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BF_3-Catalyzed Addition of Thiols to (+)-Camphene

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Abstract—BF_3-catalyzed addition of some thiols to (+)-camphene was examined. Reactions with aromatic thiols and hetaryl thiols result in terpene sulfides of camphene or bornane structure in accordance with the Markovnikov's rule, whereas with remain thiols the reaction proceeds against the Markovnikov's rules preserving the original structure of the molecule.

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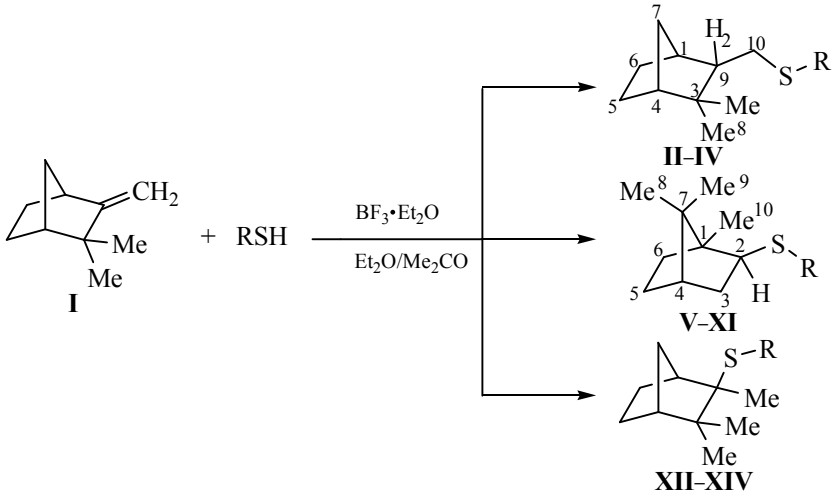
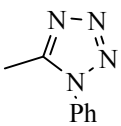
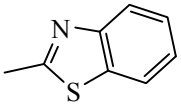
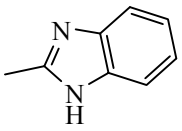
The peculiar feature of the chemical behavior of bicyclic monoterpenes in the reactions with electrophilic reagents is their tendency to various rearrangements. The most famous of them are camphene rearrangements. As a rule, the electrophilic addition to camphene is accompanied by the Wagner–Meerwein rearrangement to give the products of bornane structure [1–5]. The reactions of electrophilic addition to camphene without isomerization of the original structure of the molecule are very seldom [6].

In this work we studied BF_3-catalyzed addition of a wide range of thiols (2-mercaptoethanol, mercaptoacetic acid, methyl mercaptoacetate, benzyl mercaptan, some hetaryl thiols and thiophenols) to (+)-camphene **I**.



R = $(CH_2)_2OH$ (**II**), CH_2CO_2H (**III**), CH_2CO_2Me (**IV**), CH_2Ph (**V**),  (**VI**),  (**VII**),  (**VIII**), Ph (**IX**), *p*-FPh (**X**), *o*-FPh- (**XI**), *p*-BrPh (**XII**), *p*-ClPh (**XIII**), *o*-ClPh (**XIV**).

The reactions with mercaptoethanol, mercaptoacetic acid, and its methyl ester were found to occur against the Markovnikov's rule affording reaction products **II**–**IV** of camphene structure. The ^{1}H NMR spectra of these compounds are characterized by the presence of two singlet signals corresponding to the protons of the geminal methyl groups. The terpene sulfide **II** was found to suffer an auto-oxidation in air to form the corresponding sulfone **IIa**. One of the crystals of the sulfone was separated from the oily sulfide **II** and analyzed by XRD. Earlier cases of the auto-oxidation in air have we found for sulfides of pinane series [7]. Sulfone **IIa** crystallizes in the centrosymmetric space group *P*-1. The sulfur-containing substituent is in the *endo*-position with respect to the camphene bicycle and has almost completely unfolded conformation [torsion angles $C^3C^{10}S^1C^{11}$ and $C^{10}S^1C^{11}C^{12}$ are 169.4(1)° and 174.9(2)°, respectively], except for the last fragment [torsion angle $S^1C^{11}C^{12}O^1$ is 73.3(2)°] (Fig. 1).

The *gauche* conformation of the last fragment is determined by the so-called *gauche* effect studied in detail for the SCCO fragment [8–10]. In the crystal sulfone **IIa** molecules form cyclic dimers (Fig. 2) via the hydrogen bonds of O–H···O=S type [O^1–H^1 0.78(3), $H^1\cdots O^3$ 2.02(3), $O^1\cdots O^3$ 2.790(2) Å, $\angle O^1H^1\cdots O^3$ 170(3)°].

