Photochemical behaviour of ω-thiabicyclo[3.*n*.1]alkan-3-one: a mechanistic and exploratory study

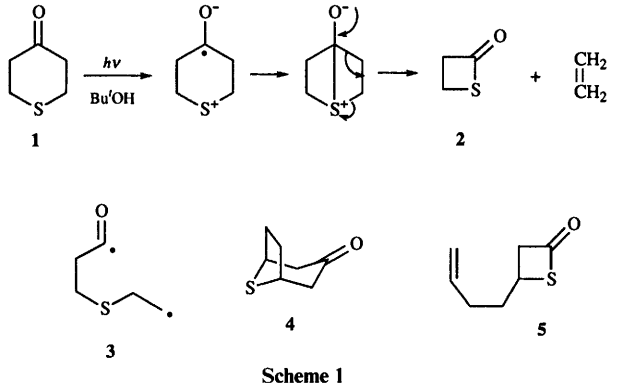
Osamu Muraoka,* Bao-Zhong Zheng, Maiko Nishimura and Genzoh Tanabe

Faculty of Pharmaceutical Sciences, Kinki University, Kowakae 3-4-1, Higashi-Osaka, Osaka 577, Japan

The photoreactivity of 9-thiabicyclo[3.3.1]nonan-3-one 9 is investigated under a variety of conditions and compared with those of its monocyclic or norbicyclic analogues 1 and 4. The principal reaction of ketone 9 on irradiation in *tert*-butyl alcohol is the Norrish type I cleavage to yield *tert*-butyl (*cis*-6-methyltetrahydrothiopyran-2-yl)acetate 10a, while compounds 1 and 4 give ring-contracted thilactones 2 and 5. The origin of the different chemoselectivity is discussed. Characteristic photoreactivity of ketone 9, observed upon direct irradiation in methanol, leading to the predominant formation of the *endo*-alcohol *endo*-11 can be explained by assuming the charge-transfer interaction between the sulfur and the carbonyl moiety in the photo-excited state.

Introduction

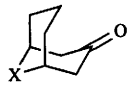
Ketone photochemistry,[1] and the Norrish type I reaction of cycloalkanones in particular, has received considerable mechanistic attention,[2] and a variety of synthetic applications to biologically active compounds have been reported.[2a,3] Characteristic photoreactivities other than the α-cleavage, such as photoreduction,[4] pinacol formation,[3a,4a,4c,4e] or enal production[5] *etc.* have also been described. On the other hand, the photolysis of thiacyclohexan-4-one **1** in *tert*-butyl alcohol has been shown to yield primarily a ring-contracted thiolactone, thiacyclobutan-2-one **2**.[6] Although the formation of this ring contraction product could be explained by direct elimination of ethylene from a sulfur-stabilized form of biradical **3**, an alternative pathway involving a charge-transfer interaction of the two chromophores, as shown in Scheme 1, has been



Scheme 1

suggested.[7] Photolysis of a bridged bicyclic γ-keto sulfide, 8-thiabicyclo[3.2.1]octan-3-one **4**, in *tert*-butyl alcohol has also been shown to afford primarily a thiolactone, 4-but-3-enylthiacyclobutan-2-one **5**.[6]

In our continuing studies on the use of bridged bicyclic compounds as synthons for biologically active natural products,[8] the authors have been exploring the photoreaction of bicyclo[3.3.1]nonan-3-one **6** and its heterocyclic analogues **7** and **8**, and revealed characteristic photochemical properties

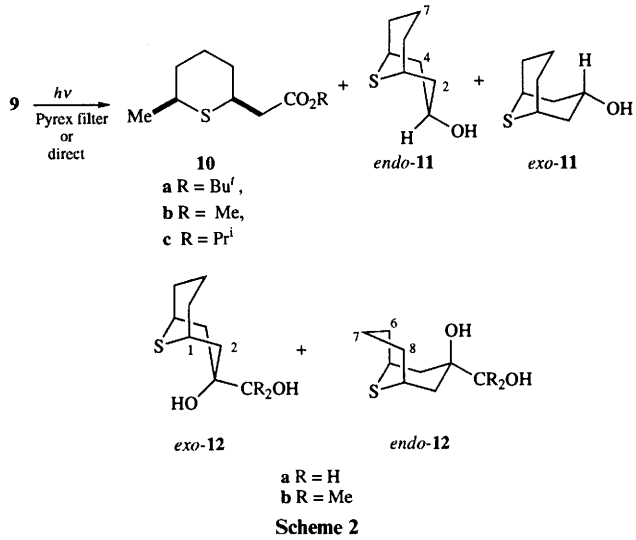


6 X = CH_2
7 X = NCO_2R
8 X = O
9 X = S

encountered in the system.[3a,3b,4b] Because of the possibility that the system might undergo an unusual photochemical reaction as a result of the interaction between the carbonyl moiety and the sulfur, the photolysis of the thia analogue, 9-thiabicyclo-[3.3.1]nonan-3-one **9**,[9] was investigated under a variety of conditions.

Results

The reactant **9** was prepared according to the method reported.[9b] Irradiation of compound **9** in *tert*-butyl alcohol through a Pyrex filter afforded mainly a type I product, *tert*-butyl (*cis*-6-methyltetrahydrothiopyran-2-yl)acetate **10a** accompanied by a small amount of photoreduced products, *endo*- and *exo*-9-thiabicyclo[3.3.1]nonan-3-ol *endo*- and *exo*-**11** (Scheme 2). Direct irradiation under the same conditions also afforded the acetate **10a** predominantly.



