BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (4), 1178—1182 (1978)

Sulfur-Carbonyl Interaction in Rigid β-Keto Sulfides

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(Received September 3, 1977)

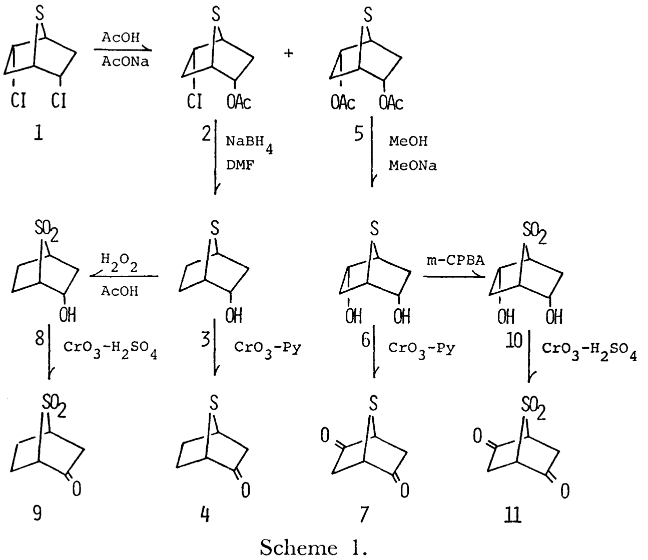
The electron donating ability of sulfur to a positively charged center through space was examined by means of ultraviolet spectroscopy. 7-Thiabicyclo[2.2.1]heptan-2-one and -2,5-dione exhibited finely separated charge transfer band (from divalent sulfide to carbonyl) at 260 nm in UV spectra, the longest wave-length for S–Cco charge transfer band so far reported. The assignment of these CT bands was confirmed by comparison with relevant reference compounds.

Recently it has been reported that the sulfur-bridge greatly accelerates the solvolysis of 2-*endo*-chloro-7-thiabicyclo[2.2.1]heptane, while it decelerates the solvolysis of 2-*exo*-chloro isomer (the former solvolyzed 4.7×10^9 times faster than the latter).[1] Spectroscopic examination of the sulfur-carbonyl interaction might give more insight into this sulfur participation. Although the interaction between sulfur (donor) and carbonyl (acceptor) has been observed in UV and IR spectroscopy,[2,3] little effort has been done to confirm under what conditions, steric and electronic, sulfur-carbonyl interaction, sulfur-positive center interaction, becomes most efficient. For this purpose, more model systems are required, especially the rigid sulfur-containing molecules of known geometry.

The aim of the present study is to examine the nature of the sulfur-carbonyl interaction in β-keto sulfides, taking 7-thiabicyclo[2.2.1]heptan-2-one (**4**),[4] 7-thiabicyclo[2.2.1]heptane-2,5-dione (**7**), and the related compounds as sterically and spacially fixed models.

