NH_2$), 7.30 m (3H, Ar). $^{13}C$ NMR spectrum ($CDCl_3$, $\delta_C$, ppm): 18.9 ($CH_3$), 20.4 ($CH_3$–Ar), 21.0 ($CH_3$–Ar), 35 ($CH_2$), 37.3 (CH), 126.3, 126.9, 128.8, 132.4, 135.4, 143.1, 169.5 (C=O). Mass spectrum [*m/z* ($I_{rl}$, %)]: 223 (5) $[M]^+$, 146 (82) $[M–HSCONH_2]^+$, 133 (100) $[M–CH_2SCONH_2]^+$.

**2-(2,4-Dimethylphenyl)propyl thiocarbamate (IIIb)** was prepared similarly to compound **IIIa** from

1070-4280/01/3704-0601$25.00 

10 ml of *m*-xylene. Yield 0.45 g (51%), mp 108–111°C. IR spectrum (KBr, ν, $cm^{-1}$): 3330, 1645, 1605. $^1H$ NMR spectrum ($CDCl_3$, δ, ppm): 1.54 d (3H, $CH_3$, *J* 6.4 Hz), 2.55 s (6H, $2CH_3$), 3.39 m (1H, CH), 5.81 s (2H, $NH_2$), 7.30 m (3H, Ar). $^{13}C$ NMR spectrum ($CDCl_3$, $\delta_C$, ppm): 19.3 ($CH_3$), 20.5 ($CH_3$), 20.8 ($CH_3$), 34.8 ($CH_2$), 37.4 (CH), 125.9, 126.9, 131.2, 135.4, 135.6, 140.3, 169.4 (C=O).

***N*-(1-Adamantyl)-2-chloropropyl thiocarbamate (IV).** To 10 ml of anhydrous dichloroethane at 0–5°C was added 1.6 g (12 mmol) of aluminum chloride, the mixture was left standing for 15 min, and then was added 1 g (4 mmol) of 2-(1-adamantylimino)-5-methyl-1,3-oxathiolane. The reaction mixture was maintained at 0–5°C for 6 h, and then poured on ice. The organic layer was separated, dried with sodium sulfate, dichloroethane was distilled off in a vacuum, and the residue was subjected to column chromatography on silica gel (eluent cyclohexane) Yield 0.8 g (69%), mp 129–131°C. IR spectrum (KBr, ν, $cm^{-1}$): 3290, 1650, 1520. $^1H$ NMR spectrum ($CDCl_3$, δ, ppm): 1.61 s (3H, $CH_3$), 1.74 m (6H, Ad), 1.81 m (6H, Ad), 1.91 m (3H, Ad), 3.31 d (2H, $CH_2$, *J* 6.2 Hz), 4.24 m (1H, CH), 5.27 s (1H, NH). $^{13}C$ NMR spectrum ($CDCl_3$, $\delta_C$, ppm): 23.7 ($CH_3$), 29.4 (Ad), 36.1 (Ad), 39.3 ($CH_2$), 41.8 (Ad), 54.1 (Ad), 57.3 (CHCl), 163.4 (C=O).

IR spectra were recorded on spectrophotometer IKS-22. $^1H$ and $^{13}C$ NMR spectra were registered on spectrometer JEOL EX90 at operating frequencies 90 and 22 MHz respectively; as internal reference served the solvent peak. Mass spectra were measured on spectrometer Finnigan MAN JNCOS50, ionizing electrons energy 70 eV.

The authors are grateful to Dr. P. Kong Thoo Lin, Robert Gordon University, Aberdeen, Scotland) for the help in the spectral research.

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