Scheme 2

Upon irradiation in methanol through a Pyrex filter, compound **9** afforded mainly the photoreduced products *endo*- and *exo*-**11**.[9b] The remaining products were the type I product **10b** and solvent adducts *endo*- and *exo*-3-hydroxymethyl-9-thiabicyclo[3.3.1]nonan-3-ol *endo*- and *exo*-**12a**. An interesting feature was observed when compound **9** was irradiated directly: the relative product ratio of these two alcohols *endo*- and *exo*-**11** was reversed, the *endo*-alcohol *endo*-**11** being predominantly produced. The product distributions are summarized in Table 1.

Table 1 Products of irradiation of compound **9**

Solvent	Filter	Yield (%) *endo*-**11**	*exo*-**11**	**10**	*endo*-**13**	*exo*-**13**	Recovered **9**
MeOH	Pyrex	10	20	13	12 (*endo*:*exo* = 1:4)[a]		17
MeOH	none	17	7	10	5 (*endo*:*exo* = 1:6)[a]		8
Pr^{i}OH	Pyrex	15	37	4	4	10	25
Pr^{i}OH	none	29	11	3	trace	3	15
Bu^{t}OH	Pyrex	6	2	32	—	—	31
Bu^{t}OH	none	5	1	22	—	—	30
MeCN (MeOH)	Pyrex	trace	trace	12	trace	trace	40
MeCN (MeOH)	none	trace	trace	27	trace	trace	38

[a] Product distributions were determined on the basis of 500 MHz ^{1}H NMR spectra.

The structure of the α-cleavage products **10a** and **10b** was easily assigned on the basis of their spectroscopic properties. Both of the photoreduced products *endo*- and *exo*-**11** were identified by comparison of their spectroscopic properties with those of authentic samples prepared by hydride or radical reduction of ketone **9**. The stereochemistry of the two isomers *endo*- and *exo*-**11** was determined on the basis of their ^{1}H and ^{13}C NMR spectral characteristics. The ^{1}H NMR spectrum of *exo*-alcohol *exo*-**11** showed a one proton triplet of triplets at δ 4.54 (J 10.5 and 6.0) arising from the axial C*H*OH proton in the rigid cyclohexane ring system. The chemical shift of δ_C 21.4 arising from C-7 was in good accord with one due to the corresponding carbon in the carbobicyclic system of the twin chair conformation.†

The large coupling constant (J 10.0) of a signal at δ_H 4.12 arising from the C*H*OH proton of the *endo*-isomer *endo*-**11** was also consistent with a diaxial relationship, implying that the tetrahydrothiopyran ring bearing the hydroxy group was in the boat conformation. The boat conformation of the ring was also supported by the considerable upfield shift of signals arising from C-7 and C-2 (C-4), which appeared at δ_C 15.8 and 35.3, respectively, possibly by the γ-gauche effect, in comparison with those of its counterpart *exo*-**11** appearing at δ_C 21.4 and 42.0.

Solvent adducts *endo*- and *exo*-**12a** were separable by gas liquid partition chromatography, and displayed their molecular ion peaks at m/z 188 in their mass spectra. The major product *exo*-**12a** displayed a singlet and a triplet, at δ_C 71.9 and 71.1, arising from its two hydroxy-bearing carbons. Appreciable upfield shift of the signals arising from C-7 and C-2 (C-4), which appeared at δ_C 15.6 and 35.6, respectively, suggested that the substituted tetrahydrothiopyran ring was in the boat conformation. In the ^{1}H NMR spectrum, a downfield shift of the signal arising from the tertiary hydroxy, which appeared at δ_H 5.04, is ascribed to the hydrogen-bonding between the sulfur and the hydroxy, supporting the conclusion that the tertiary hydroxy group is in the *exo* orientation. Further support for the stereochemistry of compound *exo*-**12a** was given by differential nuclear Overhauser effect (NOE) experiments, where a marked NOE enhancement was observed between the *endo*-proton at C-2 (C-4, δ_H 1.62) and methylene protons (δ_H 3.47) of the hydroxymethyl group. Another NOE enhancement appeared between the methine proton at C-1 (C-5, δ_H 3.13) and the *exo*-proton at C-2 (C-4, δ_H 2.24).

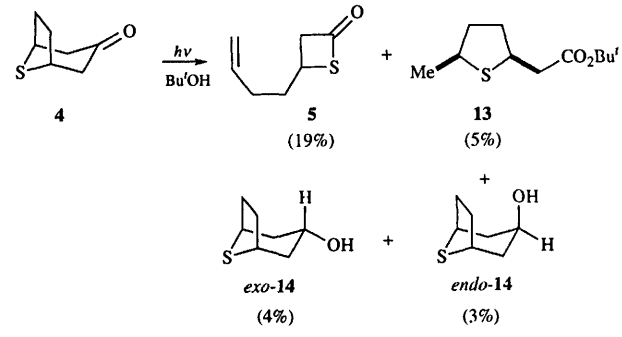
The minor isomer *endo*-**12a** showed nearly the same fragmentation pattern as that of its counterpart *exo*-**12a** in the mass spectrum. Another chair-boat conformation for compound *endo*-**12a** was evidenced both by an upfield shift of signals arising from C-3 and C-6 (C-8), which appeared at δ_C 68.7 and 32.2 respectively, and by a downfield shift, owing to the anisotropy of the sulfur, of the signal arising from the *exo*-proton at C-7, which appeared at δ_H 2.68.

The photolysis of compound **9** in propan-2-ol also gave predominantly photoreduced products *endo*- and *exo*-**11** with concomitant formation of mixed pinacols, *endo*- and *exo*-3-(2-hydroxypropan-2-yl)-9-thiabicyclo[3.3.1]nonan-3-ol *endo*- and *exo*-**12b**, and the type I product isopropyl (*cis*-6-methyltetrahydrothiopyran-2-yl)acetate **10c**. Inversion of the product ratio of the two alcohols *endo*- and *exo*-**11** in response to reaction conditions was also observed.