Results and Discussion

Syntheses of 7-Thiabicyclo[2.2.1]heptan-2-one (4) and 7-Thiabicyclo[2.2.1]heptane-2,5-dione (7); Oxidation of Hydroxy Sulfides 3 and 6 to Oxo Sulfides 4 and 7. 7-Thiabicyclo[2.2.1]heptan-2-one (**4**), 7-thiabicyclo[2.2.1]heptane-2,5-dione (**7**) and the corresponding sulfones (**9** and **11**) were prepared according to Scheme 1. Controlled acetolysis of 2,5-*endo*-*endo*-dichloro-7-thiabicyclo[2.2.1]heptane (**1**)[5] gave a mixture of 2-*endo*-acetoxy-5-*endo*-chloro-7-thiabicyclo[2.2.1]heptane (**2**) and 2,5-*endo*-*endo*-diacetoxy-7-thiabicyclo[2.2.1]heptane (**5**). After separation of **2** and **5** by means of column chromatography, **2** was reduced with $NaBH_4$ to give 2-*endo*-hydroxy-7-thiabicyclo[2.2.1]heptane (**3**). 2,5-*endo*-*endo*-Dihydroxy-7-thiabicyclo[2.2.1]heptane (**6**) was obtained by the hydrolysis of **5**. The key step in Scheme 1 consists of the selective oxidation of hydroxyl group to ketone in the presence of the sulfide linkage highly susceptible to oxidation. The oxidation of **3** to **4** was performed by chromium trioxide-pyridine complex[6] in good yield (83%) without appreciable oxidation of sulfur. Similar oxidation of **6** gave **7** in 35% yield together with 5-*endo*-hydroxy-7-thiabicyclo[2.2.1]heptan-2-one in 35% yield. This indicates that the latter considerably resists further oxidation[7] (see Experimental). On the other hand the oxidation of **3** to **4** with Jone's reagent[8] was not successful, mainly affording a mixture of sulfoxides (2-*endo*-hydroxy-7-thiabicyclo[2.2.1]heptane 7-oxides; a mixture of 38 and 62% of *syn* and *anti* sulfoxides, respectively) in *ca.* 60% yield and the expected keto sulfide **4** only in a low yield (*ca.* 10%).[9] Attempted Oppenauer oxidation of **3** and **6** with aluminium isopropoxide and cyclohexanone in refluxing toluene[10] was not successful. 7-Thiabicyclo[2.2.1]heptan-2-one 7,7-dioxide (**9**) was prepared in good yield by the oxidation with Jone's reagent from 2-*endo*-hydroxy-7-thiabicyclo[2.2.1]heptane 7,7-dioxide (**8**), which was prepared from **3** by oxidation with hydrogen peroxide in acetic acid. 7-Thiabicyclo[2.2.1]heptane-2,5-dione 7,7-dioxide (**11**) was also prepared in good yield by oxidation with Jone's reagent from **10**, which was prepared from **6** by oxidation with perbenzoic acid in chloroform. **11** decomposed readily to give hydroquinone and sulfur dioxide in the presence of acid.[11]



Scheme 1.

It seems worthwhile to note some characteristics in NMR spectra of **4** and **7** from the viewpoint of structural confirmation. For **4** the introduction of ketonic carbonyl group caused upfield shift of the bridge-head proton α to carbonyl by 0.08 ppm, while the bridge-head proton β to carbonyl shifted to downfield by 0.15 ppm as compared with 7-thiabicyclo[2.2.1]heptane (**12**) (Fig. 1). This upfield shift of bridge-head proton α to carbonyl is quite the reverse of that anticipated from the inductive effect and magnetic anisotropy of carbonyl.[12] Corey and his co-workers[13] first pointed out a similar abnormality concerning the NMR spectrum of norbornanone, *viz.*, the bridge-head proton α to carbonyl shifted down

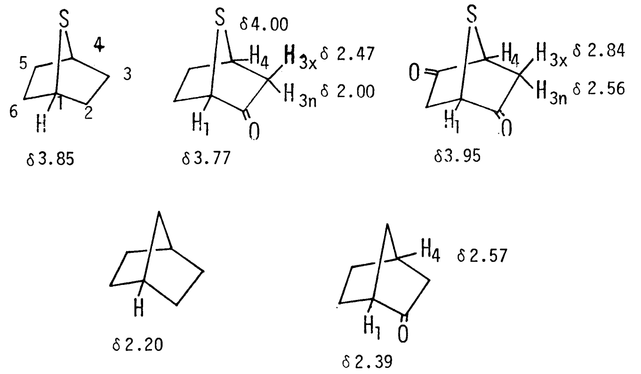


Fig. 1. Influence of carbonyl group to the bridge-head protons of bicyclo[2.2.1]heptane system.

field only by 0.19 ppm, and the bridge-head proton β to carbonyl by 0.37 ppm as compared with norbornane. The assignment was confirmed by Farnum and Mehta[14] by deuterium labeling experiments.

