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Reaction of Tricyclo[4.1.0.0^{2,7}]heptane with 1-(Arenesulfonyl)-2-phenyldiazenes

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Abstract—Tricyclo[4.1.0.0^{2,7}]heptane reacted with 1-(arenesulfonyl)-2-phenyldiazenes by radical mechanism to give bicyclo[3.1.1]heptane derivatives. Unlike analogous reactions with alkenes, the addition of diazenes occurs readily without a catalyst and yields mainly arylazosulfonation products at the C^1–C^7 bond of tricyclo-[4.1.0.0^{2,7}]heptane. The addition products are capable of undergoing thermal prototropic isomerization to 7-*endo*-(arenesulfonyl)bicyclo[3.1.1]heptan-6-one phenylhydrazones.

Keywords: 1-(arenesulfonyl)-2-phenyldiazenes, tricyclo[4.1.0.0^{2,7}]heptane, radical addition, bicyclo[3.1.1]-heptane, prototropic rearrangement

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1-(Arenesulfonyl)-2-phenyldiazenes are known [1–3] to react with some alkenes in the presence of $Pd(PPh_3)_4$ as catalyst to give mainly arylation and arenesulfonation products. The major products in the reactions with α,β-unsaturated esters are β-aryl-substituted alkenes, whereas α,β-unsaturated ketones undergo both arylation and arenesulfonation [2]. However, styrene under similar conditions gave rise to sulfonyl-substituted azo compounds in addition to the arylation products [3], whereas radical polymerization of styrene was observed under photochemical and thermal initiation [4]. It has also been found that arenesulfonyl and aryl radicals are generated in the photochemical decomposition of aryl aryldiazenyl sulfones [5]. The synthesis of substituted allylarenes via photochemical generation of aryl radicals from aryldiazenyl sulfones and their subsequent reaction with allyl sulfones has been reported [6].

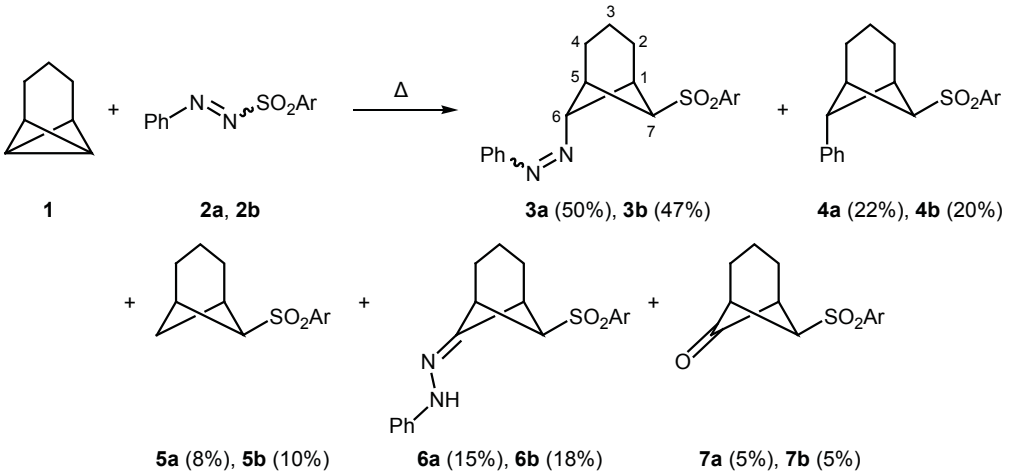
In recent years, 1-aryl-2-(methanesulfonyl)diazenes have been used in the photochemical arylation of diarylethenes [7]. Taking into account some structural similarity between the π-bond of alkenes and central C–C bond of bicyclo[1.1.0]butanes, we presumed that 1-(arenesulfonyl)-2-phenyldiazenes could also react with the latter. We selected one of the most accessible hydrocarbons of the bicyclo[1.1.0]butane series, tricyclo[4.1.0.0^{2,7}]heptane (**1**), as a model compound.