Thus, based on the X-ray data for sulfone **IIa** we proved the structure of the initial sulfide **II**.

In their turn the reactions of hetaryl thiols and benzyl mercaptan with camphene **I** proceed in accordance with the Markovnikov's rule to form the adducts of bornane structure **V**–**VIII**. The ^{1}H NMR spectra of these adducts contain three singlet signals belonging to the protons of three methyl groups and the doublet of doublets corresponding to the methine proton at the sulfur atom, which indicates the formation of terpene sulfide of bornane structure with the *exo*-position of the sulfide group relative to the bicyclic skeleton of the molecule [11]. The molecular structure of sulfide **VI** was determined by the X-ray diffraction study. XRD analysis confirmed the bornane structure of compound **VI** and *exo*-configuration of the sulfide group (Fig. 3). The bulky phenyltetrazole group is in the *trans*-position with respect to the *gem*-dimethyl fragment.

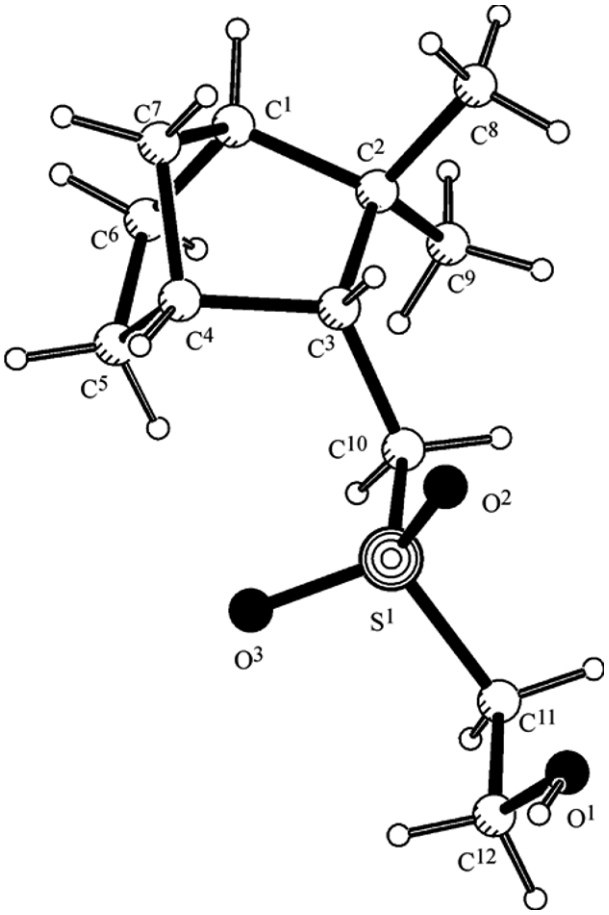


Fig. 1. General view of the molecule of **IIa** in the crystal.

In order to obtain a crystalline derivative of sulfide **V** it was oxidized by a known method to the cor-

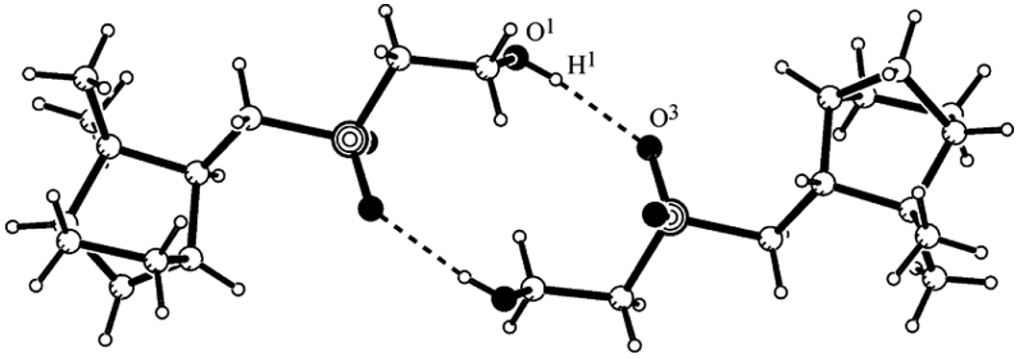


Fig. 2. General view of the dimer molecule of **IIa** in the crystal (the dashed lines show the hydrogen bonds).

