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LETTERS TO THE EDITOR

Reactions of Phosphorus Trihalides with 6-(Adamantan-1-yl)imidazo[2,1-*b*]thiazoles

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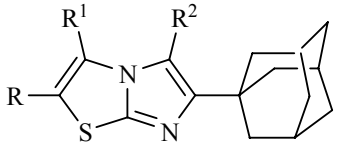
The reaction of 2-(adamantan-1-yl)imidazopyridines with phosphorus trichloride in sulfuric acid has been found to afford the corresponding (3-chloroadamantan-1-yl)imidazopyridines [1], whereas in the reaction with phosphorus tribromide, as well as with bromine, they transformed into 2-(adamantan-1-yl)-3-bromoimidazopyridine [2].

We found that 6-(adamantan-1-yl)imidazothiazoles **Ia**–**Ic** do not react with phosphorus trichloride under similar conditions. (Adamantan-1-yl)imidazothiazole **Ia** reacts with phosphorus tribromide to yield the compound **IIa**, whereas the reactions of adamantylimidazothiazoles **Ib** and **Ic** give rise to the dibromoderivatives **IIIa** and **IIIb**. Compounds **Ia**–**Ic** give the analogous products at reflux in liquid bromine. Compounds **IIa**–**IIc** were formed under milder conditions [3] in the reaction of equimolar amounts of the studied thiazoles with bromine in chloroform.



I–**III**

I, R = R^1 = R^2 = H (**a**); R = Me, R^1 = R^2 = H (**b**); R = R^2 = H, R^1 = Me (**c**); **II**, R = R^1 = H, R^2 = Br (**a**); R = Me, R^1 = H, R^2 = Br (**b**); R = H, R^1 = Me, R^2 = Br (**c**); **III**, R = Me, R^2 = Br (**a**), R = R^2 = Br, R^1 = Me (**b**).

Synthesis of (adamantan-1-yl)imidazothiazole **Ia** have been reported earlier [4]. Compounds **Ib** and **Ic** were prepared similarly.

2-Methyl-6-(adamantan-1-yl)imidazo[2,1-*b*]thiazole (Ib) was prepared from 0.04 mol of aminothiazolium bromide **IVa**. Yield 93%, mp 128–130°C. ^{1}H NMR spectrum, δ, ppm: 1.73 s (6H, 4',6',10'-CH_2), 1.87 s (6H, 2',8',9'-CH_2), 2.01 s (3H, 3',5',7'-CH), 2.34 s (3H, Me), 6.74 s (1H, 5-H), 7.37 s (1H, 3-H). Found N, %: 10.20. $C_{16}H_{20}N_2S$. Calculated N, %: 10.28.

3-Methyl-6-(adamantan-1-yl)imidazo[2,1-*b*]thiazole (Ic) was prepared from 0.04 mol of aminothiazolium bromide **IVb**. Yield 82%, mp 139–140°C. ^{1}H NMR spectrum, δ, ppm: 1.73 s (6H, 4 ', 6', 10'-CH_2), 1.91 s (6H, 2',8',9'-CH_2), 2.04 s (3H, 3',5',7'-CH) 2.35 s (3H, Me), 6.79 s (1H, 5-H), 7.38 s (1H, 2-H). Found N, %: 10.18. $C_{16}H_{20}N_2S$. Calculated N, %: 10.28.

5-Bromo-6-(adamantan-1-yl)imidazo[2,1-*b*]thiazole (IIa). *a*. Obtained from 0.002 mol of (adamantan-1-yl)imidazothiazole **Ia** and 0.0014 mol of phosphorus tribromide.Yield 92%, mp 182–184°C (ethanol). ^{1}H NMR spectrum, δ, ppm: 1.73 s (6H, 4',6',10'-CH_2), 2.05 s (6H, 2',8',9'-CH_2; 3H, 3',5',7'-CH), 7.41 d (1H, 2-H, *J* 4.4 Hz), 7.84 d (1H, 3-H, *J* 4.4 Hz). Found Br, %: 21.30. $C_{15}H_{17}BrN_2S$. Calculated Br, %: 21.69.

b and *c*. Obtained from 0.002 mol of compound **Ia** and 3 ml of bromine (*b*) [2] or equimolar amounts (0.0018 mol) of compound **Ia** and bromine in 20 ml of chloroform (*c*) [3]. Yield 84 and 70%, respectively. The spectral data and melting point are identical to those of the compound obtained by the method *a*.