In fact, compound **1** reacted with 1-(benzenesulfonyl)-2-phenyldiazene (**2a**) and 1-(4-methylbenzenesulfonyl)-2-phenyldiazene (**2b**) at 60–70°C in benzene to give multicomponent mixtures of bicyclo[3.1.1]-heptane derivatives **3**–**7** (Scheme 1). The compositions of the reaction mixtures were determined by ^{1}H NMR spectroscopy. Compounds **3a** and **3b** were isolated in the pure state by alumina column chromatography and were characterized by IR, ^{1}H and ^{13}C NMR, and mass spectra and elemental analyses. The other components (compounds **4a**, **4b**, **5a**, **5b**, **6a**, **6b**, **7a**, and **7b**) were identified in the reaction mixtures without isolation by comparing with authentic samples which were prepared by independent syntheses. In particular, sulfones **4a** and **4b** were synthesized by peroxide oxidation of the corresponding arenethiol–1-phenyltricyclo[4.1.0.0^{2,7}]-heptane (**8**) adducts [8], and sulfones **5a** and **5b** were prepared in a similar way from tricycloheptane **1** [9]. In the case of compound **8**, we obtained mixtures of stereoisomeric sulfones **4a**/**9a** and **4b**/**9b** at a ratio of ~1:5.5 (Scheme 2); the pure stereoisomers were isolated by alumina column chromatography.

Phenylhydrazones **6a** and **6b** were synthesized from ketones **7a** and **7b** which were prepared in turn by addition of the corresponding arenesulfonyl bromides to 1-(phenylsulfanyl)tricyclo[4.1.0.0^{2,7}]heptane (**10**), followed by hydrolysis (Scheme 3), according to [10]; 4-methylbenzenesulfonyl derivative **7b** and its phenylhydrazone **6b** were not reported previously.

The bicyclo[3.1.1]heptane structure of **3**–**7** is confirmed by the presence of 5 peaks in their ^{13}C NMR

Scheme 1.

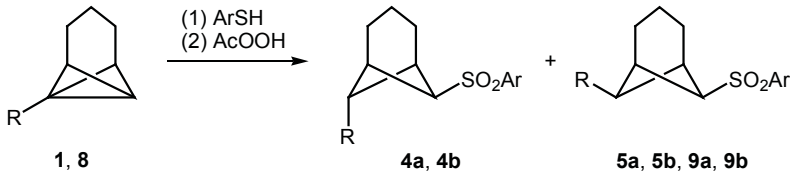


Ar = Ph (**a**), 4-MeC$_6$H$_4$ (**b**).

spectra with proper intensities and chemical shifts. The orientation of substituents in molecules **3–7** was inferred from the analysis of the positions and multiplicities of the 6-H and 7-H signals in the ^{1}H NMR spectra with account taken of known correlations [8–10]. The triplet signal of 7-H indicated *anti* orientation of that proton with respect to the trimethylene bridge. Likewise, the singlet signal of 6-H in the spectra of **3a**, **3b**, **4a**, and **4b** corresponds to its *syn* orientation. The diazenyl fragment gave rise to an IR band at 1477 cm^{-1}, and the sulfonyl group characteristically showed stretching vibration bands at ~1145 and ~1310 cm^{-1}. Compounds **6a** and **6b** were formed as a result of thermal prototropic rearrangement of azo isomers **3a** and **3b**. The occurrence of this isomerization was confirmed by independent experiment in which pure compounds **3a** and **3b** in benzene were heated at 60–70°C for 10 h; according to the ^{1}H NMR data, the conversion of **3a** and **3b** into hydrazones **6a** and **6b** was 35–40%.

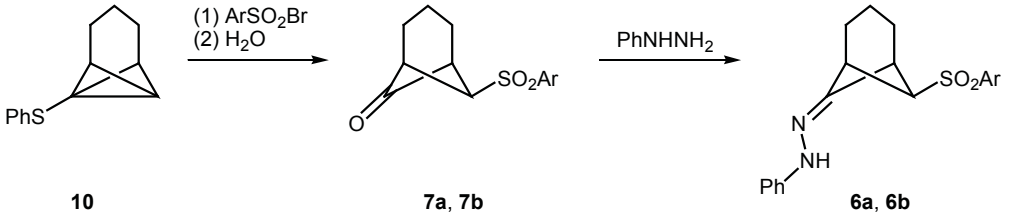
The formation of ketones **7a** and **7b** may be rationalized assuming concurrent thermally induced prototropic rearrangement of **3a** and **3b** into phenylhydrazones **6a** and **6b** and hydrolysis of the latter with traces of water present in the reaction mixture. This was confirmed by the intentional transformation of bicycloheptanes **3a** and **3b** to ketones **7a** and **7b** on heating at 50–55°C for 4 h in aqueous tetrahydrofuran (Scheme 4). The pure products were isolated by crystallization, and the structure of **7b** was assigned on the basis of its IR and ^{1}H and ^{13}C NMR spectra and the corresponding data for known analog **7a** [10].