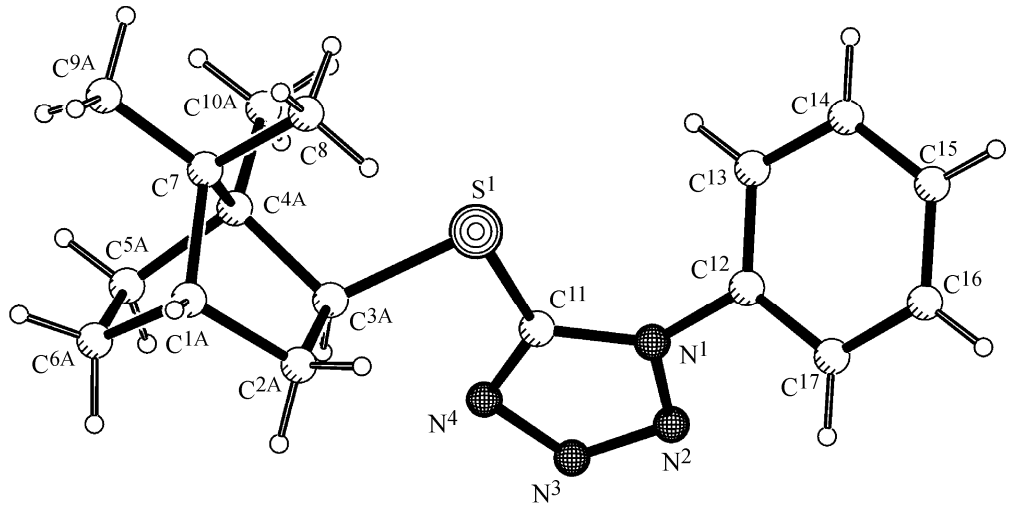


Fig. 3. General view of the molecule of **VI** in the crystal. Disorder of the bornane fragment atoms is not shown.

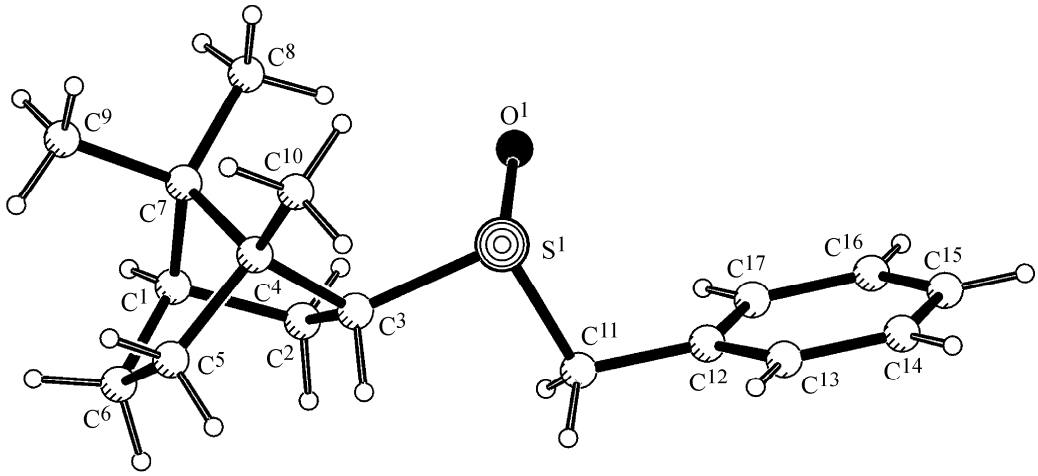


Fig. 4. General view of the molecule of **Va** in the crystal.

responding sulfoxide **Va** using Oxone as the oxidant [12]. The structure of sulfoxide **Va** was established by XRD analysis. According to XRD data the crystal of sulfoxide **Va** is diastereomerically pure (Fig. 4). In keeping with the symmetry of the *Pbca* space group, the crystal contains the enantiomeric pair with the following configurations of the chiral centers: $C^1(R)$, $C^3(R)$, $C^4(R)$, $S^1(R)$ and $C^1(S)$, $C^3(S)$, $C^4(S)$, $S^1(S)$. The XRD data of sulfoxide **Va** confirms the bornane structure and *exo*-configuration of the original sulfide **V**.

