ISSN 1070-4280, Russian Journal of Organic Chemistry, 2010, Vol. 46, No. 5, pp. 624–627. © Pleiades Publishing, Ltd., 2010.
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Regio- and Stereoselective Addition of Methane- and Bromomethanesulfonyl Bromides to 1-Phenylthiotricyclo[4.1.0.0^{2,7}]heptane

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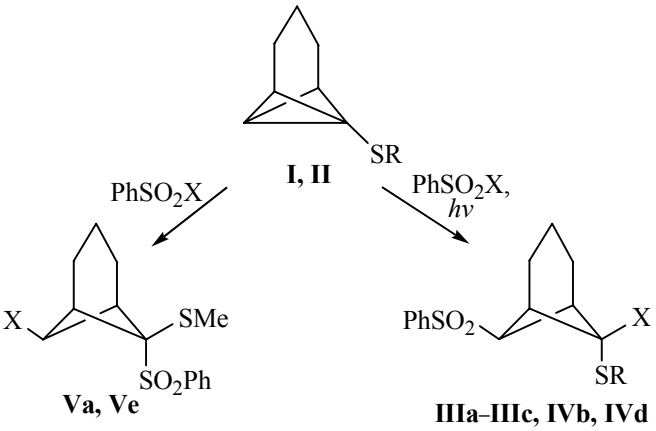
Received June 10, 2009

Abstract—1-Phenylthiotricyclo[4.1.0.0^{2,7}]heptane reacted with $MeSO_2Br$ and $BrCH_2SO_2Br$ directly at mixing at 20°C in CH_2Cl_2 along a ionic (electrophilic with respect to bromine) mechanism affording a product of an *anti*-stereoselective addition to the central bicyclobutane C^1–C^7 bond of the norpinane structure. The reaction product contains the exo-oriented sulfonyl group in the geminal position to the SPh substituent. The structure of the adduct with $MeSO_2Br$ in a single crystal was determined by XRD analysis.

DOI: 10.1134/S1070428010050027

It was shown formerly [1, 2] that 1-phenylthio- and 1-methylthiotricyclo[4.1.0.0^{2,7}]heptanes (**I**) and (**II**) under UV irradiation were subject to addition of benzenesulfonyl bromide, benzenesulfonyl chloride, S-phenylbenzenesulfonothioate, and S-methylbenzenesulfonothioate exclusively at the central bicyclobutane C^1–C^7 bond strictly regio- and stereoselectively with the formation of norpinane compounds **IIIa–IIIc** and **IVb, IVd**.

Scheme 1.

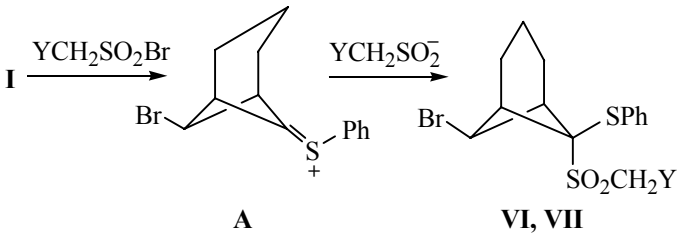


R = Ph (**I, III**), Me (**II, IV**); X = Br (a), Cl (b), SPh (c), SMe (d), SePh (e).

The reaction in the dark of compound **II** with benzenesulfonyl bromide and also with Se-phenylbenzenesulfonoselenoate resulted in another order and another stereochemistry of the reagent addition to the C^1–C^7 bond: we obtained norpinane compounds **Va** and **Ve** [2].

The difference in the behavior of the methylthioether **II** with respect to benzenesulfonyl halides was ascribed to the change in the addition mechanism from the radical at UV irradiation (benzenesulfonyl chloride) to the ionic one in the dark (benzenesulfonyl bromide). The successful reaction in the dark in this case is apparently favored by lower strength and larger polarity of the SO_2–Br bond compared with the SO_2–Cl bond and also by higher nucleophilicity of compound **II** than compound **I**.