Scheme 2.



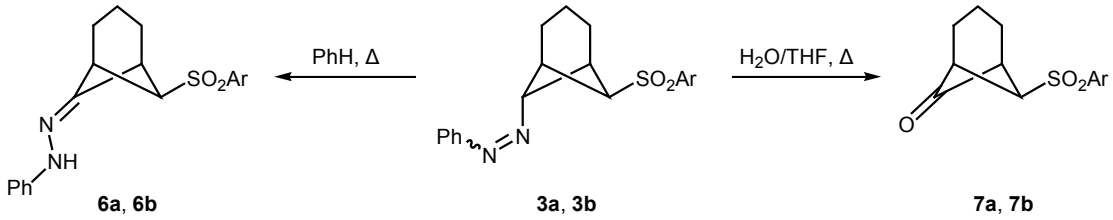
1, **5**, R = H; **4**, **8**, **9**, R = Ph; Ar = Ph (**a**), 4-MeC$_6$H$_4$ (**b**).

Scheme 3.



Ar = Ph (**a**), 4-MeC$_6$H$_4$ (**b**).

Scheme 4.



Ar = Ph (**a**), 4-MeC_6H_4 (**b**).

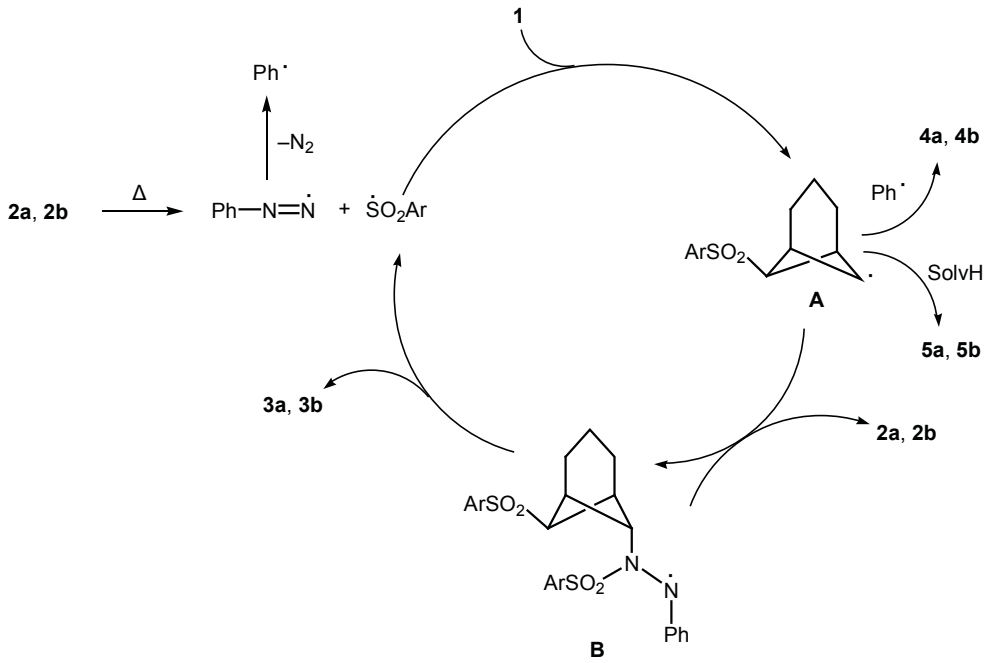
Thus, the major products in the reactions of **1** with azo sulfones **2a** and **2b** are 1:1 adducts where the azo fragment is retained; this is somewhat surprising in comparison with analogous alkene reactions. We believe that bicyclo[3.1.1]heptanes **3**–**5** are formed via a homolytic pathway (Scheme 5) starting from dissociation of the N–S bond in the reagent. Next follows *endo* attack of the liberated sulfonyl radical to the bridgehead carbon atom of tricycloheptane **1**. Intermediate bicycloheptyl radical **A** adds to azo sulfone **2** to give hydrazinyl radical **B**, and elimination of arenesulfonyl radical from **B** yields product **3**. Compound **4** is formed as a result of coupling of radical **A** and phenyl radical generated by loss of nitrogen from phenyldiazenyl radical. Small amounts of compounds **5** can appear in the reaction mixtures via abstraction of hydrogen from the solvent by radical **A**, as reported in [9] for the addition of sulfonyl chlorides to tricycloheptane **1**.