The reactions of camphene with thiophenol and its halo-derivatives are interesting. In the case of 4-bromo, 2-chloro-, and 4-chlorothiophenols, the crystalline adducts **XII**–**XIV** of camphene structure form in accordance with the Markovnikov's rule, whereas the reactions with thiophenol, 4-fluoro-, and 2-fluorothiophenols result in terpene sulfides **IX**–**XI** of bornane structure. The ^{1}H NMR spectra of the products **XII**–**XIV** contain three singlets, as in the case of the adducts of bornane structure, but they lack the characteristic signal of the methine proton. Compounds **XII** and **XIII** are crystalline, which allowed to determine their molecular structure by the X-ray diffraction method. Compounds **XIII** and **XII** form the isostructural crystals in a noncentrosymmetric $Pna2_1$ space group. *p*-Chloro(bromo)phenyl substituent is in the *trans*-position relative to the *gem*-dimethyl group (Fig. 5).

In all reactions we monitored the reaction progress by the GC-MS method, which proved that in every case only those adducts were the reaction products, which were then isolated by the column chromato-

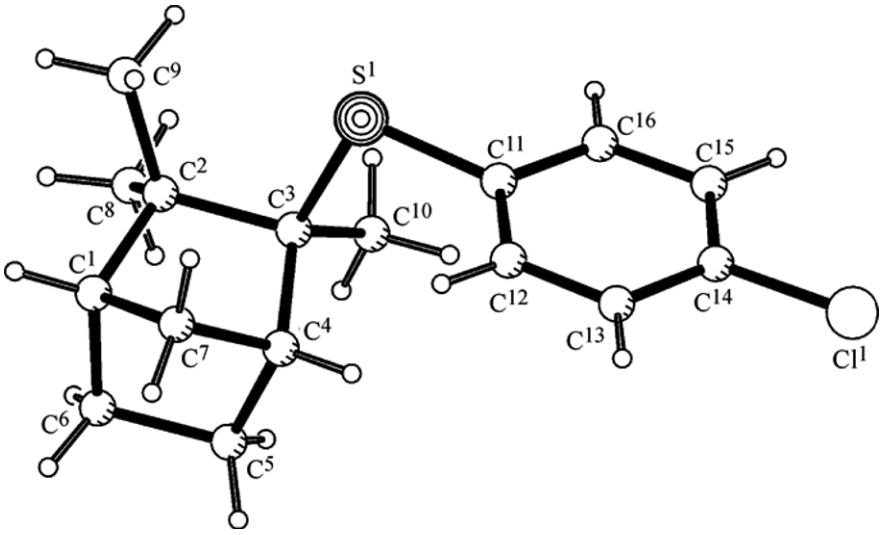


Fig. 5. General view of the molecule of **XIII** in the crystal.

graphy on silica gel. The EI mass spectra of all compounds contain the molecular ions peaks with the corresponding *m*/*z* values.

It can be assumed that the greater stability of the sulfide anion in the aromatic thiols promotes the formation of the thiolate anion or the presence of the second reagent as an "intimate ion pair," which facilitate the proton release and the Wagner–Meerwein rearrangement. Perhaps in the case of the non-aromatic thiols the addition of sulfur reagent as a complex takes place, i.e., the addition is to a certain degree a concerted process with preserving the original structure of the molecule. In favor of this assumption is the fact of the formation of the anti-Markovnikov adducts. Such a reaction process has been observed previously in the reactions of the corresponding thiols with β-pinene, which proceed against the Markovnikov's rule to form the adducts of the original pinane structure [13, 14].

All synthesized sulfides are racemates. Obviously, the rate of the reaction leading to the camphene racemization is higher than that of the reaction resulting in the adducts [15–18].

Thus, in this work we present a series of new thioterpenoids of camphene and bornane structure. The direction of the reaction is highly dependent on the nature of the using thiol.

EXPERIMENTAL

The reaction progress and the purity of compounds were monitored by the TLC using Sorbfil plates eluting with a hexane–diethyl ether mixture or methylene chloride and detecting with potassium permanganate. Preparative chromatography was performed on a silica gel (0.06–0.2 μ, Acros). (+)-Camphene (technical grade, 80%), 2-mercaptoethanol, methyl mercaptoacetate, mercaptoacetic acid, thiophenol and other thiols were purchased from Acros Organics and Aldrich. The purification of the solvents was carried out according to the known methods [19].

The ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 WB spectrometer operating at 400.13 and 100.61 MHz, respectively, internal references TMS and residual proton signals of $CDCl_3$.

The GC-MS analysis was performed on a DFS Thermo Electron Corporation instrument (Germany). The ionization method was electron impact (70 eV), the ion source temperature was 280°C. A capillary DB-5MS column (*l* 30 m, *d* 0.254 mm, Agilent) was used. Helium was used as a carrier gas with the flow rate of 1 ml min^{-1}. The processing of mass spectral data was performed using Xcalibur software. Before injecting into the spectrometer, the sample was diluted with the chromatographically pure solvent to concentration of ~1 g ml^{-1}. Conditions for GC-MS analysis: injector temperature 280°C; split ratio 1:50; the column heating was carried out in the following program mode: the initial temperature 120°C (1 min), the heating rate 10°C min^{-1}, the final temperature 280°C (15 min); the rate of the carrier gas 1 ml min^{-1}; the sample volume 1 μl.