^{1}H NMR spectra of propan-2-ol adducts *endo*- and *exo*-**12b** displayed six-proton singlets at δ_H 1.28 and 1.27, respectively, arising from geminal dimethyl groups. Other spectral properties of these two pinacols *endo*- and *exo*-**12b** were in accord with those of the corresponding methanol adducts *endo*- and *exo*-**12a**, and their stereochemistries have been proven to be the same as those of the corresponding methanol adducts, *exo*- and *endo*-**12a**, on the basis of their NMR spectroscopic properties.

Upon irradiation in acetonitrile containing a small amount of methanol as a ketene quencher, which was shown to be an adequate solvent system for the type I reaction with the 9-oxa analogue **8**,[3a] compound **10b** was also the primary product, while the reaction was retarded considerably.

Although photolysis of compound **4** in *tert*-butyl alcohol had previously been investigated,[6] we repeated the experiment and confirmed the products reported by Johnson: thiolactone **5** as the main product accompanied by concomitant formation of the α-cleavage product, *tert*-butyl (*cis*-5-methyltetrahydrothiophen-2-yl)acetate **13**,[6] and photoreduced products *endo*- and *exo*-8-thiabicyclo[3.2.1]octan-3-ol *endo*- and *exo*-**14**.[11] The product distribution in the present study is shown in Scheme 3.

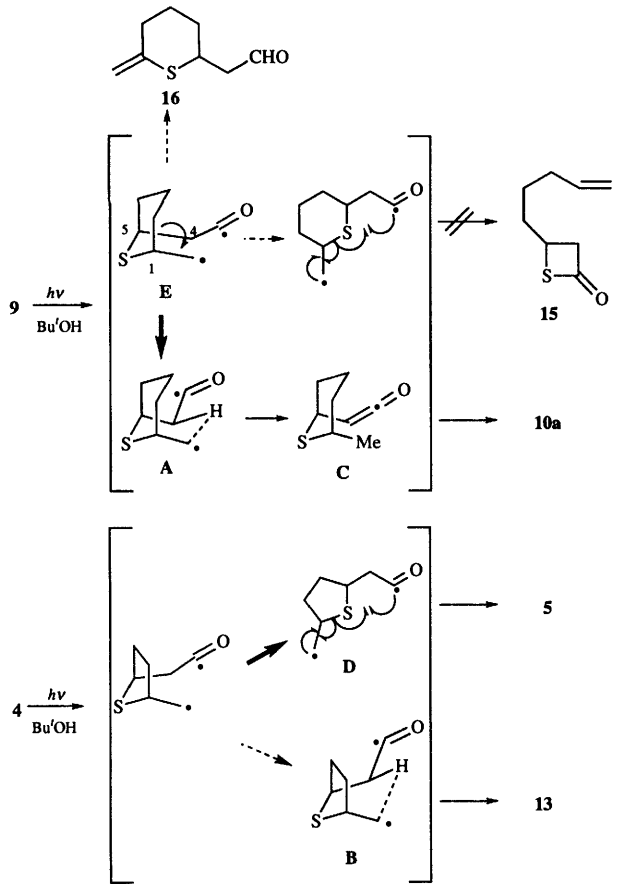


Scheme 3

Discussion

Compound **9**, when irradiated in *tert*-butyl alcohol, gave the type I product **10a**, displaying completely different photoreactivity from the nor-counterpart **4**, which afforded mainly thiolactone **5** upon irradiation under the same conditions. The

† Conformational analysis of the bicyclo[3.3.1]nonane system on the basis of ^{13}C NMR spectroscopic properties has been described (ref. 10).

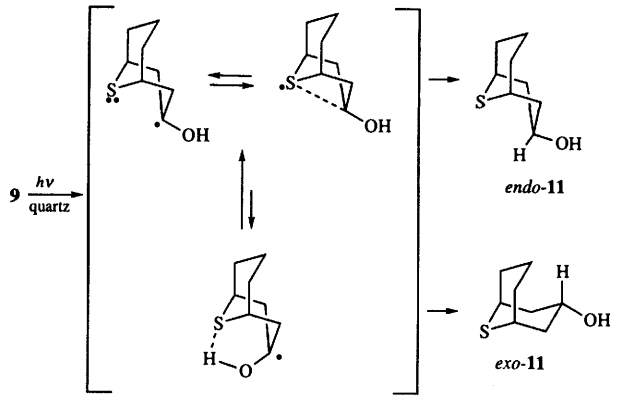


Scheme 4

gross mechanism *via* the biradical intermediates generated through the Norrish type I cleavage of ketones **4** and **9**, as shown in Scheme 4, is more satisfactory than that *via* the charge-transfer interaction, since no evidence for the formation of thiolactone **15** was detected in spite of careful examination of the products upon irradiation of ketone **9**. The different chemoselectivity observed between ketone **4** and **9** is rationalized by the different relative stereochemistry of the alkyl radical against the acyl one in the two biradical intermediates **A** and **B**. In intermediate **A**, the alkyl radical on the tetrahydrothiopyran ring is oriented in such a direction as to abstract the hydrogen in the acyl radical moiety more effectively than the one in intermediate **B**, and causes preferential formation of a ketene intermediate **C** to afford the product **10a** predominantly. On the other hand, for the alkyl radical on the tetrahydrothiophene ring (intermediate **B**), it is too far to abstract the hydrogen in the acyl radical as shown in Scheme 4, and degradation to thiolactone **5** *via* the intermediate **D** is preferred. The relief of the greater strain energy involved in the five-membered ring upon cleavage, in comparison with the six-membered one, would have forced the degradation rather than the hydrogen abstraction.