As a result of the substitution of methylene bridge for sulfur atom, the NMR spectra of bicyclo[2.2.1]-heptane system became simplified and well resolved.[15] The assignments were confirmed by using a shift reagent (europium dipivaloylmethanate), coupled with spin-decoupling experiments (see Experimental). The bridge head protons of **7** resonated in midway between the peaks of H_1 and H_4 of **4**. The following coupling constants were obtained by spin-decoupling experiments for **7**; $J_{\mathrm{H_1,H_{3x}}}=1.5$ Hz, $J_{\mathrm{H_{3x},H_{3n}}}=18$ Hz, $J_{\mathrm{H_4,H_{3x}}}=3.5$ Hz, and $J_{\mathrm{H_4,H_{3n}}}=0.75$ Hz. The computer simulation, with use of these values and $J_{\mathrm{H_1,H_4}}=0$ Hz, gave a result almost superimposable on the spectrum of **7** (Fig. 2).

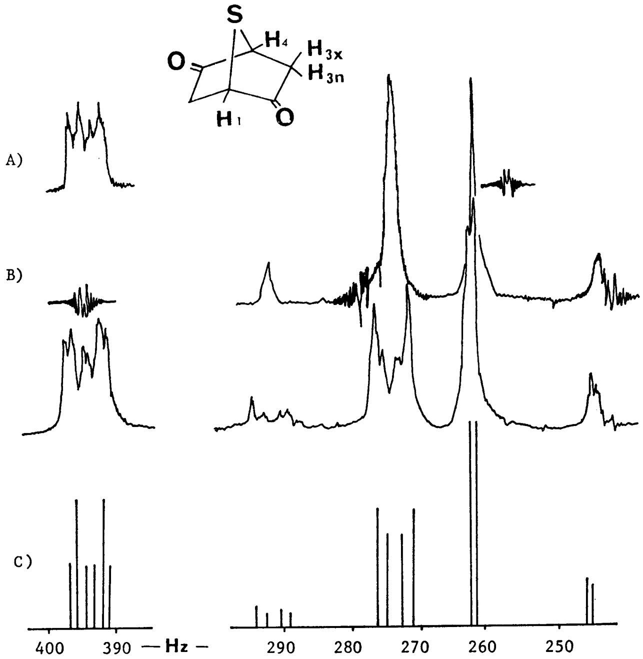


Fig 2. NMR spectra of **7** (100 MHz).
A) Saturation of H_{3n}.
B) Saturauion of $H_{1,4}$.
C) Computer simulation.

Transannular Sulfur-Carbonyl Interaction in the Ultraviolet Spectroscopy. The ultraviolet spectra of **4**, **7** and related compounds were measured in solvents of various polarities. The absorption maxima and extinction coefficients are summarized in Table 1. The keto sulfide **4** and **7** exhibited three separated absorptions at about 220, 260 and 300 nm as shown in Fig. 3. The strong absorption at about 220 nm, similar to that of 7-thiabicyclo[2.2.1]heptane (**12**), can be assigned to n, σ*,[16] although the intensity is smaller than that of

Table 1. Ultraviolet spectra[a]

Compound	Assignment	Hexane	Acetonitrile	Ethanol	Water
7-Thiabicyclo[2.2.1]heptan-2-one (**4**)	n, σ*	222.5(902)	221.6(718)	223(1060)	—[b]
	CT	255(191)	257.5(273)	259.5(233)	257.5(210)
		260(185)			
	n, π*	289(168)	296(286)	304(360)	300(393)
		298(231)	304(324)		
		308(247)	315(216)		
		319(147)			
7-Thiabicyclo[2.2.1]heptan-2,5-dione (**7**)	n, σ*	238.6(652)	238.5(733)	238.5(722)	240(644)
	CT	258(220)	261.5(261)	261.5(300)	262(306)
	n, π*	289(288)	296(466)	298(566)	300(666)
		299(402)	305(514)	305(583)	
		309(413)	315(342)		
		321(233)			
7-Thiabicyclo[2.2.1]heptan-2-one 7,7-dioxide (**9**)	n, π*			288(54)	293(68)
				297(60)	
				307(51)	
				319(23)	
7-Thiabicyclo[2.2.1]heptane	n, σ*	213(4078)		211(2970)	
		249(36.2)		248(40.9)	
Bicyclo[2.2.1]heptan-2-one	n, π*	293(22)		290(26)	

a) λ_{max} was measured in nm. Molar extinction coefficient is given in parentheses. b) This band was observed as an inflection at longer wavelength side (*ca.* 220 nm) of the main absorption band.