In summary, 1-(arenesulfonyl)-2-phenyldiazenes **2a** and **2b** react with tricyclo[4.1.0.$0^{2,7}$]heptane (**1**) to afford 6-(arenesulfonyl)-7-(phenyldiazenyl)bicyclo-[3.1.0]heptanes as the major products. The addition reaction features the same regio- and stereoselectivity as in other sulfonation reactions of compound **1**, e.g., with sulfonyl halides [9], sulfonothioic and sulfonoselenoic acid esters [11], and ethynyl [12] and allyl sulfones [13].

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded from solutions in $CDCl_3$ on a Jeol JNM-ECX400 spectrometer (Japan) at 400 and 100 MHz, respectively, using the residual proton (δ 7.26 ppm) and carbon signals (δ_C 77.16 ppm) of the solvent as reference. The IR spectra were recorded in KBr on an InfraLYuM FT-02 spectrometer (*Lyumeks* Ltd., Russia). Elemental anal-

Scheme 5.



Ar = Ph (**a**), 4-MeC_6H_4 (**b**).

ysis was carried out with an Elementar Vario MICRO CHNS analyzer (Germany). Analytical TLC was performed on Silufol UV-245 plates using light petroleum ether–ethyl acetate (4:1) as eluent; spots were visualized by treatment with iodine vapor or under UV light. Aluminum oxide (Brockmann activity grade II, 0.04–0.2 mm, *KhromLab* Ltd.) was used for column chromatography; eluent light petroleum ether–ethyl acetate, 6:1 to 3:1. The melting points were measured in sealed glass capillary tubes using a Mettler-Toledo MP-50 melting point analyzer (Switzerland). The mass spectra (electron impact, 70 eV) were obtained on a KONIK RBK-HRGC 5000B-MSQ12 instrument (Konixbert Hi-Tech, Spain).

Phenylhydrazine hydrochloride (≥99%), benzenethiol (97%), and 4-methylbenzene-1-thiol (98%) were commercial products (Sigma–Aldrich). The solvents were distilled prior to use.

Tricyclo[4.1.0.0^{2,7}]heptane (**1**) [14], 1-phenyltricyclo[4.1.0.0^{2,7}]heptane (**8**) [15], 1-(phenylsulfanyl)tricyclo[4.1.0.0^{2,7}]heptane (**9**) [16], 1-(benzenesulfonyl)-2-phenyldiazene (**2a**), 1-(4-methylbenzenesulfonyl)-2-phenyldiazene (**2b**) [17], and compounds **4a**, **9a** [8], **5a**, **5b** [9], and **7a** [10] were synthesized according to reported procedures.

Reaction of tricycloheptane 1 with 1-(arenesulfonyl)-2-phenyldiazenes 2a and 2b (*general procedure*). A flat-bottom flask equipped with a magnetic stirrer was charged with a solution of 0.51 g (5.4 mmol) of tricycloheptane **1** in 12 mL of anhydrous benzene and a solution of 2.7 mmol of **2a** or **2b** in 12 mL of anhydrous benzene. The mixture was stirred at 60–70°C for 14 h under dry argon. The solvent was removed under reduced pressure, and the residue was analyzed by TLC and ^{1}H NMR. The major product (**3a** or **3b**) was isolated by alumina column chromatography.