We investigated in this study the reactions of phenylthioether **I** with more active than $PhSO_2Br$ sources of electrophilic bromine, methane- and bromomethanesulfonyl bromides, aiming at establishing the regio- and stereoselectivity of these reagents addition. The reaction was carried out at 0°C in CH_2Cl_2 over 6–8 h using equimolar amounts of the reagents; the reaction did not require a special initiation. By column chromatography on Al_2O_3 we isolated from the reaction mixtures norpinane compounds **VI** and **VII** analogous to compounds **Va**



Y = H (**VI**), BR (**VII**).

and **Ve**. The polymeric products of the reaction were retained in the column.

The use of $MeSO_2Br$ and $BrCH_2SO_2Br$ in the reaction with methylthioether **II** under similar conditions resulted in the formation of tarry polymer products lacking sulfonyl group in their composition.

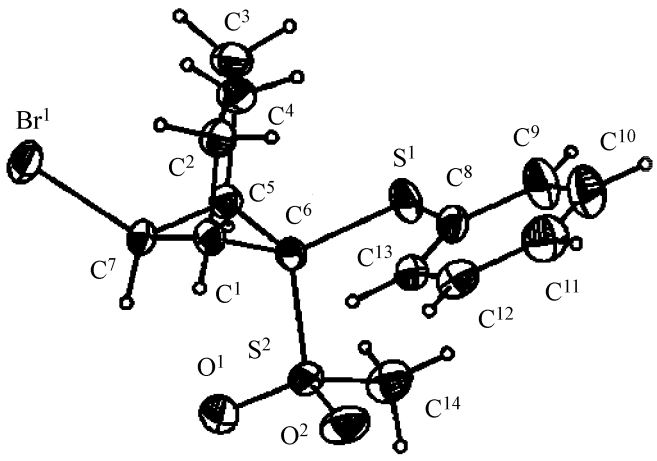
The structures of compounds **VI** and **VII** were established from the data of ^1H and ^{13}C NMR spectra taking into consideration analogous characteristics of compound **Va**. In the ^{13}C NMR spectra five characteristic peaks were observed of an expected intensity belonging to the norpinane framework of the molecules, and also the peak of the methyl (bromomethyl) group. The location of the bromine atom at the carbon framework of the molecule is indicated by the relatively large chemical shift value of the C^7 atom in the ^{13}C NMR spectra, and the *syn*-orientation of the bromine follows from the triplet signal of the proton *anti*-H^7, J 5.8 Hz, in the ^1H NMR spectra [3].

The direct proof of adduct **VI** structure was obtained by XRD analysis of its single crystal (see the figure).

The studied structure is built of discrete molecules. Only the van der Waals interaction exists between the molecules.

Among the features of the spatial arrangement of norpinane **VI** the virtually flat trimethylene bridge should be mentioned: the dihedral angle $C^1C^2C^4C^5/C^2C^3C^4$ is only 1.27°, atom C^3 insignificanly (by 0.018 Å) deviates from the plane $C^1C^2C^4C^5$ in the direction of the phenylthio group. The similar structure of the trimethylene bridge was also observed in the known 6,6,7-trisubstituted norpinanes of the *endo,syn*-configuration [2, 4]. Our estimation performed using the calculation program RICON (method ZP) [5] suggested that both six-membered rings $C^6C^1C^2C^3C^4C^5$ and $C^7C^1C^2C^3C^4C^5$ were in the *envelop* conformation with the folding parameters S 1.099, 1.072, θ 36.44, 38.49, ψ_2 0.23, 0.86 respectively. In the cyclobutane fragment the dihedral angle between the planes $C^1C^5C^6$ and $C^1C^5C^7$ (140.1°) and the nonvalence distances $C^1\cdots C^5$ (2.149 Å) and $C^6\cdots C^7$ (2.119 Å) are close to the corresponding values (137.3°, 2.140 and 2.096 Å) in an unsubstituted norpinane in the gas phase [6]. The valence distances C^1–C^6 and C^5–C^6 (average 1.573 E) are in this compound somewhat longer than the valence distances C^1–C^7 and C^5–C^7 (average 1.542 Å) evidently due to the presence of the electronegative bromine atom in the position 7. The plane of the phenyl ring is practically orthogonal to the plane $C^3C^6C^7$. This ring and the methyl group of the sulfonyl fragment have the opposite orientation with respect to the mentioned plane. The atom Br^1 deviates from the plane $C^3C^6C^7$ by 0.012 Å in the direction of C^4 atom.