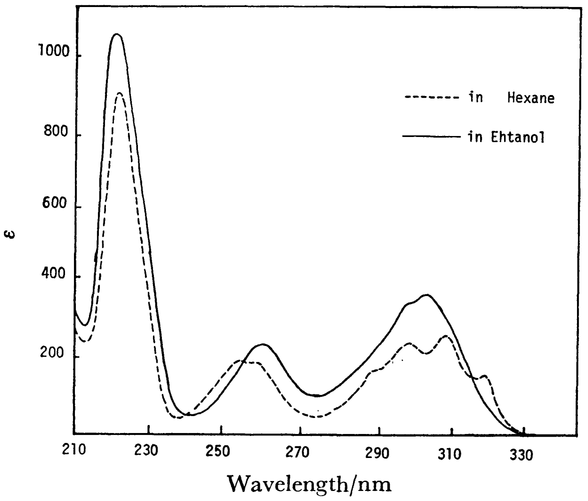
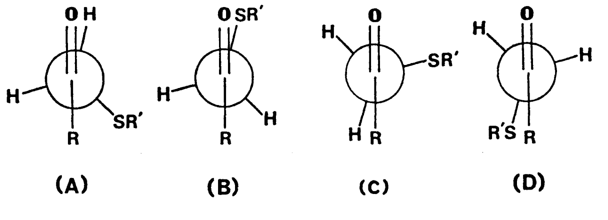


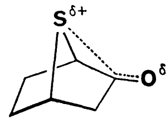
Fig. 3. Ultraviolet spectra of **4** in hexane and ethanol.

12 by a factor of three or four.[17] No absorption was observed around this region in the ultraviolet spectra of the corresponding sulfone **9**[18] or 7-thiabicyclo[2.2.1]-heptane 7,7-dioxide.

The absorption at *ca.* 300 nm, with a fine structure at intervals of *ca.* 1080 cm^{-1} for **4** and *ca.* 1130 cm^{-1} for **7** in hexane, showed a small but steady blue shift on changing the solvent from non-polar to polar. The large extinction coefficients observed for **4** (393 in water) and for **7** (666 in water) suggest that the band is due to n, π^* transition with the strong homoconjugation between sulfur and carbonyl.[19] The anomalously intense n, π^* absorption has been reported for dehydronorcamphor skeleton and was attributed to the homoconjugation between carbonyl and double bond.[20] The keto sulfides (**4** and **7**) seem to satisfy the geometrical requirements for S–CO interaction proposed by Wladislaw *et al.*[19b,19c] They suggested that of the four rotational isomers, A or C is favorable for S–CO interaction. The extinction coefficient of **7** is approximately twice as large as that of **4**.



The two bands n, σ^* and n, π^* could be assigned regarding **4** (and **7**) as a composite of 7-thiabicyclo-[2.2.1]heptane and norbornanone, but the band at 260 nm can not be explained in such a manner. The band was assigned to the charge transfer band from divalent sulfur to carbonyl based on the following. (a) The band shows a small but appreciable red shift on increasing the polarity of solvent. (b) It disappears on the oxidation of **4** to sulfone **9**. This indicates lone pair electrons on sulfur participate in the CT transition. The charge transfer band at 260 nm seems to be the longest ever reported.[21] The canonical form in the charge transfer excited state of **4** can be expressed in **13**,[2,3] which *a priori* seems to have some connection to the anchimerically assisted species by sulfur in the formation of incipient carbonium ion in solvolysis.[1]



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In order to correlate the CT band and the ability of anchimeric assistance by sulfur, more examples of well separated CT bands are requested.

Experimental

Melting points (sealed capillary) are uncorrected. The elemental analyses were performed either at the Microanalysis Center of Kyoto University or at the Faculty of Pharmaceutical Science of Kyushu University. Infrared spectra were measured with a Hitachi Model EPI-G3 grating spectrophotometer, NMR spectra with a Varian T 60 or HA-100 spectrometer, mass spectra with a Hitachi Model RMU 6C mass spectrometer, and ultraviolet spectra with a Hitachi EPS-3T recording spectrophotometer.

