At −13° there was no decomposition after 1 week although slight decomposition was noted after 5 weeks. In a refrigerator at 6° no change was noted after 1 week. At room temperature complete decomposition occurred in a few days.

The method of Choppin and Rogers was also used to obtain a crude solution of *t*-**butyl bromoformate** from carbonyl bromide.[37] Upon storage of the bromoformate solution overnight at 6° complete decomposition occurred.

Treatment of *t*-Butyl Chloroformate with Thallous Fluoride.—A mixture of 27.3 g of *t*-butyl chloroformate and 48 g of thallous fluoride was stirred at 0° for 5 days. Distillation gave 16.4 g (89%) of *t*-butyl chloride, bp 52°. After only 10 hr the chloroformate could be recovered unchanged. Similar results were obtained in methylene dichloride and tetramethylene sulfone[38] as solvent or by substitution of alkali or silver fluorides for the thallous salt. In no case could *t*-butyl fluoroformate be obtained in this way.

***t*-Butyl Fluoroformate.**—Carbonyl chlorofluoride was passed into 50 ml of methylene dichloride while cooling in a Dry Ice–ethanol bath until 11 g had been absorbed. There was then dropped in with continued cooling in the same bath over a period of 15 min a solution of 7.4 g of *t*-butyl alcohol in 7.9 g of pyridine. The mixture was stirred in the Dry Ice–ethanol bath for 1 hr, at 0° for 3 hr, and at room temperature for 24 hr. The mixture was shaken in a separatory funnel twice with 25-ml portions of ice water (ice chips present), dried over $MgSO_4$, filtered, and distilled. After removal of the solvent there was obtained 4.6 g (38%) of the fluoroformate: bp[39] 78–79° [lit.[14] bp 4° (15 mm)]; ir (neat) 5.48 μ; nmr ($CDCl_3$) δ 1.27 (s, CH_3).

(37) H. J. Schumacher and S. Lehner, *Ber.*, **61**, 1671 (1928).
(38) C. W. Tullock and D. D. Coffman, *J. Org. Chem.*, **25**, 2016 (1960).

Registry No.—α,α-Dibromo-*t*-butyl alcohol, 24482-83-5; α,α-dibromo-*t*-butyl chloroformate, 25557-88-4; α,α-dibromo-*t*-butyl carbanilate, 25557-89-5; α-bromo-*t*-butyl chloroformate, 25557-90-8; α-bromo-*t*-butyl carbamate, 25557-91-9; α-bromo-*t*-butyl N-benzylcarbamate, 25557-92-0; $(C_6H_5CH_2OCOCH_2NH)_2CO$, 25557-93-1; 2-methyl-3-butyn-2-yl chloroformate, 25557-94-2; 1,1-dimethylethylene carbonate, 4437-69-8; 5,5-dimethyl-3-phenyl-2-oxazolidinone, 25557-96-4.

Acknowledgments.—This work was generously supported by a grant from the National Institutes of Health (GM-09706). We are also indebted to Professor E. Scoffone of the Istituto di Chimica Organica, Università di Padova, in whose laboratories a portion of this work was completed, and to Mr. Jung-Hsien Tsao for checking some of the preparations.

(39) Distillation at atmospheric pressure is not recommended since some decomposition must have occurred at this point. Prior to distillation reaction of an aliquot of the crude solution with glycine gave BOC-glycine in 80% yield, mp 88–90°. Further examination of *t*-butyl fluoroformate was discontinued because of the timely appearance of the paper of Schnabel and Ugi and their collaborators[14] who provide detailed descriptions of a similar method for the large-scale synthesis of this compound

The Synthesis and Nuclear Magnetic Resonance Spectra of Some Disubstituted Derivatives of 2-Methyl-6-thiatricyclo[3.2.1.1^{3,8}]nonane[1]