2-Methyl-5-bromo-6-(adamantan-1-yl)imidazo[2,1-*b*]thiazole (IIb) was prepared by the method *c*. Yield 51%, mp 148–150°C (ethanol). ^{1}H NMR spectrum, δ, ppm: 1.72 s (6H, 4',6',10'-CH_2), 2.03 s (6H, 2',8',9'-CH_2), 2.09 s (3H, 3',5',7'-CH), 2.58 s (3H,

Me), 6.85 s (1H, 3-H). Found Br, %: 22.44. $C_{16}H_{19}Br·N_2S$. Calculated Br, %: 22.74.

3-Methyl-5-bromo-6-(adamantan-1-yl)imidazo-[2,1-*b*]thiazole (IIc) was prepared by the method *c*. Yield 60%, mp 138–140°C (ethanol). ^{1}H NMR spectrum, δ, ppm: 1.72 s (6H, 4',6',10'-CH_2), 2.05 s (6H, 2',8',9'-CH_2), 2.10 s (3H, 3',5',7-CH), 2.59 s (3H, Me), 6.87 s (1H, 2-H). Found Br, %: 22.51. $C_{16}H_{19}Br·N_2S$. Calculated Br, %: 22.74.

2-Methyl-3,5-dibromo-6-(adamantan-1-yl)-imidazo[2,1-*b*]thiazole (IIIa), 2,5-dibromo-3-methyl-6-(adamantan-1-yl)imidazo[2,1-*b*]thiazole (IIIb). *a*. Reaction of adamantanylimidazothiazoles **Ib**, **Ic** and phosphorus tribromide. Compound **IIIa**. Yield 58%, mp 156–158°C (ethanol). ^{1}H NMR spectrum, δ, ppm: 1.73 s (6H, 4',6',10'-CH_2), 2.03 s (6H, 2',8',9'-CH_2), 2.09 s (3H, 3',5',7-CH), 2.59 s (3H, Me). Found Br, %: 36.70. $C_{16}H_{18}Br_2N_2S$. Calculated Br, %: 37.15. Compound **IIIb**. Yield 62%, mp 158–160°C (ethanol). ^{1}H NMR spectrum, δ, ppm: 1.71 s (6H, 4',6',10'-CH_2), 2.03 s (6H, 2',8',9'-CH_2), 2.07 s (3H, 3',5',7-CH), 2.63 s (3H, Me). Found Br, %: 36.75. $C_{16}H_{18}Br_2N_2S$. Calculated Br, %: 37.15.

b. Reaction of 0.002 mol of compound **Ib**, **Ic** and 3 ml of bromine. Yields 88 (**IIIa**) and 81% (**IIIb**), compounds are identical to those obtained by the method *a*.

2-Amino-3-[(3-adamantan-1-yl)-2-oxoethyl]-4-methylthiazolium bromide (IVa), 2-amino-3-[(3-adamantan-1-yl)-2-oxoethyl]-5-methylylthiazolium bromide (IVb) were prepared similarly to those described in [4]. Compound **IVa**. Yield 84%, mp 245–247°C (ethanol + diethyl ether). Found Br, %: 21.25. $C_{16}H_{23}BrN_2OS$. Calculated Br, %: 21.56. Compound **IVb**. Yield 79%, mp 210–212°C (ethanol + diethyl ether). Found Br, %: 21.17. $C_{16}H_{23}BrN_2OS$. Calculated Br, %: 21.56.

The ^{1}H NMR spectra were registered in DMSO-d_6 on a Bruker WP-200 spectrometer operating at 200 MHz internal to TMS.

REFERENCES

1. Yurchenko, R.I. and Savina, N.S., *Zh. Obshch. Khim*., 2005, vol. 75, no. 4, p. 700.
2. Yurchenko, R.I., Ponomarenko, A.D., Svarovskaya, N.N., and Tolmachev, A.A., *Khim. Geterotsikl. Soedin.*, 2005, no. 5, p. 761.
3. Saldabol, N.O., Zeligman, L.L., Giller, S.A., Popelis, Yu.Yu., Abele, A.E., and Alekseeva, L.N., *Khim. Geterotsikl. Soedin.*, 1972, no. 10, p. 1353.
4. Makarova, N.V., Zemtsova, M.N., and Moiseev, I.K., *Khim. Geterotsikl. Soedin.*, 1993, no. 11, p. 1580.