6-*syn*-(Benzenesulfonyl)-7-*exo*-(phenyldiazenyl)-bicyclo[3.1.1]heptane (3a). Yield 240 mg (26.2%), yellow crystals, mp 130–131°C (decomp., from acetone–petroleum ether). IR spectrum, ν, cm^{-1}: 2955 w, 1477 w (N=N), 1447 m, 1308 s (SO_2, asym.), 1285 s, 1146 v.s (SO_2, sym.), 1088 m, 721 v.s, 687 s, 617 v.s. ^{1}H NMR spectrum, δ, ppm: 1.87–1.98 m (1H, *endo*-3-H), 2.05–2.21 m (3H, *exo*-3-H, *endo*-2-H, *endo*-4-H), 2.82–2.89 m (2H, *exo*-2-H, *exo*-4-H), 3.04 br.s (2H, 1-H, 5-H), 4.20 s (1H, *endo*-6-H), 4.60 t (1H, *anti*-7-H, J = 5.8 Hz), 7.42–7.44 m (3H, H_{arom}), 7.56–7.65 m (5H, H_{arom}), 7.94–7.96 m (2H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 14.6 (C^3), 23.3 (C^2, C^4), 44.2 (C^1, C^5), 60.4 (C^7), 79.5 (C^6), 122.2 (2C, C_{arom}), 127.5 (2C, C_{arom}), 129.0 (2C, C_{arom}), 129.3 (2C, C_{arom}), 130.8 (C_{arom}), 133.4 (C_{arom}), 140.5 (C_{arom}), 151.7 (C_{arom}). Mass spectrum, m/z (I_{rel}, %): 340 (2) $[M]^+$, 235 (20), 199 (33), 142 (68), 105 (68), 93 (100). Found, %: C 67.09; H 5.88; N 8.29. $C_{19}H_{20}N_2O_2S$. Calculated, %: C 67.03; H 5.92; N 8.23.

6-*syn*-(4-Methylbenzenesulfonyl)-7-*exo*-(phenyldiazenyl)bicyclo[3.1.1]heptane (3b). Yield 200 mg (21%), yellow–orange crystals, mp 159–161°C (decomp., from acetone–petroleum ether). IR spectrum, ν, cm^{-1}: 2955 w, 1477 w (N=N), 1448 w, 1311 s (SO_2, asym.), 1285 s, 1142 s (SO_2, sym.), 1088 m, 818 m, 764 w, 671 v.s, 606 m. ^{1}H NMR spectrum, δ, ppm: 1.86–1.97 m (1H, *endo*-3-H), 2.03–2.201 m (3H, *exo*-3-H, *endo*-2-H, *endo*-4-H), 2.44 s (3H, C**H**$_3$C$_6$H$_4$), 2.81–2.88 m (2H, *exo*-2-H, *exo*-4-H), 3.03 br.s (2H, 1-H, 5-H), 4.20 s (1H, *endo*-6-H), 4.58 t (1H, *anti*-7-H, J = 5.9 Hz), 7.36 d (2H, H_{arom}, J = 7.9 Hz), 7.42–7.44 m (3H, H_{arom}), 7.62–7.65 m (2H, H_{arom}), 7.82 d (2H, H_{arom}, J = 8.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 14.6 (C^3), 21.6 (**C**H$_3$C$_6$H$_4$), 23.3 (C^2, C^4), 44.2 (C^1, C^5), 60.5 (C^7), 79.5 (C^6), 122.3 (2C, C_{arom}), 127.6 (2C, C_{arom}), 129.0 (2C, C_{arom}), 130.0 (2C, C_{arom}), 130.8 (C_{arom}), 137.6 (C_{arom}), 144.3 (C_{arom}), 151.7 (C_{arom}). Mass spectrum, m/z (I_{rel}, %): 300 (30) $[M]^+$, 285 (25), 272 (33), 246 (34), 194 (100), 167 (40), 103 (40), 63 (50). Found, %: C 67.80; H 6.29; N 7.88. $C_{20}H_{22}N_2O_2S$. Calculated, %: C 67.77; H 6.26; N 7.90.

Independent synthesis of compounds 4b and 9b. A solution of 1.70 g (10 mmol) of 1-phenyltricycloheptane **8** in 12 mL of carbon tetrachloride was mixed with a solution of 1.51 g (12 mmol) of 4-methylbenzenethiol in 12 mL of carbon tetrachloride, and the mixture was kept in a tightly capped flask at 20°C for 24 h. The mixture was washed with 10 mL of 5% aqueous sodium hydroxide to remove excess thiol, dried over $CaCl_2$, and evaporated under reduced pressure. The residue was cooled to –10°C, and 10 mL of acetic acid, 10 mL of acetic anhydride, and 5 mL of 30% aqueous hydrogen peroxide were added at that temperature. The mixture was stirred on a magnetic stirrer at –10 to 0°C for 5 h and at 20°C for 24 h. The solvent was removed under reduced pressure, the residue was dissolved in 20 mL of chloroform, and the solution was washed with a saturated aqueous solution of $NaHCO_3$ and dried over $CaCl_2$. The solvent was removed under reduced pressure, and the solid residue was subjected to alumina chromatography.