PELHAM WILDER, JR., AND ROY F. GRATZ

Paul M. Gross Chemical Laboratory, Duke University, Durham, North Carolina 27706

Received March 6, 1970

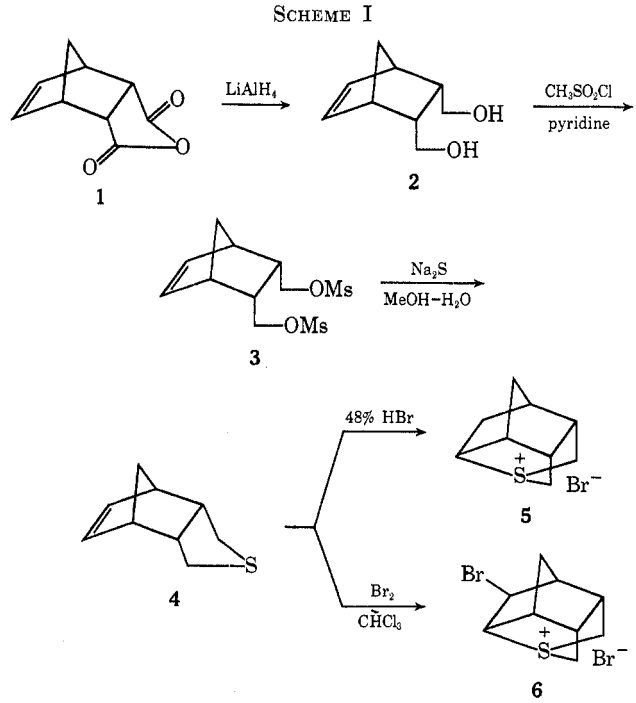
2-Methyl-6-thiatricyclo[3.2.1.1^{3,8}]nonane (**8**) has been prepared by reduction of sulfonium salt **5** with lithium aluminum hydride. A series of 4,10-disubstituted derivatives (**10a–e**) of **8** has been prepared by the reaction of several nucleophiles with bromosulfonium salt **6**. Nmr chemical shifts are presented for the tricyclic compounds, for sulfonium salts **5** and **6**, and for some symmetrical norbornene(ane) derivatives. Spin-decoupling techniques have been used on two of the compounds (**2** and **10a**) to confirm the assignment of chemical shifts. A mechanism for the formation of **10** *via* thiiranium ion **12** has been proposed.

The synthesis of 2-thia-1,2-dihydro-*endo*-dicyclopentadiene (**4**) from *endo-cis*-5-norbornene-2,3-dicarboxylic anhydride (**1**) *via* diol **2** and dimesylate **3** has previously been described.[2] The facile cyclization of **4** to the sulfonium salts **5** and **6** with 48% hydrobromic acid and bromine in chloroform, respectively, has also been reported from this laboratory.[2,3] These reactions are summarized in Scheme I.

The sulfonium salt **5** has been found to react with various nucleophilic reagents to yield monosubstituted products,[4] and the bromosulfonium salt **6** has been reported to react with aqueous lithium carbonate to yield *exo-cis*-2-thiatetrahydro-*endo*-dicyclopentadiene-9,10-diol (**7a**).[3]

At this time we wish to report the preparation and nmr spectrum of 2-methyl-6-thiatricyclo[3.2.1.1^{3,8}]-

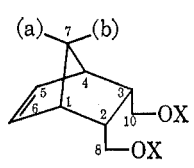
SCHEME I



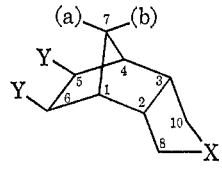
(1) (a) The support of this research by Research Grant CA-4298 from the National Cancer Institute of the National Institutes of Health, U. S. Public Health Service, is gratefully acknowledged. (b) This work represents part of the research of R. F. G., partially fulfilling the requirements for the degree of Doctor of Philosophy at Duke University.
(2) P. Wilder, Jr., and L. A. Feliu-Otero, *J. Org. Chem.*, **30**, 2560 (1965).
(3) P. Wilder, Jr., and L. A. Feliu-Otero, *ibid.*, **31**, 4264 (1966).
(4) L. A. Feliu-Otero, Ph.D. Thesis, Duke University, Durham, N. C., 1965.

TABLE I

CHEMICAL SHIFTS FOR SOME NORBORNENE(ANE) DERIVATIVES[a]



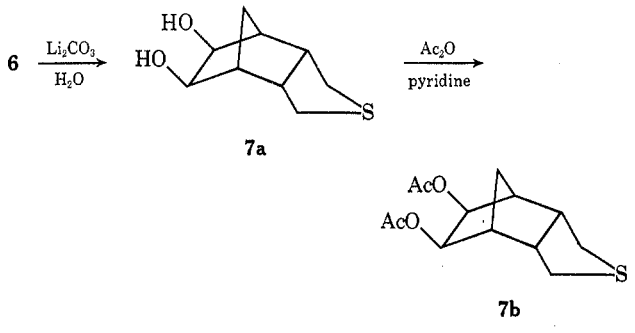
2,3



1, 4, 7a-b, 9

Compd	X	Y	Chemical shift, δ[b] 1,4	2,3exo	5,6olef	5,6endo	7(a)	7(b)	8,10
1	O	C=C	3.50	3.60	6.31		1.82	1.57	[c]
2	H[d]	C=C	2.80	2.52	6.05		1.40[e]	1.40[e]	~3.47
3	SO_2CH_3[f]	C=C	3.00	2.74	6.24		1.65	1.42	~4.01
4	S	C=C	~3.21	~2.44	6.18		1.77[g]	1.77[g]	~2.76
7a	S	OH[h]	2.84	2.21		4.36	1.98	1.32	2.84
7b	S	OAc[i]	2.88	2.33		5.44	2.02	1.45	2.88
9	S	H	2.70	2.17		~1.45[j]	1.48[k]	1.48[k]	2.70