Preparation and structural determination of 2-*endo*-acetoxy-5-*endo*-chloro-7-thiabicyclo[2.2.1]heptane (**2**), 2-*endo*-hydroxy-7-thiabicyclo[2.2.1]heptane (**3**), and 2,5-*endo*-*endo*-diacetoxy-7-thiabicyclo[2.2.1]heptane (**5**) have been reported.[1]

Oxidation of 3 with Jone's Reagent. Cold Jone's reagent, prepared from 114 mg (1.14 mmol) of CrO_3, 186 mg of concd H_2SO_4 and 0.5 ml of distilled water, was added dropwise with ice cooling and stirring to a solution of 174 mg (1.34 mmol) of **3** in 1.5 ml of acetone. The color of the reaction mixture turned from red to green. After being stirred for 30 min at 0 °C, the reaction mixture was diluted with 2 ml of water and extracted with 2 portions of 5 ml of dichloromethane. The combined dichloromethane extracts were dried over magnesium sulfate and condensed to 60 mg of colorless oil.

On the basis of NMR, IR, and VPC analyses, the oily product was found to consist of *ca.* 30% of 7-thianorbornan-2-one (**4**), *ca.* 50% of **3** and 20% of sulfoxide. The water layer was neutralized with sodium hydrogencarbonate and allowed to stand at room temperature to evaporate water. The solid residue was washed twice with 15 ml of acetone. Acetone extracts were evaporated and adsorbed on silica gel. Elution was benzene (10)–ethanol (2) afforded 70 mg of a *syn* and *anti* mixture of 2-*endo*-hydroxy-7-thiabicyclo[2.2.1]heptane 7-oxides. The structures of these products were confirmed by a comparison of spectra (NMR, IR) with those of sulfoxides derived from **3** by oxidation with equimolar amount of *m*-chloroperbenzoic acid. Further structural confirmation was given by the oxidation of a mixture of sulfoxides with H_2O_2 in acetic acid to give 2-*endo*-hydroxy-7-thiabicyclo[2.2.1]heptane 7,7-dioxide **8** as a sole product.

$\nu_{\mathrm{max}}^{\mathrm{KBr}}$ (*syn*, *anti* mixture) 3330 cm^{-1} (S), 2930 cm^{-1} (M), 1072 cm^{-1} (sh), 1030 cm^{-1} (v.s., $\nu_{\mathrm{S-O}}$ and $\nu_{\mathrm{C-O}}$), and 1005 cm^{-1} (sh). $\delta_{\mathrm{CDCl_3}}^{\mathrm{TMS}}$ (*syn*, *anti* mixture) 5.06 (multiplet, α proton to OH of *syn*-sulfoxide, area intensity 8), 4.20 (double triplets, J=10 and 4 Hz, α proton to OH of *anti*-sulfoxide, 13), 3.6 (narrow multiplet, bridgehead protons and OH, 67) and 2.5—1.3 (multiplet, methylene and ethylene protons, 113). The composition ratio of *anti* to *syn* was determined on the basis of area intensities of α protons[22] to OH to be *ca.* 1.6.

*2-*endo*-Hydroxy-7-thianorbornane 7-Oxide.* *m*-Chloroperbenzoic acid (156 mg, 0.77 mmol, 85% assay) was added at room temperature to a solution of 100 mg (0.77 mmol) of **3** in 10 ml of dichloromethane. After being stirred for 1 day, the solvent was removed and the solid residue was washed with two portions of 1 ml of water to transfer sulfoxides to the water layer. Evaporation of water gave transparent solid, which was adsorbed on silica gel. Elution with benzene (10)–ethanol (2) gave 102 mg of a mixture of sulfoxides. The composition ratio of *anti*- to *syn*-sulfoxide determined by NMR spectroscopy was *ca.* 1.0.