6-*syn*-(4-Methylbenzenesulfonyl)-7-*exo*-phenylbicyclo[3.1.1]heptane (4b). Yield 195 mg (6.1%),

colorless crystals, mp 134–135°C (from $CHCl_3$–petroleum ether). IR spectrum, ν, cm^{-1}: 2956 m, 1599 w, 1312 s (SO_2, asym.), 1290 s, 1144 s (SO_2, sym.), 1084 m, 827 m, 770 w, 680 v.s, 601 m. ^1H NMR spectrum, δ, ppm: 1.88–1.97 m (1H, *endo*-3-H), 2.04–2.26 m (1H, *exo*-3-H), 2.43 s (3H, C**H**$_3C_6H_4$), 2.66–2.79 m (2H, *endo*-2-H, *endo*-4-H), 2.81–2.88 m (2H, *exo*-2-H, *exo*-4-H), 3.02 br.d (2H, 1-H, 5-H), 3.19 s (1H, *endo*-6-H), 3.61 t (1H, *anti*-7-H, J = 5.9 Hz), 7.33 d (2H, H_{arom}, J = 7.9 Hz), 7.40–7.44 m (3H, H_{arom}), 7.60–7.64 m (2H, H_{arom}), 7.79 d (2H, H_{arom}, J = 8.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 14.6 (C^3), 21.6 (**C**$H_3C_6H_4$), 24.6 (C^2, C^4), 43.0 (C^1, C^5), 44.8 (C^6), 60.0 (C^7), 122.3 (2C, C_{arom}), 126.9 (2C, C_{arom}), 127.5 (2C, C_{arom}), 130.0 (2C, C_{arom}), 130.8 (C_{arom}), 137.6 (C_{arom}), 139.3 (C_{arom}), 144.7 (C_{arom}). Mass spectrum, m/z (I_{rel}, %): 326 (4) $[M]^+$, 171 (45), 156 (38), 145 (20), 129 (22), 91 (100). Found, %: C 73.55; H 6.76. $C_{20}H_{22}O_2S$. Calculated, %: C 73.58; H 6.79.

6-*syn*-(4-Methylbenzenesulfonyl)-7-*endo*-phenylbicyclo[3.1.1]heptane (9b). Yield 1.66 g (50.8%), colorless crystals, mp 150–151°C (from $CHCl_3$–petroleum ether). IR spectrum, ν, cm^{-1}: 2957 m, 1600 w, 1315 s (SO_2, asym.), 1291 s, 1147 s (SO_2, sym.), 1085 m, 830 m, 775 w, 685 v.s, 608 m. ^1H NMR spectrum, δ, ppm: 0.63–0.86 m (1H, *endo*-3-H), 1.44–1.59 m (1H, *exo*-3-H), 2.44 s (3H, C**H**$_3C_6H_4$), 1.78–1.95 m (2H, *endo*-2-H, *endo*-4-H), 2.42–2.65 m (2H, *exo*-2-H, *exo*-4-H), 3.15 br.d (2H, 1-H, 5-H), 2.91 t (1H, *exo*-6-H, J = 5.9 Hz), 3.38 t (1H, *anti*-7-H, J = 5.9 Hz), 7.28 d (2H, H_{arom}, J = 7.9 Hz), 7.36–7.42 m (3H, H_{arom}), 7.57–7.61 m (2H, H_{arom}), 7.71 d (2H, H_{arom}, J = 8.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 13.6 (C^3), 21.0 (**C**$H_3C_6H_4$), 20.4 (C^2, C^4), 40.4 (C^6), 41.8 (C^1, C^5), 60.7 (C^7), 121.9 (2C, C_{arom}), 126.4 (2C, C_{arom}), 127.0 (2C, C_{arom}), 129.8 (2C, C_{arom}), 130.1 (C_{arom}), 136.2 (C_{arom}), 138.9 (C_{arom}), 142.0 (C_{arom}). Mass spectrum, m/z (I_{rel}, %): 326 (4) $[M]^+$, 171 (40), 156 (35), 145 (25), 129 (30), 91 (100). Found, %: C 73.55; H 6.76. $C_{20}H_{22}O_2S$. Calculated, %: C 73.58; H 6.79.