[a] The numbering shown above for compounds 1, 4, 7a-b, and 9, is not correct as far as nomenclature is concerned; *i.e.*, these compounds are derivatives of 2-oxa- or 2-thiadicyclopentadiene. However, the incorrect numbering system is used in order to focus on the relationship of these compounds to their norbornyl analogs. [b] δ values are measured relative to TMS = δ 0.00. Solvent is $CDCl_3$ except for 9 for which it is CCl_4. [c] Compound 1 is an anhydride. [d] OH protons at δ 4.52 (2 H). [e] Center of a triplet, $S \approx 4$ Hz. [f] SO_2CH_3 protons at δ 3.00 (6 H). [g] Center of a triplet, $S \approx 4$ Hz. [h] OH protons at δ 3.77 (2 H). [i] $COCH_3$ protons at δ 2.02 (6 H). [j] Two resonances appear at ~δ 1.78 and ~δ 1.45 for the $5,6_{exo}$ and $5,6_{endo}$ protons. Assignment is indefinite, but the upfield protons are assumed to be *endo*. See ref 8. [k] Center of a quartet, $S \approx 5$ Hz.



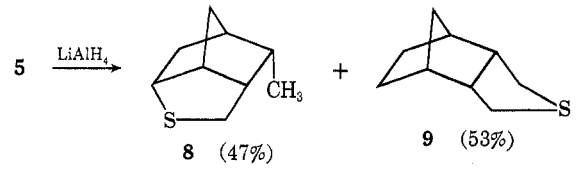
7a

7b

nonane (**8**) and also to report the preparation and nmr spectra of several 4,10-disubstituted derivatives, **10a–e**, of **8**.

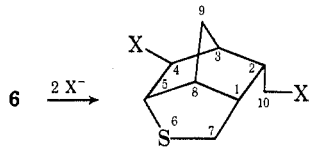
Results

The parent compound **8** was prepared by the reaction of lithium aluminum hydride with **5**. The mixture of compound **8** and 2-thiatetrahydro-*endo*-dicyclopentadiene (**9**)[2,5] which resulted was separated by preparative glpc.



8 (47%) **9** (53%)

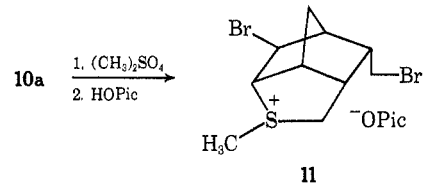
The disubstituted derivatives of **8** were prepared from the bromosulfonium bromide **6**. 4-Bromo-2-bromomethyl-6-thiatricyclo[3.2.1.$1^{3,8}$]nonane (**10a**), a yellow oil, appeared after **6**, a white crystalline solid, was kept for several days at room temperature. The remaining derivatives, **10b–e**, were prepared by the reaction of the sodium or potassium salt of the anion with **6** in an aqueous medium (glacial acetic acid for **10e**).



10a, X = Br
b, X = OPh
c, X = SPh
d, X = 2-SPyr
e, X = OAc

The assignment of structures to compounds **8** and **10a–e** was based primarily upon interpretation of their nmr spectra, which were in no way similar to the spectra of the symmetrical compounds **1–4**, **7a–b**, and **9**, but which were much more closely related to the spectra of the sulfonium salts **5** and **6**. The chemical shift data for the symmetrical compounds are summarized in Table I and for compounds **5**, **6**, **8**, and **10a–e** in Table II.

As a final proof of structure, the methyl picrate salt **11** was prepared from the dibromide **10a** and was subjected to X-ray analysis.[6] This evidence confirmed the structure as written for **11** and eliminated the possibility of sulfur being present in a six-membered sulfide ring.



11

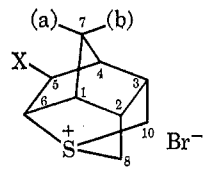
Nmr Spectra.—The assignment of chemical shifts to the protons of the symmetrical norbornene deriva-

(5) S. F. Birch, N. J. Hunter, and D. T. McAllan, *J. Org. Chem.*, **21**, 970 (1956).

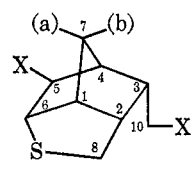
(6) The details of this analysis will be published separately.

TABLE II

CHEMICAL SHIFTS FOR SOME 2-METHYL-6-THIATRICYCLO[3.2.1.1^{3,8}]NONANE DERIVATIVES[a]



5,6



8, 10a–e

Compd	X	Chemical shift, δ[b] 1,4	2,3$_{exo}$	5$_{exo}$	5$_{endo}$	6$_{exo}$	7(a)	7(b)	8	10
5	H	3.04	2.75	1.40	1.90	4.13	2.17	1.63	3.69	3.35
6	Br	3.17	3.00		5.05	4.40	2.40	2.10	3.94	3.50
8	H	2.74	1.97	~1.73[c]	~1.73[c]	3.17	~1.52[d]	~1.52[d]	2.62	1.00
10a	Br	2.92	2.68		4.08	3.74	2.27	1.76	2.84	3.58
10b	OPh[e]	2.97	2.62		4.30	3.24	2.20	1.63	2.80	4.20
10c	SPh[f]	2.95	2.38		3.47	3.27	1.97	1.55	2.74	3.12
10d	2-SPyr[g]	2.98	2.48		4.00	3.32	2.05	1.58	2.74	3.52
10e	OAc[h]	2.83	2.32		4.53	3.10	1.93	1.57	2.72	4.18