No evidence for the formation of the corresponding enal, 2-(6-methylidenetetrahydrothiopyran-2-yl)ethanal **16**, was obtained under any of the conditions studied. This result is attributable to the prohibited rotation of the C-1–S bond in the intermediate **E**, which is essential for enal formation, by incorporation with the trimethylene bridge between C-1 and C-5. Facile rotation of the C-4–C-5 bond resulted in the preferential formation of the intermediate **A**, affording primarily the ester **10a**.

Characteristic photoreduction with predominance of *endo*-hydrogenation leading to the corresponding *exo*-alcohol has been observed in the photolysis of homo- and hetero-bicyclic analogues **6**,[4b] **7** [4b] and **8**.[3a] Preferential formation of the *endo*-isomer *endo*-**11**, observed upon direct irradiation of compound **9** in methanol or in propan-2-ol, can be explained by assuming the charge-transfer interaction of the carbonyl with the sulfur in the excited state as shown in Scheme 5. Direct irradiation,



Scheme 5

which covers wavelengths short enough for the excitation of two chromophores (*ca.* 230–240 nm),[6] might form the weak S–C-3 bond, which caused the predominant formation of the *endo*-isomer *endo*-**11**.

On the other hand, the coupling reaction of the ketyl radical with solvent-based radicals leading to the mixed pinacols *endo*- and *exo*-**12** gave the *endo*-adduct *exo*-alcohol **12** as the major product even upon direct irradiation. As the molecular energy of the *exo*-adduct *endo*-**12b** calculated was higher by *ca.* 1.5 kcal mol^{-1} than that of the *endo*-adduct *exo*-**12b**,‡ the process might have been thermodynamically controlled.

The lack of pinacol dimer, which had been reported to be the main product on irradiation of monocyclic γ-oxa and γ-aza analogues,[4c] was attributable to serious steric hindrance around C-3, which prohibited the self-coupling reaction.

In conclusion, compound **9** showed different photoreactivity from its monocyclic and norbicyclic analogues **1** and **4**, and gave the type I cleavage product **10a** upon irradiation in *tert*-butyl alcohol. Characteristic *exo*-hydrogenation observed upon direct irradiation in methanol or in propan-2-ol would be an interesting manifestation of the charge-transfer interaction between the carbonyl and the sulfur encountered in the bicyclo[3.3.1]nonane system. Attempts to utilize compound **9** for the synthesis of biologically active natural compounds are in progress.

Experimental

Mps (Yanagimoto MP-35 micromelting point apparatus) and bps are uncorrected. IR spectra were measured on a Shimadzu IR-435 grating infrared spectrophotometer. NMR spectra were recorded on either a JEOL JNM-GSX 270 (270 MHz ^1H, 67.5 MHz ^{13}C) or a JEOL JNM-GSX 500 (500 MHz ^1H, 125 MHz ^{13}C) spectrometer. Chemical shifts (δ) and coupling constants (J) are given in ppm and Hz, respectively. All the NMR spectra were taken as $CDCl_3$ solutions with tetramethylsilane as internal standard. Low- and high-resolution mass spectra (electron impact) were recorded on either a Shimadzu QP 1000EX spectrometer or a JEOL JMS-HX 100 instrument. Column chromatography was effected over Merck Kieselgel 60 (230–400 mesh) with a pump (FMI model RP). All the organic extracts were dried over anhydrous magnesium sulfate prior to evaporation.

Starting materials

Ketones **4** and **9** were prepared according to the methods reported.[9b,c]

‡ Minimization of these compounds employed the MM2 forcefield using Chem 3D Plus™.

8-Thiabicyclo[3.2.1]octan-3-one 4. Needles, mp 112–114 °C (from aq. MeOH) (lit.,[6a] 155–157 °C, lit.,[9a] 150–153 °C, lit.,[9c] 155–156 °C, lit.,[11a] 155–157 °C).

9-Thiabicyclo[3.3.1]nonan-3-one 9. Plates, mp 195–197 °C (from methanol) (lit.,[9b] 194–197 °C, lit.,[9c] 210–211 °C); λ_{max}(MeOH)/nm 232 and 285 (ε/dm^3 mol^{-1} cm^{-1} 422 and 43).

Spectral properties of both the ketones **4** [6a,9a] and **9**[9b] were in accord with those reported.

Photochemical studies

General procedure. All photochemical reactions were carried out under argon using an Ishii UV-HT 200 W high-pressure mercury lamp in a water-cooled quartz immersion-well apparatus. Ketone **4** (100 mg, 0.70 mmol) and **9** (100 mg, 0.64 mmol) were dissolved in the appropriate degassed solvent (10 cm^3), the solution placed in a Pyrex or a quartz test tube, which was held in place around the immersion-well apparatus, and all solutions were irradiated for 15 h (product distribution is given in Table 1). Products were isolated by column chromatography of the residue left after removal of the solvent. Column chromatography was carried out using hexane–ethyl acetate (10 : 1) as eluent.