*Oxidation of **3** with Chromium Trioxide-Pyridine Complex.* Chromium trioxide (280 mg, 2.8 mmol) was added in portions to 2.5 ml of dry pyridine with stirring in a 10 ml flask fitted with a KOH drying tube. To a yellow suspension of chromium trioxide-pyridine complex was added in one portion a solution of 150 mg (1.15 mmol) of **3** in 2.0 ml dry pyridine at room temperature. The solution was allowed to stand overnight and then poured into 50 ml of ether. The filtrate was washed with dilute hydrochloric acid and then with water saturated with NaCl. Evaporation of ether through a 10 cm Vigreux column under atmospheric pressure left 122 mg (82.5 %) of 7-thiabicyclo[2.2.1]heptan-2-one (**4**) as a white waxy solid, which was purified by preparative VPC, followed by sublimation (80 °C/760 mmHg). 7-Thiabicyclo[2.2.1]heptan-2-one (**4**): Mp 115.8—116.6 °C (in a sealed tube). $\delta^{\mathrm{TMS}}_{\mathrm{CCl_4}}$ 4.00 (broad singlet, H_4, 1H), 3.77 (broad singlet, H_1, 1H), 2.47 (double doublets, J=16 and 4 Hz, H_{3x}, 1H), 2.00 (doublet, J=16 Hz, H_{3n}, 1H) and 2.03 (multiplet, H_5, H_6, 4H).

To a solution of 12 mg of **4** in 0.5 ml of CCl_4 was added europium dipivaloylmethanate progressively. The downfield shifts observed were: for H_1, by 0.50 and 1.16 ppm (for 4.5 mg and 9.0 mg of dipivaloylmethanate, respectively); H_{3x}, by 0.56 and 1.16 ppm; H_{3n}, 0.53 and 1.10 ppm; H_4, by 0.16 and 0.36 ppm; H_5, H_6, by *ca.* 0.2 and 0.43 ppm.

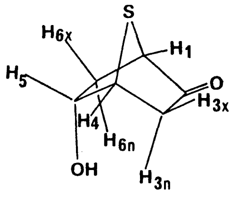
Saturation of H_4 proton resulted in the collapse of proton H_{3x} to a doublet (J=16 Hz). $\nu^{\mathrm{KBr}}_{\mathrm{max}}$ 1745 cm^{-1} (S), 1060 cm^{-1} (M) and 446 cm^{-1} (M). *m/e*; 128 (M$^+$, 36), 100 (18), 85 (88), 71 (8), 67 (100), 58 (20) and 55 (35).

Found: C, 56.30; H, 6.00%. Calcd for C_6H_8OS: C, 56.22; H, 6.29%.

*2,5-*endo-endo*-Dihydroxy-7-thiabicyclo[2.2.1]heptane (**6**).* 11.5 g (50 mmol) of **5** and 50 mg of sodium were dissolved in 200 ml of absolute methanol under nitrogen. After being refluxed overnight, methanol and methyl acetate were distilled off to give a white solid. Recrystallization from benzene gave 6.95 g (95%) of white crystals of **6**. The physical and spectral properties are the same as those in the literature.[5]

*Thiabicyclo[2.2.1]hepthane-2,5-dione (**7**).* To a yellow suspension of chromium trioxide-pyridine complex (30 mmol) in 20 ml of dry pyridine was added 1.0 g (6.85 mmol) of solid **6** at room temperature. After being stirred overnight at room temperature, the reaction mixture was poured into 100 ml of ether. After the inorganic materials had been filtered off the ether extract was washed with dilute hydrochloric acid. Evaporation of ether gave 710 mg of a colorless waxy solid. The solid was adsorbed on silica gel and eluted with benzene (5)–ethanol (1) to give 350 mg of **7** and 330 mg of 5-*endo*-hydroxy-7-thiabicyclo[2.2.1]heptan-2-one. Prolonged reaction time did not affect the product ratio significantly. Dioxo sulfide **7** was recrystallized from benzene–hexane–dichloromethane: Mp 130.0—131.0 °C. $\delta^{\mathrm{TMS}}_{\mathrm{CDCl_3}}$ (100 MHz) 3.94 (triple doublets, J=3.5 and 1.5 Hz, H_1 and H_4, 2H), 2.79 (double quartets, J=18, 3.5 and 1.5 Hz, H_{3x} and H_{6x}, 2H) and 2.57 (double doublets, J=18 and 0.75 Hz, H_{3n} and H_{6n}, 2H). $\nu^{\mathrm{KBr}}_{\mathrm{max}}$ 1765 cm^{-1} (sh), 1742 cm^{-1} (S), 1720 cm^{-1} (sh), 1414 cm^{-1} (M), 1200 cm^{-1} (S), 1053 cm^{-1} (M), 941 cm^{-1} (M), 901 cm^{-1} (M), 540 cm^{-1} (S), and 428 cm^{-1} (M). *m/e* 142 (M$^+$, 33), 114 (6) 100 (10), 98 (9), 86 (25), 72 (13), 59 (20), 58 (20), 55 (100) and 45 (30).