[a] See footnote *a* to Table I; the salts are dimethanocyclopenta[*c*]thiolium derivatives, and the other compounds are 6-thiatricyclo[3.2.1.1^{3,8}]nonane derivatives. [b] δ values are measured relative to TMS = δ 0.00. Solvent is $CDCl_3$ except for **5** and **6** for which it is D_2O and **8** and **10e** for which it is CCl_4. [c] Center of a multiplet, W_h = 7 Hz. [d] Center of a multiplet, W_h = 8 Hz. [e] Ph protons centered at δ 7.07 (10 H). [f] Ph protons centered at δ 7.24 (10 H). [g] Pyr protons centered at δ 8.44 (2 H) and 7.24 (6 H). [h] $COCH_3$ protons at δ 1.98 (3 H) and 1.95 (3 H).

tives (Table I) is relatively straightforward since different magnetic environments influence each type of proton and give rise to resonances at five or six separate frequencies. The spectrum of compound **1**[7] shows the C_2- and C_3-*exo* protons as a multiplet somewhat downfield from the more complex multiplet of the C_1 and C_4 protons. The deshielding of the C_2- and C_3-*exo* protons is due to the adjacent *endo*-carboxyl functions.[8] In the remaining examples, the C_2- and C_3-*exo* protons occur upfield from the C_1 and C_4 protons with the most shielding in the fully saturated compounds **7a–b** and **9**. The C_5 and C_6 olefinic protons appear in all cases as an "irregular" triplet with a separation (S) between the outer lines of ~4 Hz in agreement with previously reported examples.[8] The C_5- and C_6-*endo* protons in the diol **7a** appear as a doublet (J = 3 Hz) at δ 4.36, and upon acylation the doublet is shifted downfield 1.08 ppm as would be expected.[9] 2-Thiatetrahydro-*endo*-dicyclopentadiene (**9**) exhibits multiplets at ~δ 1.78 and ~1.45 which also overlap with the sharper resonances due to the C_7 protons. These multiplets were assigned to the C_5- and C_6-*exo* and C_5- and C_6-*endo* protons, respectively.[8] The nature of the resonances due to the $C_{7(a)}$ and $C_{7(b)}$ protons varies considerably from compound to compound. Diol **2** and unsaturated sulfide **4** exhibit two-proton triplets with $S \approx 5$ Hz. The remaining compounds have separate resonances for the $C_{7(a)}$ and $C_{7(b)}$ protons with coupling constants J_{ab} = 8–10 Hz. In two of these cases, assignment of chemical shifts to the $C_{7(a)}$ and $C_{7(b)}$ protons is relatively unambiguous. For diol **7a**, the doublet at δ 1.32 may be assigned to the $C_{7(b)}$ proton on the basis of additional small coupling (absent for the doublet at δ 1.98) with the C_5- and C_6-*endo* protons.[8] The diacetate **7b** should be analogous; however, the downfield doublet is hidden under the methyl resonances of the acetate groups and cannot be compared directly with the doublet at δ 1.45.

In the case of anhydride **1** and dimesylate **3**, the upfield doublet is also assigned to the $C_{7(b)}$ proton. Here each line of the downfield doublet shows additional coupling in the form of a triplet ($S \approx 4$ Hz) indicating $J_{C_{7(a)}-C_1} = J_{C_{7(a)}-C_4} \approx 2$ Hz. These results are in agreement with those reported by Laszlo and Schleyer for *cis-endo*-2,3-dichloro-5-norbornene.[8] The interpretation of the resonances due to the C_1, C_4, C_8, and C_{10} protons is difficult. In anhydride **1**, the C_1 and C_4 protons appear as a broad multiplet coupled with C_2- and C_3-*exo* protons, the olefinic protons, and the C_7 proton. In diol **2** the C_1 and C_4 protons appear as a broad singlet at δ 2.80 (W_h = 8 Hz); the C_8 and C_{10} protons exhibit a complex group of lines centered about δ 3.47. Dimesylate **3** has a similar complex multiplet at about δ 4.01. Its bridgehead protons, however, are obscured under the methyl resonances of the methanesulfonate groups. 2-Thia-1,2-dihydro-*endo*-dicyclopentadiene (**4**) has two very complex multiplets at δ 3.21 and 2.76 for the bridgehead and C_8, C_{10} protons, respectively. In the remaining compounds **7a–b** and **9**, a six-proton singlet (W_h = 3–5 Hz) appears for these protons. The simplicity of the signal for the C_8, C_{10}, and bridgehead protons in these latter cases must be due to a fortuitous overlap of the various signals and perhaps to a reduction in the magnitude of the geminal coupling at C_8 and C_{10} caused by the adjacent sulfur atom.[10] So, although there are complications in some of the individual cases, the assignment of chemical shifts to the protons of the symmetrical compounds is feasible.