The melting points were determined on the Koeffler heating block and reported uncorrected.

The X-ray diffraction studies of the crystals of **IIa**, **VI**, **Va**, **XII** and **XIII** were carried out on a Bruker SMART Apex II diffractometer (graphite monochromator, λMoK_α 0.71073 Å) at 293 (**IIa**, **VI**, **Va**) and 150 K (**XII**, **XIII**). A semi-empirical account of extinction was performed using SADABS software [20]. The structure was solved by the direct method using SHELXS software [21]. The nonhydrogen atoms were refined in isotropic and then in anisotropic approximations by SHELXL-97 software [22]. In the structure of **VI** the bornane C^1, C^2, C^3, C^4, C^6, C^9 atoms are disordered over two positions with equal occupancy, which cannot be avoided by going to the space groups with lower symmetry ($P2_1$, P-1, $P1$). The hydrogen atoms bonded to the carbon atoms were placed into the calculated positions and refined by a *rider* model. The hydroxyl hydrogen atom in the structure of **IIa** was identified from the difference Fourier series. At the final stage its position was refined in the isotropic approximation. All the calculations were performed using the WinGX [23] and APEX2 programs [24]. The figures were made using PLATON software [25].

The XRD data on the structures of **IIa**, **VI**, **Va**, **XII** and **XIII** were deposited in the Cambridge Structural Database (CCDC 883962, 883958, 883961, 883959, 883960, respectively).

Crystals of compound IIa are triclinic, $C_{12}H_{22}O_3S$, at 20°C: *a* 6.10380(10), *b* 7.4328(9), *c* 14.7441(18) Å, α 85.631(1), β 82.1810(10), γ 75.7690(1)°, *V* 641.72 (11) (6) $Å^3$, *Z* 2, d_{calc} 1.275 g cm^{-3}, space group *P*-1, μMo 2.43 cm^{-1}. The intensity of 5375 reflections was measured, for 2085 of which $I \geq 2\sigma$. The final values of the divergence factors are *R* 0.0449, R_w 0.1084.

Crystals of compound VI are monoclinic, $C_{17}H_{22}N_4S$; at 20°C: *a* 6.9065(14), *b* 7.2626(15), *c* 33.434(7) Å, β 94.038(3)°, *V* 1672.8(6) $Å^3$, *Z* 4, d_{calc} 1.249 g cm^{-3}, space group $P2_1/c$, μMo 1.96 cm^{-1}. The intensity of 13121 reflections was measured, for 2107 of which $I \geq 2\sigma$. The final values of the divergence factors are *R* 0.0525, R_w 0.1569.

Crystals of compound Va are rhombic, $C_{17}H_{24}OS$; at 20°C: *a* 12.22(1), *b* 10.55(1), *c* 23.93(2) Å, *V* 3086(5) $Å^3$, *Z* 8, d_{calc} 1.190 g cm^{-3}, space group *Pbca*, μMo 2.01 cm^{-1}. The intensity of 23438 reflections was measured, for 1598 of which $I \geq 2\sigma$. The final values of the divergence factors are *R* 0.0734, R_w 0.1875.

Crystals of compound XII are rhombic, $C_{16}H_{21}BrS$; at 20°C: *a* 10.5510(18), *b* 19.247(3), *c* 7.1695(12) Å, *V* 1456.0(4) $Å^3$, *Z* 4, d_{calc} 1.484 g cm^{-3}, space group $Pna2_1$, μMo 29.48 cm^{-1}. The intensity of 12671 reflections was measured, for 2650 of which $I \geq 2\sigma$. The final values of the divergence factors are *R* 0.0407, R_w 0.0784, Flake parameter 0.081(9).

Crystals of compound XIII are rhombic, $C_{16}H_{21}ClS$; at 20°C: *a* 10.3077(8), *b* 19.0746(14), *c* 7.1529(5) Å, *V* 1406.37(18) $Å^3$, *Z* 4, d_{calc} 1.326 g cm^{-3}, space group $Pna2_1$, μMo 4.00 cm^{-1}. The intensity of 11432 reflections was measured, for 3195 of which $I \geq 2\sigma$. The final values of the divergence factors are: *R* 0.0272, R_w 0.0655, Flake parameter 0.15(5).