To understand the origin of norpinanes **VI** and **VII** we suggest that the addition occurs by the ionic mechanism where the methane- and bromomethane-sulfonyl bromides operate as the sources of the electrophilic bromine. The attack of Br^+ is strictly *endo*-directed on the unsubstituted nodal carbon atom of the tricycloheptane **I** in conformity with the characteristic feature of the ionic reactions of the bicyclobutane derivatives [7, 8] and leads to the formation of a norpinanyl carbocation A stabilized by the mesomeric involvement of the sulfur atom. The subsequent transfer of the sulfonyl anion on the carbocation A proceeds highly selectively into the *anti*-position. The main reason of the latter we believe to be in the shielding of the reaction site of the



Perspective view of molecule of *syn*-7-bromo-*exo*-6-(methylsulfonyl)-*endo*-6-(phenylthio)bicyclo[3.1.1]-heptane (**VI**).

intermediate A by the fragment C^3H_2 considerably deviating from the plane $C^1C^2C^4C^5$ in the direction of atom C^6 because of the repulsion by the bulky bromine atom attached to C^7.

Hence the studied new reactions of sulfobromination of 1-phenylthiotricycloheptane **I** like the formerly reported [2] addition of $PhSO_2Br$ and $PhSO_2SePh$ to tricycloheptane **II** with respect to the regio- and stereoselectrivity of the addition are completely resembling the addition reactions to 1-phenyltricyclo[4.1.0.$0^{2,7}$]-heptane initialed by the electrophilic bromine, namely the bromomethoxy(hydroxy)lation [9, 10] and *N*-halo-succinimides addition in the aprotic solvent [11].

EXPERIMENTAL

Elemental analysis was carried out on a CHN-analyzer HP-185B. ^1H and ^{13}C NMR spectra of compounds were registered on a spectrometer Bruker AC-300 (300.130 and 75.468 MHz respectively) in $CDCl_3$. The conditions of analytical TLC were as follows: adsorbent Silufol UV-254, eluent hexane–ethyl ether, 1 : 1. Development in iodine chamber. The column chromatography was performed on Al_2O_3 of II activity grade, eluent low-boiling petroleum ether–ethyl ether, 3 : 1.

Tricycloheptane **I** [12], $MeSO_2Br$ [13], and $BrCH_2SO_2Br$ [14] were obtained by published procedures.

Reaction of tricycloheptane I with methanesulfonyl bromides. At cooling with an ice bath a solution of 0.708 g (3.5 mmol) of tricycloheptane **I** in 5 ml of anhydrous CH_2Cl_2 was mixed with 3.5 mmol of $MeSO_2Br$ or $BrCH_2SO_2Br$ in 5 ml of the same solvent, and 100 mg of anhydrous Na_2CO_3 was added. The mixture was kept in a tightly stoppered flask for 30 h at 20°C, then the reaction mixture was filtered, the solvent was evaporated in a vacuum of the water-jet pump. The oily residue was subjected to column chromatography on Al_2O_3.