The nmr spectra of the derivatives of 2-methyl-6-thiatricyclo[3.2.1.1^{3,8}]nonane (**8**, **10a-e**) and of the two salts (**5** and **6**) have certain similarities which led to the postulation of the tricyclic structure for **8** and **10a–e** Bromosulfonium salt **6** has a singlet ($W_h \approx 4$ Hz) at δ 5.05 for the C_5-*endo* proton; all of the other C_5-*exo* substituted compounds have an appropriately positioned singlet (W_h = 3–4 Hz) representing this proton. The C_6-*exo* proton of the salt **6** appears as a doublet (J =

(7) M. Green and E. A. C. Lucken, *Helv. Chim. Acta*, **45**, 1870 (1962).

(8) P. Laszlo and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1171 (1964), and references therein.

(9) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, p 55.

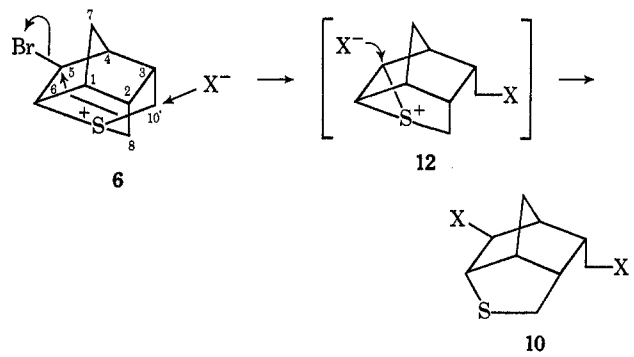
(10) Y. Allingham, R. C. Cookson, and T. A. Crabb, *Tetrahedron*, **24**, 1989 (1968).

5 Hz) at 4.40 coupled to the C_1 proton; in the dibromide **10a**, it is a doublet (J = 5 Hz) at δ 3.74; and, in the remaining compounds, it is also a doublet (J = 4–5 Hz) at δ 3.10 to 3.32 (except for the parent compound **8** where the lack of a C_5-*exo* substituent allows additional coupling). These results are in agreement with those obtained for the 6-oxatricyclo[3.2.1.1^{3,8}]nonane derivatives studied by Ramey, *et al.*[11] In all but one of these unsymmetrical compounds, the $C_{7(a)}$ and $C_{7(b)}$ protons appear as a pair of doublets (J = 11 Hz) near δ 2.00, the exception being the parent compound **8** where overlapping resonances obscure the details. The downfield resonance is assigned to the $C_{7(a)}$ proton in each case.[11] Also, the upfield doublet is generally less sharp owing to long range coupling with the C_5-*endo* proton. The other main diagnostic feature present in all of the 6-thiatricyclo[3.2.1.1^{3,8}]nonane derivatives is a doublet ($J \approx 7$ Hz) for the C_{10} protons. In the parent compound **8** this appears upfield at δ 1.00. In the other compounds, it appears at an appropriate position downfield owing to the variation in substituents at C_{10}. The remaining protons appear between δ 2 and 3, frequently as two broad singlets (W_h = 8–10 Hz) and one sharper singlet (W_h = 3–4 Hz) near δ 3. Decoupling experiments (see below) have helped somewhat to unravel these resonances, but no unequivocal interpretation can be given. In particular the ABX splitting observed for the C_8 protons in the 6-oxa analog[11,12] is not seen because of overlapping resonances.

In order to gain more confidence in the assignment of chemical shifts to the C_1, C_4, C_2- and C_3-*exo*, and the $C_{8(10)}$ protons, decoupling experiments were run on several samples. For diol **2** irradiation of the broad multiplet at δ 2.52 simplifies considerably the complex pattern of the $C_{8(10)}$ protons at $\sim\delta$ 3.47, which indicates that this multiplet represents the C_2- and C_3-*exo* protons. Irradiation of the sharper multiplet at δ 2.80 sharpens both the olefinic resonance and the C_7 proton resonances which indicates that this multiplet represents the C_1 and C_4 protons. In the case of dibromide **10a** the spectrum was run in benzene solution to provide better separation of the various resonances, an exception being part of the doublet for the $C_{7(a)}$ proton which is lost under the broad resonance due to the C_2- and C_3-*exo* protons at δ 2.10 The pertinent experiments here are (1) irradiation of the $C_{7(b)}$ proton at δ 1.22 with observed sharpening of the signal for the C_5-*endo* proton at δ 3.87, (2) irradiation of the resonance due to the C_1 and C_4 protons at δ 2.47 with the observation of the collapse of the doublet for the C_6-*exo* proton at δ 3.53 into a singlet, and (3) irradiation of the resonance due to the C_2- and C_3-*exo* protons at δ 2.10 with the observation of the collapse of the doublet for the C_{10} protons at δ 3.05 into a singlet. Thus, these decoupling experiments have been helpful in assigning the resonances found between δ 2 and 3.