The X-ray diffraction analysis was performed in the Federal collective spectral analysis center for physical and chemical investigations of structure, properties and composition of substances and materials (Kazan).

General procedure for the preparation of compounds II–XIV. To a solution of 0.01 mol of (+)-camphene **I** in 10 ml of Et_2O [for the preparation of compounds **VI–VIII**, in a diethyl ether–acetone mixture, 1:1] at room temperature was added 0.01 mol of the corresponding thiol and a catalytic amount of $BF_3 \cdot Et_2O$. After 10–15 h the solvent was distilled off under a reduced pressure. The reaction products were purified by the column chromatography on silica gel eluting with hexane or hexane–diethyl ether mixture.

2-[({(2*S*)-3,3-Dimethylbicyclo[2.2.1]hept-2-yl}-methyl)sulfanyl]ethanol (II). Yield 57%. ^{1}H NMR spectrum, δ, ppm: 0.85 s and 0.98 s (6H, $H^{8,9}$), 1.18 d (1H, H^1, *J* 9.54 Hz), 1.28 s (2H, H^7), 1.54–1.64 m (4H, $H^{5,6}$), 1.76 br.s (1H, H^4), 2.03 br.s (1H, H^2), 2.28 br.s (1H, OH), 2.45–2.55 m (2H, H^{10}), 2.73 t (2H, $\underline{CH_2}CH_2OH$, *J* 5.96 Hz), 3.72 t (2H, CH_2OH, *J* 5.95 Hz). ^{13}C NMR spectrum, δ_C, ppm: 20.93, 32.27 ($C^{8,9}$), 19.91, 24.56, 30.02 (C^{5-7}), 35.87, 36.82 (CH_2SCH_2), 37.57 (C^3), 41.37 (C^2), 49.10, 49.90 ($C^{1,4}$), 59.98 (CH_2OH). Mass spectrum (EI), *m*/*z* (I_{rel}, %): 214 (16) $[M]^{+\cdot}$, 183 (2) $[M - CH_2OH]^+$, 169 (18) $[M - CH_2CH_2OH]^+$, 137 (34) $[M - SCH_2CH_2OH]^+$, 95 (52) $[C_7H_{11}]^+$, 81 (100) $[C_6H_9]^+$, 67 (50) $[C_5H_7]^+$, 41 (58) $[C_3H_5]^+$.

2-[({(2*S*)-3,3-Dimethylbicyclo[2.2.1]hept-2-yl}-methyl)sulfanyl]acetic acid (III). Yield 54%. ^{1}H NMR spectrum, δ, ppm: 0.86 s and 0.97 s (6H, $H^{8,9}$), 1.19 d (1H, H^1, *J* 9.54 Hz), 1.22–1.32 m (2H, H^7), 1.55–1.64 m (4H, $H^{5,6}$), 1.77 br.s (1H, H^4), 2.26 br.s (1H, H^2), 2.60–2.71 m (2H, H^{10}), 3.25 s (2H, CH_2CO). Mass spectrum (EI), *m*/*z* (I_{rel}, %): 228 (2) $[M]^{+\cdot}$, 185 (2) $[M - CH_3CO]^+$, 169 (25) $[M - CH_2CO_2H]^+$, 136 (40)

$[M - SCH_2CO_2H - H]^+$, 95 (49) $[C_7H_{11}]^+$, 81 (100) $[C_6H_9]^+$, 67 (45) $[C_5H_7]^+$, 41 (42) $[C_3H_5]^+$.

Methyl 2-[({(2*S*)-3,3-dimethylbicyclo[2.2.1]hept-2-yl}methyl)sulfanyl]acetate (IV). Yield 56%. ^{1}H NMR spectrum, δ, ppm: 0.85 s and 0.97 s (6H, $H^{8,9}$), 1.16–1.21 m (1H, H^1), 1.24–1.33 m (2H, H^7), 1.54–1.63 m (4H, $H^{5,6}$), 1.75 br.s (1H, H^4), 2.24 br.s (1H, H^2), 2.57–2.67 m (2H, H^{10}), 3.22 s (2H, CH_2CO), 3.74 s (3H, OCH_3). Mass spectrum (EI), *m*/*z* (I_{rel}, %): 242 (2) $[M]^{+\cdot}$, 199 (2) $[M - COCH_3]^+$, 183 (5) $[M - CO_2CH_3]^+$, 169 (45) $[M - CH_2CO_2CH_3]^+$, 137 (23) $[M - SCH_2CO_2CH_3]^+$, 95 (59) $[C_7H_{11}]^+$, 81 (100) $[C_6H_9]^+$, 67 (64) $[C_5H_7]^+$, 43 (26) $[COCH_3]^+$, 41 (78) $[C_3H_5]^+$.