Photolysis of compound 9 in *tert*-butyl alcohol. The type I product, tert-*butyl* (cis-6-*methyltetrahydrothiopyran*-2-*yl*)-*acetate* **10a**, and photoreduced product, *endo*-9-thiabicyclo[3.3.1]nonan-3-ol *endo*-**11** and its exo-*isomer exo*-**11**, were obtained with the recovery of a small amount of the starting material **9**.

tert-Butyl (*cis*-6-methyltetrahydrothiopyran-2-yl)acetate **10a**: oil, bp 62–64 °C/8 mmHg (Found: M$^+$, 230.1368. $C_{12}H_{22}O_2S$ requires *M*, 230.1340); ν_{max}(CHCl$_3$)/cm^{-1} 1722; δ_H 1.17 (3 H, d, $J_{CH_3.6}$ 7.0, CH_3), 1.21–1.30 (2 H, m, 3- and 5-H_{ax}), 1.39 (1 H, qt, $J_{4ax.4eq} = J_{4ax.3ax} = J_{4ax.5ax} = 13.0$, $J_{4ax.3eq} = J_{4ax.5eq} = 3.0$, 4-$H_{ax}$), 1.45 [9 H, s, C(CH$_3$)$_3$], 1.87–1.96 (2 H, m, 4- and 5-H_{eq}), 2.01 (1 H, dtd, $J_{3eq.3ax}$ 13.0, $J_{3eq.4eq} = J_{3eq.4ax} = 3.0$, $J_{3eq.2}$ 2.5, 3-H_{eq}), 2.30 (1 H, dd, J_{gem} 15.5, J_{vic} 7.5, C*H*HCO$_2$), 2.34 (1 H, dd, J_{gem} 15.5, J_{vic} 7.0, CH*H*CO$_2$), 2.87 (1 H, dqd, $J_{6.5ax}$ 11.5, $J_{6.CH_3}$ 7.0, $J_{6.5eq}$ 2.5, 6-H) and 3.15 (1 H, dddd, $J_{2.3ax}$ 11.5, $J_{2.CHHCO_2}$ 7.5, $J_{2.CHHCO_2}$ 7.0, $J_{2.3eq}$ 2.5, 2-H); δ_C 21.5 (q), 26.6 (t), 28.1 (q), 33.5 (t), 35.9 (t), 38.4 (d), 39.5 (d), 41.9 (t), 80.7 (s) and 170.6 (s); *m*/*z* 230 (M$^+$, 11%), 174 (38), 155 (17), 127 (79), 115 (100) and 81 (31).

endo-**11**: Needles, mp 132–134 °C (from hexane–AcOEt) (lit.,[9b] 142–145 °C) (Found: C, 60.5; H, 8.7; M$^+$, 158.0762. $C_8H_{14}OS$ requires C, 60.72; H, 8.92%; *M*, 158.0766); ν_{max}(CHCl$_3$)/cm^{-1} 3579 and 3433; δ_H 1.37 [2 H, ddd, $J_{2(4)endo.2(4)exo}$ 13.5, $J_{2(4)endo.3}$ 10.0, $J_{2(4)endo.1(5)}$ 2.0, 2(4)-H_{endo}], 1.50 (1 H, br s, exchangeable with D$_2$O), 1.58–1.65 (1 H, m, 7-H_{exo}), 1.78 [2 H, dm, $J_{6(8)endo.6(8)exo}$ 14.0, 6(8)-H_{endo}], 1.93 [2 H, ddt, $J_{6(8)exo.6(8)endo}$ 14.0, $J_{6(8)exo.7endo}$ 13.5, $J_{6(8)exo.1(5)} = J_{6(8)exo.7exo}$ 3.5, 6(8)-H_{exo}], 2.06 [1 H, qt, $J_{7endo.7exo} = J_{7endo.6(8)exo}$ = 13.5, $J_{7endo.6(8)endo}$ 4.0, 7-H_{endo}], 2.46–2.53 [2 H, m, 2(4)-H_{exo}], 3.10 [2 H, br d-like, $J_{1(5).2(4)exo}$ 11.0, 1(5)-H] and 4.12 [1 H, tt, $J_{3.2(4)endo}$ 10.0, $J_{3.2(4)exo}$ 7.0, 3-H]; δ_C 15.8 (t), 33.0 (d), 34.3 (t), 35.3 (t) and 66.7 (d); *m*/*z* 158 (M$^+$, 82%), 125 (30), 87 (83), 67 (69) and 55 (100).

exo-**11**: Needles, mp 114.5–116.5 °C (from hexane–AcOEt) (Found: C, 60.5; H, 8.7; M$^+$, 158.0781); ν_{max}(CHCl$_3$)/cm^{-1} 3586 and 3436; δ_H 1.76–1.82 (3 H, m, 7-H and OH), 1.94 [2 H, dm, $J_{6(8)endo.6(8)exo}$ 14.0, 6(8)-H_{endo}], 2.04 [2 H, dddd, $J_{2(4)exo.2(4)endo}$ 13.0, $J_{2(4)exo.3}$ 10.5, $J_{2(4)exo.1(5)}$ 5.0, $J_{2(4)exo.6(8)exo}$ 2.0, 2(4)-H_{exo}], 2.10–2.18 [2 H, m, 6(8)-H_{exo}], 2.33 [2 H, ddd, $J_{2(4)endo.2(4)exo}$ 13.0, $J_{2(4)endo.3}$ 6.0, $J_{2(4)endo.1(5)}$ 3.5, 2(4)-H_{endo}], 3.08 [2 H, br s, 1(5)-H] and 4.54 [1 H, tt, $J_{3.2(4)exo}$ 10.5, $J_{3.2(4)endo}$ 6.0, 3-H]; δ_C 21.4 (t), 31.7 (t), 34.9 (d), 42.0 (t) and 66.1 (d); *m*/*z* 158 (M$^+$, 70%), 125 (8), 101 (51), 87 (100), 67 (52) and 55 (60).

