Russian Journal of Organic Chemistry, Vol. 40, No. 4, 2004, pp. 591–592. Translated from Zhurnal Organicheskoi Khimii, Vol. 40, No. 4, 2004, pp. 617–618.

SHORT COMMUNICATIONS

Aryl 2,3-Dibromopropyl Sulfones in S,N-Tandem Heterocyclizations. New Synthesis of Benzimidazothiazolidines

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Received July 17, 2003

In the recent years, extensive development in the chemistry of saturated heterocycles containing nitrogen and sulfur atoms, specifically thiazine and thiazolidine derivatives, resulted primarily from their high pharmacological activity [1–3]. Thiazolidine ring constitutes a structural fragment of many biologically important compounds, in particular penicillin derivatives. However, methods of synthesis of such heterocycles are few in number, multistep, and fairly laborious [4–7]. We now propose a convenient procedure for synthesizing benzimidazothiazolidines via S,N-tandem alkylation of 2-sulfanylbenzimidazole with aryl 2,3-dibromopropyl sulfones (Scheme 1).

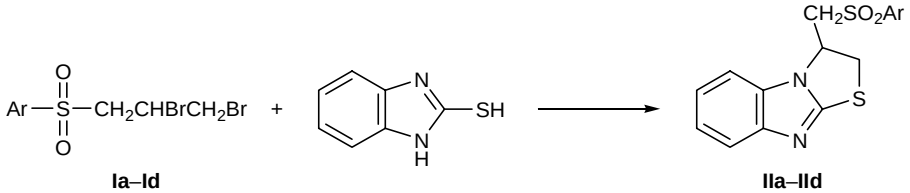
The reactions were carried out by stirring a mixture of the corresponding sulfone **Ia**–**Id**, 2-sulfanylbenzimidazole, and potassium hydroxide (reactant molar ratio 1:2:4) in ethanol at 20–25°C (reaction time 8 h). The yields of products **IIa**–**IId** were 85–95%. Their structure was proved by ^{1}H NMR spectroscopy and mass spectrometry. Compounds **IIa**–**IId** showed in the ^{1}H NMR spectra signals from protons of the CH_2CHCH_2 group as an *AA'MM'X* spin system. Nonequivalence of the CH_2S protons confirms the formation of thiazolidine ring having two chiral centers. The mass spectra of **IIa**–**IId** contained the following characteristic fragment ion peaks, *m*/*z*: 188 $[M - ArS(O)OH]^+$, 175 $[M - ArSO_2CH_2]^+$, 150, $[M - ArSO_2CH{=}CH_2]^+$, 130 $[M - ArSO_2CH_2 - CH{=}S]^+$. The fragmentation pattern was proposed with account taken of the data in [8, 9]. The absence of isomeric compounds among the products indicates high chemo- and regioselectivity of the reaction, typical of tandem processes [10].

3-Phenylsulfonylmethyl-2,3-dihydro[1,3]thiazolo[3,2-*a*]benzimidazole (IIa). Yield 90%, mp 162–163°C (from ethanol). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.27 d (1H, CH), 3.56 d.d (1H, CH), 4.09 d (1H, CH), 4.26 d.d (1H, CH), 5.24 t (1H, CH), 7.01–7.96 m (9H, H_{arom}). Mass spectrum, *m*/*z*, (I_{rel}, %): 330 (66.4) $[M]^+$, 188 (100), 175 (50.2), 150 (8.2), 130 (16.4), 117 (24.5), 90 (17.2).

3-(4-Methylphenylsulfonylmethyl)-2,3-dihydro-[1,3]thiazolo[3,2-*a*]benzimidazole (IIb). Yield 95%, mp 174–175°C (from ethanol). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.46 s (3H, CH_3), 3.26 d (1H, CH), 3.54 d.d (1H, CH), 4.07 d (1H, CH), 4.26 d.d (1H, CH), 5.21 t (1H, CH), 7.39 d (2H, H_{arom}), 7.55 d (2H, H_{arom}). Mass spectrum, *m*/*z*, (I_{rel}, %): 344 (76.6) $[M]^+$, 188 (100), 175 (54.6), 150 (9.8), 130 (17.1), 117 (25.2), 90 (16.8).

3-(4-Nitrophenylsulfonylmethyl)-2,3-dihydro-[1,3]thiazolo[3,2-*a*]benzimidazole (IIc). Yield 92%,

Scheme 1.



Ia–**Id** **IIa**–**IId**

Ar = Ph (**a**), 4-MeC_6H_4 (**b**), 4-$O_2NC_6H_4$ (**c**), 2-naphthyl (**d**).

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mp 238°C (from ethanol). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.91 d (1H, CH), 4.09 d (1H, CH), 4.12–4.15 m (1H, CH), 4.30 t (1H, CH), 5.29 m (1H, CH), 7.04–7.29 m (4H, H_{arom}), 8.17 d (2H, H_{arom}), 8.29 d (2H, H_{arom}). Mass spectrum, *m*/*z*, (I_{rel}, %): 375 (78.3) $[M]^+$, 188 (100), 175 (64.5), 150 (8.8), 130 (18.8), 117 (22.7), 90 (15.6).

3-(2-Naphthylsulfonylmethyl)-2,3-dihydro[1,3]-thiazolo[3,2-*a*]benzimidazole (IId). Yield 85%, mp 167–168°C (from ethanol). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.38 d (1H, CH), 3.63 d.d (1H, CH), 4.14–4.18 m (2H, 2CH), 5.29 t (1H, CH), 7.04–7.56 m (4H, H_{arom}), 7.67–8.03 m (7H, H_{arom}). Mass spectrum, *m*/*z*, (I_{rel}, %): 380 (100) $[M]^+$, 188 (80.1), 175 (79.2), 150 (8.4), 130 (21.1), 117 (36.4), 90 (18.2).

The GC–MS data were obtained on a Micromass ZDM-2000 instrument (electrospray ionization, positive ions). The mass spectra (70 eV) were run on an MKh-1321 spectrometer with direct sample admission into the ion source. The ^{1}H NMR spectra were measured from solutions in DMSO-d_6 and $CDCl_3$ on a Bruker AM-500 spectrometer (500.13 MHz) using signals from residual protons in the solvents as internal reference.

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