Mechanism.—Several possible mechanisms may be proposed for the reaction of the bromosulfonium salt **6** with the various nucleophiles reported above. It is apparent that the reaction of **6** with aqueous lithium carbonate which produces the symmetrical diol **7a**[3] proceeds by a different route, probably one in which the lithium cation coordinates with the unshared electrons of the bromine at C_5 leading to loss of bromide ion and nucleophilic attack in a concerted process.

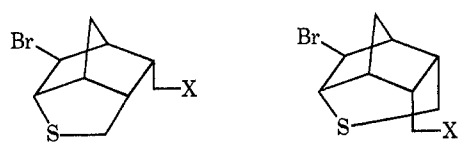
In the present example, the following sequence is proposed.



6 **12** **10**

Nucleophilic attack at C_8 or C_{10} predominates since these positions are less sterically hindered than C_6. Concerted loss of bromide ion leads to the formation of a thiiranium ion (episulfonium ion)[13] intermediate, **12**. The subsequent addition of a second mole of X^- at C_5 yields the product containing the five-membered sulfide ring.[14]

Since these reactions are run in refluxing aqueous solution, generally for 12 hr or more, it is probable that the thermodynamically favored products are formed. Additional intermediates such as **13** and **14** may be



13 **14**

involved although **14** does appear to suffer from excessive nonbonded interactions and no products analogous to it are observed. Concerted loss of bromide ion in the formation of **12** is not necessary. Initial attack of X^- at C_6 is not likely because of steric hindrance to its approach by the C_5 bromine and the $C_{7(a)}$ hydrogen and also no symmetrical products analogous to **7a** are observed.

Experimental Section[15]

2-Thia-1,2-dihydro-*endo*-dicyclopentadiene (4) was prepared by the method previously described:[2] bp 55–57° (0.3 mm) [lit.[2] bp 57° (0.45 mm)]; nmr ($CDCl_3$) δ 6.18 (2 H), ~3.21 (2 H), ~2.76 (4 H), ~2.44 (2 H), and 1.77 (2 H).

Hexahydro-1H-1,5:2,4-dimethanocyclopenta[*c*]thiolium bromide (5)[2] was prepared from **4** and 48% hydrobromic acid: mp 243–245° dec (lit.[2] mp 245–247° dec); nmr (D_2O) δ 4.13 (1 H), 3.69 (2 H), 3.35 (2 H), 3.04 (2 H), 2.75 (2 H), 2.17 (1 H), 1.90 (1 H), 1.63 (1 H), and 1.40 (1 H).

(11) K. C. Ramey, D. C. Lini, R. M. Moriarty, H. Gopal, and H. G. Welsh, *J. Amer. Chem. Soc.*, **89**, 2401 (1967).

(12) D. J. Goldsmith, B. C. Clark, Jr., and R. C. Joines, *Tetrahedron Lett.*, **11**, 1149 (1966).

(13) W. H. Mueller, *Angew. Chem., Int. Ed. Engl.*, **8**, 482 (1969), and references therein.

(14) F. Lautenschlaeger, *J. Org. Chem.*, **33**, 2620 (1968).

(15) Melting points and boiling points are uncorrected. Analyses are by Galbraith Laboratories, Knoxville, Tenn., or M-H-W Laboratories, Garden City, Mich. Analytical glpc analyses were performed on a Varian-Aerograph Series 1200 instrument; preparative glpc analyses were performed on an Aerograph Model A-700 Autoprep. Nmr spectra were recorded on a Varian A-60 or Varian T-60 spectrometer; decoupling experiments were done on the T-60. Mass spectra were recorded on a Bendix time-of-flight spectrometer.

endo-**7-Bromohexahydro-1H-1,5:2,4-dimethanocyclopenta[*c*]-thiolium bromide** (**6**)[3] was prepared from **4** and bromine in $CHCl_3$: mp 117–118° (lit.[3] mp 117–118°); nmr (D_2O) δ 5.05 (1 H), 4.40 (1 H), 3.94 (2 H), 3.50 (2 H), 3.17 (2 H), 3.00 (2 H), 2.40 (1 H), and 2.10 (1 H).

exo-cis-**2-Thiatetrahydro-*endo*-dicyclopentadiene-9,10-diol** (**7a**)[3] was prepared from **6** and aqueous lithium carbonate: mp 106–108° (lit.[3] mp 102–106); nmr ($CDCl_3$) δ 4.36 (2 H), 3.77 (2 H), 2.84 (6 H), 2.21 (2 H), 1.98 (1 H), and 1.32 (1 H).

exo-cis-**2-Thiatetrahydro-*endo*-dicyclopentadiene-9,10-diacetate** (**7b**).—To a solution of 3 ml of acetic anhydride in 15 ml of dry pyridine (distilled from BaO) was added a solution of 100 mg (0.00054 mol) of diol **7a** in 15 ml of dry pyridine. The mixture was stirred and refluxed overnight. The reaction mixture was poured into 100 ml of ice water and the aqueous solution extracted with three 25-ml portions of ether. The ethereal extract was washed with dilute HCl, dried over $MgSO_4$, and concentrated. Final purification was accomplished by preparative glpc on a 5 ft × $^3/_8$ in. 20% SE-30 column at 175° (200-ml/min He flow): nmr ($CDCl_3$) δ 5.44 (2 H), 2.88 (6 H), 2.33 (2 H), 2.02 (7 H), and 1.45 (1 H).