Photolysis of compound 9 in methanol. Photoreduced products, *endo*-9-thiabicyclo[3.3.1]nonan-3-ol *endo*-**11** and its exo-*isomer exo*-**11**, the type I product, *methyl* (cis-6-*methyltetrahydrothiopyran*-2-*yl*)*acetate* **10b**, and a 1 : 4 mixture of solvent adducts, 3β-*hydroxymethyl*-9-*thiabicyclo*[3.3.1]-*nonan*-3α-*ol endo*-**12a** and its *stereoisomer exo*-**12a**, were obtained with a recovery of a small amount of the starting material **9**.

Methyl (*cis*-6-methyltetrahydrothiopyran-2-yl)acetate **10b**: oil, bp 61–63 °C/8 mm Hg (Found: M$^+$, 188.0854. $C_9H_{16}O_2S$ requires *M*, 188.0871); ν_{max}(CHCl$_3$)/cm^{-1} 1733; δ_H 1.17 (3 H, d, $J_{CH_3.6}$ 7.0, CH_3), 1.22–1.32 (2 H, m, 3- and 5-H_{ax}), 1.40 (1 H, qt, $J_{4ax.4eq} = J_{4ax.3ax} = J_{4ax.5ax} = 13.0$, $J_{4ax.3eq} = J_{4ax.5eq} = 3.0$, 4-$H_{ax}$), 1.88–1.97 (2 H, m, 4- and 5-H_{eq}), 2.01 (1 H, dtd, $J_{3eq.3ax}$ 13.0, $J_{3eq.4eq} = J_{3eq.4ax} = 3.0$, $J_{3eq.2}$ 2.5, 3-H_{eq}), 2.43 (2 H, d, $J_{2.CH_2CO_2}$ 7.0, CH_2CO_2), 2.88 (1 H, dqd, $J_{6.5ax}$ 11.5, $J_{6.CH_3}$ 7.0, $J_{6.5eq}$ 2.5, 6-H), 3.20 (1 H, dtd, $J_{2.3ax}$ 11.5, $J_{2.CH_2CO_2}$ 7.0, $J_{2.3eq}$ 2.5, 2-H) and 3.70 (3 H, s, CO_2CH_3); δ_C 21.5 (q), 26.6 (t), 33.5 (t), 35.8 (t), 38.4 (d), 39.3 (d), 40.6 (t), 51.7 (q) and 171.7 (s); *m*/*z* 188 (M$^+$, 54%), 128 (68), 115 (100) and 81 (65).

endo- and *exo*-**12a**: oil, ν_{max}(CHCl$_3$)/cm^{-1} 3548 and 3407; δ_H 1.54–1.66 (1 H, m, 7-H_{endo}), 1.62 [1.6 H, br d, $J_{2(4)exo.2(4)endo}$ 14.0, 2(4)-H_{endo}, for *exo*-**12a**], 1.70–2.12 [5.2 H, m, 6(8)-H, 7-H_{exo}, for *exo*-**12a**, 2(4)-H_{endo} for *endo*-**12a**], 2.19–2.24 [0.4 H, m, 2(4)-H_{endo} for *endo*-**12a**], 2.24 [1.6 H, dd-like, $J_{2(4)exo.2(4)endo}$ 14.0, $J_{2(4)exo.1(5)}$ 10.0, 2(4)-H_{exo} for *exo*-**12a**], 2.27–2.35 (1 H, br s, exchangeable with D$_2$O, CH_2OH), 2.62–2.74 (0.2 H, m, 7-H_{exo} for *endo*-**12a**), 3.02 [0.4 H, br s, 1(5)-H for *endo*-**12a**], 3.13 [1.6 H, br d-like, $J_{1(5).2(4)exo}$ 10.0, 1(5)-H for *exo*-**12a**], 3.47 (2 H, s, CH_2OH), 3.70 (0.2 H, s, exchangeable with D$_2$O, C^3-OH for *endo*-**12a**) and 5.04 (0.8 H, s, exchangeable with D$_2$O, C^3-OH *exo*-**12a**); δ_C (*exo*-**12a**/*endo*-**12a**) 15.6/17.0 (t), 31.2/32.5 (d), 34.3/32.2 (t), 35.6/40.4 (t), 71.9/68.7 (s) and 71.1/74.4 (t). The two isomers *endo*-**12a** and *exo*-**12a** were separated by GC–MS; for the major isomer *exo*-**12a** (Found: M$^+$, 188.0873. $C_9H_{16}O_2S$ requires *M*, 188.0871); *m*/*z* 188 (M$^+$, 33%), 157 (88), 115 (19) and 99 (100); for the minor isomer *endo*-**12a** (Found: M$^+$, 188.0881); *m*/*z* 188 (M$^+$, 18%), 157 (82), 115 (9) and 99 (100).

Photolysis of compound 9 in propan-2-ol. Photoreduced products *endo*- and *exo*-**11**, a type I product, *propan*-2-*yl* (cis-6-*methyltetrahydrothiopyran*-2-*yl*)*acetate* **10c**, and solvent adducts, 3α-(2-*hydroxypropan*-2-*yl*)-9-*thiabicyclo*[3.3.1]-*nonan*-3β-*ol exo*-**12b** and its *stereoisomer endo*-**12b**, were obtained with a recovery of a small amount of the starting material **9**.