Independent synthesis of 7-*endo*-(4-methylbenzenesulfonyl)bicyclo[3.1.1]heptan-6-one (7b). A solution of 1.01 g (5 mmol) of 1-(phenylsulfanyl)tricyclo[4.1.0.0^{2,7}]heptane (**10**) in 4 mL of methylene chloride was mixed with a solution of 1.17 g (5 mmol) of 4-methylbenzenesulfonyl bromide in 4 mL of methylene chloride, and the mixture was irradiated in a hermetically closed quartz test tube for 10 h. The solvent was removed under reduced pressure, the residue was dissolved in 20 mL of THF, and a solution of 1 g of sodium carbonate in 10 mL of water was added. The mixture was refluxed with stirring on a magnetic stirrer for 3 h. The solvent was removed under reduced pressure, the residue was dissolved in 15 mL of chloroform, and the solution was washed with 5 mL of 5% aqueous sodium hydroxide to remove benzenethiol and dried over $CaCl_2$. The solvent was removed under reduced pressure, and the residue was recrystallized from acetone–petroleum ether. Yield 0.82 g (62%), mp 136–137°C. IR spectrum, ν, cm^{-1}: 2955 w, 1782 v.s (C=O), 1597 w, 1319 m (SO_2, asym.), 1288 s, 1146 v.s (SO_2, sym.), 1088 m, 694 m, 671 s, 586 m. ^1H NMR spectrum, δ, ppm: 1.68–1.77 m (1H, *endo*-3-H), 2.91–1.98 m (1H, *exo*-3-H), 2.22–2.27 m (2H, *endo*-2-H, *endo*-4-H), 2.45 s (3H, C**H**$_3C_6H_4SO_2$), 3.25–3.30 m (4H, *exo*-2-H, exo-4-H, 1-H, 5-H), 3.45 t (1H, *anti*-7-H, J = 6.0 Hz), 7.37 d (2H, H_{arom}, J = 8.0 Hz), 7.80 d (2H, H_{arom}, J = 8.1 Hz). ^{13}C NMR spectrum, δ_C, ppm: 16.7 (C^3), 21.6 (**C**$H_3C_6H_4$), 27.5 (C^2, C^4), 53.1 (C^1, C^5), 60.2 (C^7), 127.3 (2C, C_{arom}), 130.2 (2C, C_{arom}), 138.0 (C_{arom}), 145.0 (C_{arom}), 206.1 (C^6=O). Mass spectrum, m/z (I_{rel}, %): 264 (3) $[M]^+$, 249 (10), 156 (41), 109 (50), 91 (100). Found, %: C 63.59; H 6.13. $C_{14}H_{16}O_3S$. Calculated, %: C 63.61; H 6.10.

Phenylhydrazones 6a and 6b (*general procedure*). A solution of 3 mmol of ketone **7a** or **7b** in 7 mL of dioxane was added in small portions under continuous stirring to a solution of 477 mg (3.3 mmol) of phenylhydrazine hydrochloride and 250 mg (3 mmol) of anhydrous sodium acetate in 7 mL of water. The mixture was stirred at room temperature for 2 h, and the precipitate was filtered off, dried in air, and recrystallized from ethanol.