Anal. Calcd for $C_{13}H_{16}O_4S$: C, 57.75; H, 6.71. Found: C, 57.99; H, 6.73.

Lithium Aluminum Hydride Reduction of 5.[4] Preparation of 2-Methyl-6-thiatricyclo[3.2.1.1^{3,8}]nonane (8) and 2-Thiatetrahydro-*endo*-dicyclopentadiene (**9**).—A suspension of 0.25 g (0.066 mol) of lithium aluminum hydride and 1.5 g (0.065 mol) of sulfonium salt **5** in 50 ml of anhydrous ether (dried over Na) was refluxed overnight. Water (25 ml) was carefully added to the reaction mixture to destroy excess lithium aluminum hydride, and 10% HCl was added to solubilize the aluminum salts. The aqueous layer was extracted with two 50-ml portions of ether. The extracts were combined with the original ether layer, dried over $MgSO_4$, and concentrated. Analytical glpc on a 5 ft × $^1/_8$ in. 3% SE-30 column at 100° indicated two components to be present in the ratio 47:53. Preparative glpc on a 10 ft × $^3/_8$ in. 20% SE-30 column at 165° (200-ml/min He flow) was used to separate the mixture.

The 53% component (longer glpc retention time) was identified as 2-thiatetrahydro-*endo*-dicyclopentadiene (**9**) by comparison with an authentic sample: mp 123.5–124.5° (lit.[5] mp 123.5–125); nmr (CCl_4) δ 2.70 (6 H), 2.17 (2 H), ~1.78 (2 H), 1.48 (2 H), and ~1.45 (2 H).

The 47% component (shorter glpc retention time) was identified as 2-methyl-6-thiatricyclo[3.2.1.1^{3,8}]nonane (**8**): mp 143–144°; nmr (CCl_4) δ 3.17 (1 H), 2.74 (2 H), 2.62 (2 H), 1.97 (2 H), ~1.73 (2 H), ~1.52 (2 H), and 1.00 (3 H).

Anal. Calcd for $C_9H_{14}S$: C, 70.06; H, 9.14. Found: C, 69.72; H, 8.97.

A methiodide derivative was prepared by dissolving the sulfide in dry ether and adding a large excess of methyl iodide: mp 158° on recrystallization from EtOH–Et_2O.

Anal. Calcd for $C_{10}H_{17}IS$: C, 40.54; H, 5.79. Found: C, 40.28; H, 5.91.

4-Bromo-2-bromomethyl-6-thiatricyclo[3.2.1.1^{3,8}]nonane (**10a**) was formed when bromosulfonium salt **6** was allowed to stand at room temperature for about 1 week. The yellow oil which appeared was distilled: bp 137–142° (0.4 mm); nmr ($CDCl_3$) δ 4.08 (1 H), 3.74 (1 H), 3.58 (2 H), 2.92 (2 H), 2.84 (2 H), 2.68 (2 H), 2.27 (1 H), and 1.76 (1 H); mass spectrum *m/e* (rel intensity) 310 (42), 312 (73), 314 (58), 233 (100), 231 (92), 201 (38), 199 (38), and 152 (88).

Anal. Calcd for $C_9H_{12}Br_2S$: C, 34.63; H, 3.88; Br, 51.21; S, 10.27. Found: C, 34.72; H, 3.79; Br, 51.22; S, 10.10.

A methylsulfonium picrate **11** was prepared by treating **10a** with excess dimethyl sulfate in anhydrous ether, dissolving the resulting precipitate in absolute ethanol, and adding an ethanolic solution of picric acid. This derivative, mp 172–173° (from MeOH), was used in the X-ray analysis.

Anal. Calcd for $C_{16}H_{17}Br_2N_3O_7S$: C, 34.61; H, 3.09. Found: C, 34.45; H, 2.96.

4-Phenoxy-2-phenoxymethyl-6-thiatricyclo[3.2.1.1^{3,8}]nonane (**10b**).—To a solution of 3.36 g (0.06 mol) of potassium hydroxide and 5.64 g (0.06 mol) of phenol in 40 ml of water was added 1.6 g (0.0051 mol) of sulfonium salt **6**. The mixture was stirred and refluxed overnight. The oily material which separated from the aqueous solution was recrystallized from 95% EtOH four times: mp 69.5–71°; nmr ($CDCl_3$) δ 7.07 (10 H), 4.30 (1 H), 4.20 (2 H), 3.24 (1 H), 2.97 (2 H), 2.80 (2 H), 2.62 (2 H), 2.20 (1 H), and 1.63 (1 H); mass spectrum *m/e* (rel intensity) 338 (16), 261 (10), 245 (100), 184 (63), 168 (73), and 152 (96).