Propan-2-yl (*cis*-6-methyltetrahydrothiopyran-2-yl)acetate **10c**: oil, bp 64–66 °C/8 mmHg (Found: M$^+$, 216.1181. $C_{11}H_{20}O_2S$ requires *M*, 216.1184); ν_{max}(CHCl$_3$)/cm^{-1} 1724; δ_H 1.17 (3 H, d, $J_{CH_3.6}$ 7.0, CH_3), 1.24 [6 H, d, J_{bis} 6.0, CH(C*H*$_3$)$_2$], 1.20–1.32 (2 H, m, 3- and 5-H_{ax}), 1.40 (1 H, qt, $J_{4ax.4eq} = J_{4ax.3ax} = J_{4ax.5ax} = 13.0$, $J_{4ax.3eq} = J_{4ax.5eq} = 3.0$, 4-$H_{ax}$), 1.88–1.97 (2 H, m, 4- and 5-H_{eq}), 2.01 (1 H, dtd, $J_{3eq.3ax}$ 13.0, $J_{3eq.4eq} = J_{3eq.4ax} = 3.0$, $J_{3eq.2}$ 2.5, 3-H_{eq}), 2.36 (1 H, dd, J_{gem} 15.5, J_{vic} 7.5, C*H*HCO$_2$), 2.39 (1 H, dd, J_{gem} 15.5, J_{vic} 7.0, CH*H*CO$_2$), 2.87 (1 H, dqd, $J_{6.5ax}$ 11.5, $J_{6.CH_3}$ 7.0, $J_{6.5eq}$ 2.5, 6-H), 3.19 (1 H, dddd, $J_{2.3ax}$ 11.5, $J_{2.CHHCO_2}$ 7.5, $J_{2.CHHCO_2}$ 7.0, $J_{2.3eq}$ 2.5, 2-H) and 5.03 [1 H, hept, J_{vic} 6.0, C*H*(CH$_3$)$_2$]; δ_C 21.5 (q), 21.8 (q), 26.6 (t), 33.5 (t), 35.9 (t), 38.4 (d), 39.4 (d), 41.1 (t), 68.0 (d) and 170.8 (s); *m*/*z* 216 (M$^+$, 30%), 173 (33), 155 (20), 127 (100), 115 (99) and 81 (38).

exo-**12b**: Needles, mp 107–107.5 °C (from hexane–AcOEt) (Found: C, 60.9; H, 9.2; M$^+$, 216.1157. $C_{11}H_{20}O_2S$ requires C, 61.07; H, 9.32%; *M*, 216.1184); ν_{max}(CHCl$_3$)/cm^{-1} 3535 and 3402; δ_H 1.27 [6 H, s, C(C*H*$_3$)$_2$OH], 1.58–1.64 (1 H, m, 7-H_{exo}), 1.75–1.86 [3 H, m, 7-H_{endo}, 6(8)-H_{endo}], 1.80 [2 H, d-like, $J_{2(4)endo.2(4)exo}$ 14.5, 2(4)-H_{endo}], 1.98 [2 H, tm, $J_{6(8)exo.6(8)endo} = J_{6(8)exo.7endo}$ = 14.0, 6(8)-H_{exo}], 2.23 [2 H, dd-like, $J_{2(4)exo.2(4)endo}$ 14.5, $J_{2(4)exo.1(5)}$ 10.5, 2(4)-H_{exo}], 2.57 [1 H, s, exchangeable with D$_2$O, C(CH$_3$)$_2$O*H*], 3.11 [2 H, br d, $J_{1(5).2(4)exo}$ 10.5, 1(5)-H] and 5.16 (1 H, s, exchangeable with D$_2$O, C^3-OH); δ_C 15.8 (t), 24.8 (q), 31.5 (d), 33.2 (t), 34.7 (t), 75.3 (s) and 75.9 (s); *m*/*z* 216 (M$^+$, 10%), 157 (46), 125 (8), 113 (11), 99 (90) and 59 (100).

endo-**12b**: Needles, mp 98–99.5 °C (from hexane–AcOEt) (Found: M^+, 216.1203); $\nu_{max}(CHCl_3)/cm^{-1}$ 3535 and 3427; δ_H 1.28 [6 H, s, $C(CH_3)_2OH$], 1.55 [1 H, dtt, $J_{7endo.7exo}$ 14.5, $J_{7endo.6(8)endo}$ 6.5, $J_{7endo.6(8)exo}$ 3.0, 7-H_{endo}], 1.73 (1 H. br s, exchangeable with D_2O), 1.85 [2 H, dd, $J_{2(4)endo.2(4)exo}$ 15.0, $J_{2(4)endo.1(5)}$ 2.0, 2(4)-H_{endo}], 1.93 [2 H, dm, $J_{6(8)exo.6(8)endo}$ 14.0, 6(8)-H_{exo}], 2.08 [2 H, tt, $J_{6(8)endo.6(8)exo} = J_{6(8)endo.7exo}$ = 14.0, $J_{6(8)endo.7endo} = J_{6(8)endo.1(5)}$ = 6.5, 6(8)-H_{endo}], 2.23 (1 H, br s, exchangeable with D_2O), 2.42 [2 H, dd, $J_{2(4)exo.2(4)endo}$ 15.0, $J_{2(4)exo.1(5)}$ 6.0, 2(4)-H_{exo}], 2.80 [1 H, dtt, $J_{7exo.7endo}$ 14.5, $J_{7exo.6(8)endo}$ 14.0, $J_{7exo.6(8)exo}$ 6.0, 7-H_{exo}] and 3.06 [2 H, br s, 1(5)-H]; δ_C 17.3 (t), 24.8 (q), 31.6 (t), 32.9 (d), 39.1 (t), 72.4 (s) and 75.0 (s); *m/z* 216 (M^+, 2%), 157 (48), 125 (12), 113 (13) and 99 (100).