Found: C, 50.58; H, 4.48; O, 22.39. Calcd for $C_6H_6O_2S$: C, 50.68; H, 4.25; O, 22.50%.



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*5-*endo*-Hydroxy-7-thiabicyclo[2.2.1]heptan-2-one (**14**):* $\delta^{\mathrm{TMS}}_{\mathrm{CDCl_3}}$ 4.76 (double triplets, J=10 and 3.5 Hz, H_5, 1H) 3.93 (singlet, OH, 1H), 3.9—3.6 (multiplet, H_1 and H_4, 2H), 3.00 (doublet, J=17 Hz, H_{3n}, 1H), 2.43 (double doublets, J=17 and 4 Hz, H_{3x}, 1H), 2.8—2.4 (multiplet, H_{6x}, 1H) and 1.63 (double doublets, J=15 and 3.5 Hz, H_{6n}, 1H). $\nu^{\mathrm{KBr}}_{\mathrm{max}}$ 3420 cm^{-1} (S), 1742 cm^{-1} (sh), 1728 cm^{-1} (S), 1118 cm^{-1} (W), 1096 cm^{-1} (W), 1051 cm^{-1} (M), 1032 cm^{-1} (M), and 1000 cm^{-1} (W). *m/e* 144 (M$^+$, 73), 57 (100).

*2-*endo*-Hydroxy-7-thiabicyclo[2.2.1]heptane 7,7-Dioxide (**8**).* With water cooling and stirring, 1.5 ml (13 mmol) of 30% hydrogen peroxide was added dropwise to a solution of 297 mg (2.28 mmol) of **3** in 2 ml of acetic acid. The mixture was then heated at 70—80 °C overnight. After cooling, methyl mercaptan was introduced at moderate speed into this reaction mixture until peroxide test became negative (KI-starch). Evaporation of the solvent gave 330 mg of a waxy solid. Column chromatography on silica gel eluted with benzene (10)–ethanol (1) gave 290 mg (79.5%) of **8**: Mp 227.5—229.0 °C (in a sealed tube). $\delta^{\mathrm{TMS}}_{\mathrm{CDCl_3}}$ 4.80 (double triplets, J=9 and 3 Hz, 1H), 3.03 (narrow multiplet, 2H) 2.6 (singlet, 1H), 2.7—1.9 (multiplet, 5H) and 1.50 (double doublets, J=14 and 2.5 Hz, 1H). $\nu^{\mathrm{KBr}}_{\mathrm{max}}$ 3485 cm^{-1} (S), 1297 cm^{-1} (VS), 1161 cm^{-1} (S), 1126 cm^{-1} (S), 1043 cm^{-1} (M), and 514 cm^{-1} (M).