***syn*-7-Bromo-*exo*-6-(sulfonyl)-*endo*-6-(phenylthio)bicyclo[3.1.1]heptane (VI)**. Yield 30%, mp 110–111°C (CH_2Cl_2–hexane). ^1H NMR spectrum, δ, ppm: 1.72–1.90 m (2H, H^3), 2.13–2.43 m (4H, $H^{2,4}$), 3.12 s (3H, CH_3), 3.48 br.s (2H, $H^{1,5}$), 5.67 t (1H, H^7, *J* 6 Hz), 7.24–7.38 m ($3H_{arom}$), 7.48–7.52 m ($2H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 12.5 (C^3), 26.3 (2C, $C^{2,4}$), 38.4 (CH_3), 49.3 ($C^{1,5}$), 49.8 (2C, C^7), 79.1 (C^6); 127.2, 128.7 (2C), 129.1 (2C), 132.17 (C_{arom}). Found, %: C 46.77; H 4.88. $C_{14}H_{17}BrO_2S_2$. Calculated, %: C 46.54; H 4.74.

***syn*-7-Bromo-*exo*-6-(bromosulfonyl)-*endo*-6-(phenylthio)bicyclo[3.1.1]heptane (VII)**. Yield 29%, mp 96°C ($CHCl_3$–hexane). ^1H NMR spectrum, δ, ppm: 1.76–1.94 m (2H, H^3), 2.15–2.38 m (4H, $H^{2,4}$), 3.61 d (2H, $H^{1,5}$, J 6 Hz), 4.84 s (2H, CH_2Br), 5.66 t (1H, H^7, *J* 6 Hz), 7.30–7.40 m ($3H_{arom}$), 7.54 d ($2H_{arom}$, *J* 7.5 Hz). ^{13}C NMR spectrum, δ, ppm: 12.6 (C^3), 26.1 (2C, $C^{2,4}$), 42.3 (CH_2Br), 48.4 (C^7), 49.9 (2C, $C^{1,5}$), 78.4 (C^6), 127.7, 129.1 (2C), 129.4 (2C), 131.6 (C_{arom}). Found, %: C 38.38; H 3.78. $C_{14}H_{16}Br_2O_2S_2$. Calculated, %: C 38.20; H 3.66.

XRD analysis of compound VI. Experimental set of intensities of 3141 reflections was obtained from a colorless prismatic single crystal of the size 1.0 × 0.4 × 0.3 mm on an automatic four-circle diffractometer Siemens P3/PC at 293 K (graphite monochromator, MoK_a-radiation, λ 0.71073 Å, θ-5/3θ scanning, $2\theta_{max}$ 55.76°, spherical segment $-9 \le h \le 25$, $0 \le k \le 8$, $-27 \le l \le 27$). After the averaging of equivalent reflections 2846 (R_{int} 0.0180) independent reflections were obtained that were used in solving and refining the structure. Crystals monoclinic, *a* 20.423(11), *b* 6.783(6), *c* 22.176(8) Å, β108.29(4)°, *V* 2917(9) $Å^3$, M 361.31, Z 8, d_{calc} 1.646 g/cm^3, μ 3.099 mm^{-1}, *F*(000) 1472, space group C 2/*c*. The structure was solved by the direct method. All atoms were localized by successive syntheses of the electron density. The refinement was performed by F^2_{hkl} in the anisotropic approximation for all nonhydrogen atoms and in the isotropic approximation for hydrogen atoms. The final divergence factors are as follows: R_1 0.0519 [calculated by F_{hkl} for 2336 reflections with $I > 2\sigma(I)$], wR_2 0.1443 (calculated by F^2_{hkl} for 3141 reflections used in the refining). The number of independent refined parameters 172, GOOF 1.070. The residual electron density from the difference Fourier series was 1.718 and –1.1.474 e/$Å^{-3}$. The correcton for extinc-tion was not done. All calculations were performed using the software SHELXTL ver.5.1 [15]. Weight scheme $w^{-1} = \sigma^2(F_O^2) + (0.1066P)^2 + 2.6728P$ where $P = 1/3(F_O^2 + 2F_O^2)$. The XRD data for compound **VI** are deposited in the Cambridge Crystallographic Data Center (no. CCDC 733628) and can be obtained free at the address www.ccdc.cam.ac.uk/conts/retrieving.html or by post at The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44)-1223-336033; e-mail: deposit@ccdc.cam.ac.uk.

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