7-*endo*-(Benzenesulfonyl)bicyclo[3.1.1]heptan-2-one phenylhydrazone (6a). Yield 0.84 g (82.3%), mp 174–175°C. IR spectrum, ν, cm^{-1}: 2961 w, 1602 s, 1505 w, 1449 m, 1312 s (SO_2, asym.), 1291 s, 1150 v.s (SO_2, sym.), 1091 m, 720 v.s, 680 s, 622 v.s. ^1H NMR spectrum, δ, ppm: 1.32–1.36 m (1H, *endo*-3-H), 1.44–1.49 m (1H, *exo*-3-H), 1.52–1.74 m (4H, *endo*-2-H, *endo*-4-H), 2.02–2.11 m (2H, *exo*-2-H, *exo*-4-H), 3.44 br.d (2H, 1-H, 5-H), 3.68 t (1H, *exo*-7-H, J = 5.8 Hz), 7.42–7.44 m (3H, H_{arom}), 7.06–7.31 m (5H, H_{arom}), 7.94–7.96 m (2H, H_{arom}), 9.87 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 13.9 (C^3), 24.3 (C^2, C^4), 42.2 (C^1, C^5), 58.1 (C^7), 118.2 (2C, C_{arom}), 125.2 (2C, C_{arom}), 128.1 (2C, C_{arom}), 129.2 (2C, C_{arom}), 129.8 (C_{arom}), 138.4 (C_{arom}), 144.7 (C_{arom}), 151.7 (C_{arom}),

153.6 (C^6). Mass spectrum, *m*/*z* (I_{rel}, %): 340 (4) $[M]^+$, 235 (15), 222 (34), 199 (58), 157 (39), 142 (100), 107 (50). Found, %: C 67.09; H 5.88; N 8.29. $C_{19}H_{20}N_2O_2S$. Calculated, %: C 67.03; H 5.92; N 8.23.

7-*endo*-(4-Methylbenzenesulfonyl)bicyclo[3.1.1]-heptan-2-one phenylhydrazone (6b). Yield 0.90 g (85%), mp 189–190°C. IR spectrum, ν, cm^{-1}: 2959 m, 1599 s, 1504 w, 1450 m, 1316 s (SO_2, asym.), 1290 s, 1156 v.s (SO_2, sym.), 1094 m, 718 v.s, 675 s, 620 v.s. ^{1}H NMR spectrum, δ, ppm: 1.30–1.34 m (1H, *endo*-3-H), 1.41–1.45 m (1H, *exo*-3-H), 1.53–1.70 m (2H, *endo*-2-H, *endo*-4-H), 2.06–2.14 m (2H, *exo*-2-H, *exo*-4-H), 2.45 s (3H, C**H**$_3$C$_6$H$_4$), 3.14 br.d (2H, 1-H, 5-H), 3.48 t (1H, *exo*-7-H, J = 5.8 Hz), 7.28 d (2H, H_{arom}, J = 7.9 Hz), 7.28–7.39 m (3H, H_{arom}), 7.47–7.51 m (2H, H_{arom}), 7.71 d (2H, H_{arom}, J = 8.2 Hz), 9.86 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 14.9 (C^3), 21.3 (**C**H$_3$C$_6$H$_4$), 25.3 (C^2, C^4), 50.2 (C^1, C^5), 59.6 (C^7), 118.2 (2C, C_{arom}), 124.2 (2C, C_{arom}), 126.7 (2C, C_{arom}), 129.7 (2C, C_{arom}), 130.1 (C_{arom}), 136.4 (C_{arom}), 138.7 (C_{arom}), 142.7 (C_{arom}), 152.9 (C^6). Mass spectrum, *m*/*z* (I_{rel}, %): 354 (4) $[M]^+$, 339 (18), 199 (45), 171 (30), 156 (100), 107 (43). Found, %: C 67.75; H 6.28; N 7.87. $C_{20}H_{22}N_2O_2S$. Calculated, %: C 67.77; H 6.26; N 7.90.

Isomerization of bicyclo[3.1.1]heptanes 3a and 3b to phenylhydrazones 6a and 6b (*general procedure*). A solution of 0.1 mmol of compound **3a** or **3b** in 2 mL of benzene was heated in a sealed ampule at 60–70°C for 10 h. The ampule was cooled and opened, the solvent was removed under reduced pressure, and the residue was analyzed by ^{1}H and ^{13}C NMR.

Hydrolysis of compounds 3a and 3b (*general procedure*). A flat-bottom flask equipped with a magnetic stirrer was charged with a solution of 0.3 mmol of compound **3a** or **3b** in a mixture of 15 mL of THF and 1 mL of water. The mixture was heated at 50–55°C for 4 h (TLC), the solvent was removed under reduced pressure, and the residue was recrystallized from acetone–petroleum ether. Yield: **7a**, 61 mg (82%); **7b**, 63 mg (80%).

CONFLICT OF INTEREST

The authors declare the absence of conflict of interest.

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