2-*exo*-(Benzylsulfanyl)-1,7,7-trimethylbicyclo-[2.2.1]heptane (V). Yield 57%. ^{1}H NMR spectrum, δ, ppm: 0.81 s (3H, H^{10}), 0.98 s and 0.99 s (6H, $H^{8,9}$), 1.09 d (1H, H^4, *J* 7.95 Hz), 1.55–1.82 m (6H, $H^{3,5,6}$), 2.55–2.64 m (1H, H^2), 3.73 s (2H, $\underline{CH_2}Ph$), 7.28–7.35 m (5H, Ph). Mass spectrum (EI), *m*/*z* (I_{rel}, %): 260 (9) $[M]^{+\cdot}$, 169 (76) $[M - CH_2Ph]^+$, 137 (19) $[M - SCH_2Ph]^+$, 95 (18) $[C_7H_{11}]^+$, 91 (100) $[C_7H_7]^+$, 81 (25) $[C_6H_9]^+$, 41 (10) $[C_3H_5]^+$.

1-Phenyl-5-({(2*R*)-1,7,7-trimethylbicyclo[2.2.1]-hept-2-yl}sulfanyl)-1*H*-tetrazole (VI). Yield 61%, mp 100°C. ^{1}H NMR spectrum, δ, ppm: 0.87 s (3H, H^{10}), 0.94 s and 1.00 s (6H, $H^{8,9}$), 1.25–1.29 m, 1.46–1.50 m, 1.75–1.81 m, 1.94–1.98 m (6H, $H^{3,5,6}$), 2.19–2.25 m (1H, H^4), 4.23 d.d (1H, H^2, *J* 9.54, 5.56 Hz), 7.52–7.57 m (5H, Ph). Mass spectrum (EI), *m*/*z* (I_{rel}, %): 314 (4) $[M]^{+\cdot}$, 168 (7) $[M - C_7H_5N_4]^+$, 137 (96) $[M - SC_7H_5N_4]^+$, 81 (100) $[C_6H_9]^+$, 41 (26) $[C_3H_5]^+$.

2-({(2*R*)-1,7,7-Trimethylbicyclo[2.2.1]hept-2-yl}-sulfanyl)-1,3-benzothiazole (VII). Yield 40%. ^{1}H NMR spectrum, δ, ppm: 0.88 s (3H, H^{10}), 1.00 s and 1.04 s (6H, $H^{8,9}$), 1.22–2.04 m (7H, H^{3-6}), 4.11 d.d (1H, H^2, *J* 9.54, 5.56 Hz), 7.25–7.42 m (2H, H_{Ar}), 7.73 d and 7.86 d (2H, H_{Ar}, *J* 7.95 Hz).

2-({(2*R*)-1,7,7-Trimethylbicyclo[2.2.1]hept-2-yl}-sulfanyl)-1*H*-benzimidazole (VIII). Yield 45%. ^{1}H NMR spectrum, δ, ppm: 0.82 s (3H, H^{10}), 0.95 s and 0.96 s (6H, $H^{8,9}$), 1.15–2.00 m (7H, $H^{3,5,6}$), 2.12–2.18 m (1H, H^4), 3.97 d.d (1H, H^2, *J* 9.54, 5.36 Hz), 7.26 d.d (2H, H_{Ar}, *J* 5.96, 3.58 Hz), 7.59–7.61 m (2H, H_{Ar}), 8.00 br.s (1H, NH).

Phenyl (2*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl sulfide (IX). Yield 66%. ^{1}H NMR spectrum, δ, ppm: 0.86 s (3H, H^{10}), 1.02 s and 1.05 s (6H, $H^{8,9}$), 1.18–1.79 m (6H, $H^{3,5,6}$), 2.00 d (1H, H^4, *J* 7.95 Hz), 3.23 t (1H, H^2, *J* 7.55 Hz), 7.13–7.51 m (5H, Ph). Mass spectrum (EI), *m*/*z* (I_{rel}, %): 246 (3) $[M]^{+\cdot}$, 137 (76) $[M - SPh]^+$, 95 (23) $[C_7H_{11}]^+$, 81 (100) $[C_6H_9]^+$, 67 (18) $[C_5H_7]^+$, 41 (13) $[C_3H_5]^+$.