Photolysis of compound 9 in acetonitrile in the presence of methanol. Compound **9** was irradiated in acetonitrile (10 cm^3) containing methanol (129 mm^3, 3.20 mmol) for 15 h, and worked up to give a type I product **10b**, and 38–40% of the starting material was recovered. Formation of a trace amount of photoreduced products *endo*- and *exo*-**11** and solvent adducts *endo*- and *exo*-**12a** was detected by GC–MS analysis.

Reduction of compound 9

With sodium boranuide. According to the method described,[9b] compound **9** (300 mg, 1.92 mmol) was treated with sodium boranuide (145 mg, 3.84 mmol) to afford a 10:1 mixture of alcohols *endo*- and *exo*-**11** (298 mg). The product distribution was determined on the basis of the 500 MHz ^1H NMR spectrum of the crude mixture. Recrystallization of the crude product from a mixture of hexane and AcOEt gave compound *endo*-**11** (240 mg, 79%) as needles, the physical and spectral properties of which were completely in accord with those of the specimen obtained by the irradiation of compound **9**.

With sodium. A solution of compound **9** (300 mg, 1.92 mmol) in ethanol (6 cm^3) was added dropwise to a suspension of sodium (900 mg, 39.1 mmol) in benzene (15 cm^3) under reflux with vigorous stirring. After being stirred for 2.5 h, the mixture was poured into ice–water (30 cm^3), and extracted with diethyl ether. The extract was washed with brine, and the solvent evaporated to give a pale yellow oil (321 mg), which, on column chromatography (benzene), gave alcohol *exo*-**11** (218 mg, 71%) and its stereoisomer *endo*-**11** (44 mg, 14%). Recrystallization of the major alcohol *exo*-**11** from hexane–AcOEt gave needles, the physical and spectral properties of which were completely in accord with those of the specimen obtained by the irradiation of compound **9**.

Photolysis of compound 4 in *tert*-butyl alcohol

Thiolactone 4-but-3-enyl thiacyclobutan-2-one **5**, the type I product *tert*-butyl (*cis*-5-methyltetrahydrothiophen-2-yl)-acetate **13**, and photoreduced products *endo*- and *exo*-8-thiabicyclo[3.2.1]octan-3-ol *endo*- and *exo*-**14**, were obtained with a recovery of a small amount of the starting material.

Thiolactone **5**: oil, bp 95–97 °C/2 mmHg (lit.,[6a] 66 °C/0.75 mmHg).

tert-Butyl (*cis*-5-methyltetrahydrothiophen-2-yl)acetate **13**: oil, bp 68–70 °C/4 mmHg.

Spectral properties of compounds **5** and **13** obtained in the present study were in accord with those reported.[6a] Compounds *endo*- and *exo*-**14** were identical with authentic specimens synthesized *via* the sodium boranuide reduction of ketone **4**.

Sodium boranuide reduction of compound 4

According to the method described,[6a] compound **4** (200 mg, 1.41 mmol) was treated with sodium boranuide (54 mg, 1.43 mmol) to give two stereoisomeric alcohols *endo*-**14** (64 mg, 31%) and *exo*-**14** (100 mg, 49%).

endo-**14**: Needles, mp 132–133 °C (from hexane–AcOEt) (lit.,[6a] 239–240 °C, lit.,[9a] 240–241 °C, lit.,[11b] 238–239 °C) (Found: C, 58.0; H, 8.1; M^+, 144.0595. $C_8H_{14}OS$ requires C, 58.29; H, 8.39%; *M*, 144.0609); $\nu_{max}(CHCl_3)/cm^{-1}$ 3587 and 3447; δ_H 1.35 (1 H, br s, exchangeable with D_2O), 2.00–2.08 [4 H, m, 6(7)-H_{exo}, 2(4)-H_{exo}], 2.27 [2 H, dm, $J_{2(4)endo.2(4)exo}$ 15.0, 2(4)-H_{endo}], 2.44–2.50 [2 H, m, 6(7)-H_{endo}], 3.56–3.61 [2 H, m, 1(5)-H] and 4.13§ [1 H, tt, $J_{3.2(4)endo}$ 5.0, $J_{3.2(4)exo}$ 1.0, 3-H]; δ_C 33.7 (t), 42.5 (t), 45.0 (d) and 65.9 (d); *m/z* 144 (M^+, 91%), 110 (62), 95 (59), 85 (84) and 67 (100).

exo-**14**: Needles, mp 150–152 °C (from cyclohexane) (lit.,[6a] 145–148 °C, lit.,[9a] 140–141 °C, lit.,[11b] 158–159 °C) (Found: C, 58.1; H, 8.3; M^+, 144.0595); $\nu_{max}(CHCl_3)/cm^{-1}$ 3581 and 3432; δ_H 1.40 (1 H, br d, $J_{OH.3}$ 5.5, exchangeable with D_2O), 1.74 [2 H, dd, $J_{2(4)exo.2(4)endo}$ 12.0, $J_{2(4)exo.3}$ 12.0, 2(4)-H_{exo}], 1.94–2.07 [4 H, m, 6(7)-H], 2.27 [2 H, dt, $J_{2(4)endo.2(4)exo}$ 12.0, $J_{2(4)endo.1(5)}$ 5.5, 2(4)-H_{endo}], 3.61 [2 H, br m, 1(5)-H] and 3.92 [1 H, ttd, $J_{3.2(4)exo}$ 12.0, $J_{3.2(4)endo} = J_{3.OH}$ = 5.5, 3-H]); δ_C 33.4 (t), 44.0 (t), 45.7 (d) and 65.7 (d); *m/z* 144 (M^+, 76%), 97 (26), 87 (100) and 67 (93).

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§ A discrepancy has appeared between our data and the literature data: δ_H 4.50 (*J* 4.5 and 2.5) [ref. 9(*a*)].

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