Anal. Calcd for $C_{21}H_{22}O_2S$: C, 74.53; H, 6.55; S, 9.46. Found: C, 74.84; H, 6.76; S, 9.68.

4-Thiophenoxy-2-thiophenoxymethyl-6-thiatricyclo[3.2.1.1^{3,8}]-nonane (**10c**).[16]—To a solution of 3.36 g (0.06 mol) of potassium hydroxide and 6.61 g (0.06 mol) of thiophenol in 40 ml of water was added 2.18 g (0.007 mol) of sulfonium salt **6**. The mixture was stirred and refluxed overnight. The oily material which separated from the aqueous solution was recrystallized from absolute EtOH: mp 80–80.5°; nmr ($CDCl_3$) δ 7.24 (10 H), 3.47 (1 H), 3.27 (1 H), 3.12 (2 H), 2.95 (2 H), 2.74 (2 H), 2.38 (2 H), 1.97 (1 H), and 1.55 (1 H); mass spectrum *m/e* (rel intensity) 370 (37), 261 (100), and 152 (76).

Anal. Calcd for $C_{21}H_{22}S_3$: C, 68.06; H, 5.98; S, 25.96. Found: C, 67.88; H, 5.97; S, 25.93.

4-(2-Thiopyridyl)-2-(2-thiopyridylmethyl)-6-thiatricyclo[3.2.-1.1^{3,8}]nonane (**10d**).—To a solution of 5.39 g (0.096 mol) of potassium hydroxide and 10.68 g (0.096 mol) of 2-mercaptopyridine in 50 ml of water was added 1.5 g (0.0048 mol) of sulfonium salt **6**. The mixture was stirred and refluxed overnight. The black oily material which separated from the aqueous solution was taken up in ether and decolorized with Norit. The ether solution was evaporated, and the white solid which remained was recrystallized from absolute EtOH: mp 86.5–88°; nmr ($CDCl_3$) δ 8.44 (2 H), 7.24 (6 H), 4.00 (1 H), 3.52 (2 H), 3.32 (1 H), 2.98 (2 H), 2.74 (2 H), 2.48 (2 H), 2.05 (1 H), and 1.58 (1 H); mass spectrum *m/e* (rel intensity) 372 (10), 264 (64), and 152 (100).

Anal. Calcd for $C_{19}H_{20}N_2S_3$: C, 61.28; H, 5.41; N, 7.52; S, 25.78. Found: C, 61.32; H, 5.46; N, 7.52; S, 25.97.

A dipicrate was prepared by dissolving the sulfide in 95% ethanol and adding a saturated solution of picric acid: mp 173.5–175° on recrystallization from 95% EtOH.

Anal. Calcd for $C_{31}H_{26}N_8O_{14}S_3$: C, 44.81; H, 3.15. Found: C, 45.28; H, 3.21.

4-Acetoxy-2-acetoxymethyl-6-thiatricyclo[3.2.1.1^{3,8}]nonane (**10e**).—To a solution of 1.50 g (0.018 mol) of anhydrous sodium acetate in 25 ml of glacial acetic acid was added 0.5 g (0.0016 mol) of sulfonium salt **6**. The mixture was stirred and refluxed overnight. The reaction mixture was poured into 100 ml of water, neutralized with sodium carbonate, and the aqueous solution extracted with three 25-ml portions of ether. The extracts were dried over $MgSO_4$ and concentrated. Final purification was accomplished by preparative glpc on a 5 ft × $^3/_8$ in. 20% SE-30 column at 175° (200-ml/min He flow): nmr (CCl_4) δ 4.53 (1 H), 4.18 (2 H), 3.10 (1 H), 2.83 (2 H), 2.72 (2 H), 2.32 (2 H), 1.98 (3 H), 1.95 (3 H), 1.93 (1 H), and 1.57 (1 H); mass spectrum *m/e* (rel intensity) 270 (49), 211 (70), 184 (44), and 152 (100).

Anal. Calcd for $C_{13}H_{18}O_4S$: C, 57.75; H, 6.71. Found: C, 57.90; H, 6.55.

Registry No.—**1**, 129-64-6; **2**, 699-97-8; **3**, 2590-37-6; **4**, 2434-67-5; **5**, 2433-70-7; **6**, 25630-10-8; **7a**, 14751-18-9; **7b**, 25558-28-5; **8**, 25558-29-6; **8** methyl iodide, 25558-30-9; **9**, 2590-39-8; **10a**, 25558-32-1; **10a** methylsulfonium picrate, 25558-33-2; **10b**, 25558-34-3; **10c**, 25558-35-4; **10d**, 25558-36-5; **10d** dipicrate, 25558-37-6; **10e**, 25558-38-7.

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