2-*exo*-[(4-Fluorophenyl)sulfanyl]-1,7,7-trimethylbicyclo[2.2.1]heptane (X). Yield 75%. ^{1}H NMR spectrum, δ, ppm: 0.85 s (3H, H^{10}), 1.00 s and 1.03 s (6H, $H^{8,9}$), 1.14–1.21 m, 1.68–1.75 m, 1.94–1.98 m (7H, H^{3-6}), 3.09–3.12 d.d (1H, H^2, *J* 8.7, 6.3 Hz), 6.96–7.37 m (4H, H_{Ar}). Mass spectrum (EI), *m*/*z* (I_{rel}, %): 264 (8) $[M]^{+\cdot}$, 263 (51) $[M - H]^+$, 137 (30) $[M - SPhF]^+$, 121 (35) $[M - SPhF - CH_4]^+$, 93 (85) $[C_7H_9]^+$, 81 (100) $[C_6H_9]^+$, 67 (48) $[C_5H_7]^+$, 41 (90) $[C_3H_5]^+$.

2-*exo*-[(2-Fluorophenyl)sulfanyl]-1,7,7-trimethylbicyclo[2.2.1]heptane (XI). Yield 70%. ^{1}H NMR spectrum, δ, ppm: 0.86 s (3H, H^{10}), 1.02 s and 1.07 s (6H, $H^{8,9}$), 1.16–1.25 m, 1.68–1.76 m, 1.93–2.01 m (7H, H^{3-6}), 3.21 d.d (1H, H^2, *J* 8.9, 6.0 Hz), 7.01–7.4 m (4H, H_{Ar}). Mass spectrum (EI), *m*/*z* (I_{rel}, %): 264 (4) $[M]^{+\cdot}$, 137 (100) $[M - SPhF]^+$, 109 (11) $[M - SPhF - C_2H_4]^+$, 95 (45) $[C_7H_{11}]^+$, 81 (59) $[C_6H_9]^+$, 41 (17) $[C_3H_5]^+$.

2-*exo*-[(4-Bromophenyl)sulfanyl]-2,3,3-trimethylbicyclo[2.2.1]heptane (XII). Yield 60%, mp 90–92°C. ^{1}H NMR spectrum, δ, ppm: 0.99 s, 1.21 s, 1.29 s (9H, $H^{8,9,10}$), 1.62 m, 1.81 br.s, 1.97 m, 2.14 br.s, 2.50 m (8H, $H^{1,4-7}$), 7.35 m, 7.41 m (4H, H_{Ar}).

2-*exo*-[(4-Chlorophenyl)sulfanyl]-2,3,3-trimethylbicyclo[2.2.1]heptane (XIII). Yield 79%, mp 91–93°C. ^{1}H NMR spectrum, δ, ppm: 1.02 s, 1.21 s, 1.29 s (9H, $H^{8,9,10}$), 1.33 m, 1.62 m, 1.81 br.s, 2.14 br.s, 2.50 m (8H, $H^{1,4-7}$), 7.27 m, 7.43 m (4H, H_{Ar}). ^{13}C NMR spectrum, δ_C, ppm: 22.43, 23.60, 23.81 ($C^{8,9,10}$), 23.96, 27.87 ($C^{5,6}$), 35.54 (C^7), 44.06 (C^3), 49.24 (C^4), 51.59 (C^1), 62.49 (C^2), 128.48 (2 $C^{3'}$), 132.92 ($C^{1'}$), 134.80 ($C^{4'}$), 139.00 (2 $C^{2'}$).

2-*exo*-[(2-Chlorophenyl)sulfanyl]-2,3,3-trimethylbicyclo[2.2.1]heptane (XIV). Yield 72%. ^{1}H NMR spectrum, δ, ppm: 1.05 s, 1.29 s, 1.36 s (9H, $H^{8,9,10}$), 1.34 m, 1.59–1.69 m, 1.82 br.s, 2.24 br.s, 2.59 m (8H, $H^{1,4-7}$), 7.22–7.57 m (4H, H_{Ar}). Mass spectrum (EI), *m*/*z* (I_{rel}, %): 280 (4) $[M]^{+\cdot}$, 170 (5) $[M - C_6H_4Cl]^+$, 137 (73) $[M - SPhCl]^+$, 108 (15) $[M - SPhCl - C_2H_5]^+$, 95 (34) $[C_7H_{11}]^+$, 81 (100) $[C_6H_9]^+$, 41 (43) $[C_3H_5]^+$.

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