*7-Thiabicyclo[2.2.1]heptan-2-one 7,7-Dioxide (**9**).* To a solution of 100 mg (0.62 mmol) of **8** in 2 ml of acetone chilled with ice and stirred was added dropwise Jone's reagent prepared from 470 mg (4.7 mmol) of chromium trioxide, 760 mg of concd H_2SO_4 and 1.5 ml of distilled water. After completion of addition stirring was continued for 40 min in ice and then at room temperature for 40 min. The excess oxidizing reagent was treated with 2-propanol with ice cooling. The reaction mixture was extracted with three portions of 20 ml of dichloromethane and the combined dichloromethane extracts were washed with 5 ml of water saturated with NaCl. Evaporation of the solvent gave 74 mg (74%) of white solid **9**. Recrystallization from CCl_4–hexane and sublimation under reduced pressure gave 50 mg of pure **9**; mp *ca.* 229 °C (dec in a sealed tube). $\delta^{\mathrm{TMS}}_{\mathrm{CDCl_3}}$ 3.53 (narrow multiplet, 2H), 3.20 (double doublets, J=18.0 and 3.5 Hz, 2H), 2.66 (doublet, J=18.0 Hz, 1H), 2.7—1.9 (multiplet, 4H). *m/e* 160 (M$^+$, 32), 96 (M$^+$ $-SO_2$, 80). 68 (100), 64 (62), and 55 (85).

Found: C, 44.91; H, 5.15; S, 19.84; O, 29.75%. Calcd for $C_6H_8SO_3$: C, 44.99; H, 5.03; S, 20.02; O, 29.96%.

*2,5-*endo-endo*-Dihydroxy-7-thianorbornane 7,7-Dioxide (**10**).* To a solution of 5.0 g (34.2 mmol) of **6** in 1250 ml of $CHCl_3$ was added dropwise a solution of 11.3 g (81.9 mmol) of perbenzoic acid in 150 ml of $CHCl_3$ at room temperature with stirring. After the completion of addition (3 h), the reaction mixture was refluxed for 5—6 h and then allowed to stand overnight at room temperature. After filtration of transparent crystalline precipitate (5.30 g) of **10**, the solution was condensed to *ca.* 200 ml and into this residue was passed methyl mercaptan vigorously to destroy the excess peroxide. The mixture was cooled with ice to give additional 0.38 g of **10**: Mp 277 °C (dec, in a sealed tube) $\delta^{\text{TMS}}_{\text{pyridine-}d_5}$ 6.44 (singlet, 2H), 5.00 (quintet, J=4 Hz, 2H), 3.2 (narrow multiplet, 2H) and 2.6 (narrow multiplet, 4H). $\nu^{\text{KBr}}_{\text{max}}$ 3570 (S), 1295 (M), 1160 (S), 920 (M), and 860 cm^{-1} (M).

Found: C, 40.53; H, 5.64%. Calcd for $C_6H_{10}SO_4$: C, 40.44; H, 5.66%.

7-Thiabicyclo[2.2.1]heptane-2,5-dione 7,7-Dioxide (11). To a 1.5 ml of aqueous solution of 200 mg (1.12 mmol) of **10** chilled with ice and stirred was added dropwise Jone's reagent prepared from 7.52 mmol of chromium trioxide, 1.2 g of concd H_2SO_4 and 3.2 ml of distilled water. After completion of addition (30 min), stirring was continued for 1 h in ice and then at room temperature for 4 h. The reaction mixture was extracted with four portions of 10 ml of dichloromethane and the combined extracts were dried over calcium chloride. Evaporation of the solvent gave 90 mg of crystals. Yellow crystals of hydroquinone sublimed at the neck of the flask. Recrystallization from chloroform gave 74 mg of **11**: Mp 160 °C (dec in a sealed tube). $\delta^{\text{TMS}}_{\text{CDCl}_3}$ 4.10 (quartet, J=4.5 and 1.5 Hz, 2H), 3.44 (double quartets, J=1.5, 4.5, and 19 Hz, 2H) and 2.84 (doublet, J=19 Hz, 2H). $\nu^{\text{KBr}}_{\text{max}}$ 3000 (M), 1760 (S), 1416 (M), 1322 (S), 1218 (M), 1118 (S), 586 (S), 586 (S), and 450 cm^{-1} (M).

Found: C, 41.47; H, 3.74; S, 18.45%. Calcd for $C_6H_6SO_4$: C, 41.38; H, 3.47; S, 18.41%.

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