Transannular Addition of Sulfur Dichloride to Cyclooctadienes

Edward D. Weil,[1] Keith J. Smith, and R. J. Gruber

The Hooker Chemical Corporation, Research Department, Niagara Falls, New York

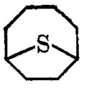
Received November 9, 1965

Transannular addition of sulfur dichloride to 1,5-cyclooctadiene yielded 2,6-dichloro-9-thiabicyclo[3.3.1]-nonane which was readily converted to 2,6-disubstituted derivatives by displacement of both chlorine atoms. Thermal dehydrochlorination of the adduct yielded 6-chloro-9-thiabicyclo[3.3.1]-2-nonene, which also was subject to facile displacement of chlorine. By contrast, the chlorine atoms of 7,8-dichloro-9-thiabicyclo[4.2.1]-nonane, produced by transannular addition of sulfur dichloride to 1,3-cyclooctadiene, were unreactive. By routes precluding skeletal rearrangement, both the 1,3- and 1,5-cyclooctadiene–sulfur dichloride adducts were converted to the parent 9-thiabicyclo[4.2.1]- and -[3.3.1]nonanes. Infrared bands in the vicinity of 1490 and 2990 cm^{-1} were shown to be characteristic of the 3.3.1 ring system and served to establish its twin-chair conformation.

The 9-thiabicyclo[3.3.1]nonane structure (I) was tentatively assigned by Birch and co-workers to a sulfide isolated from Middle East petroleum and also synthesized in very low yield from hydrogen sulfide and N-methylgranatanine.[2] The 9-thiabicyclo[3.3.1]-nonane 9,9-dioxide ring system has been described as the structural unit in the 2:1 copolymer of sulfur dioxide with 1,5-cyclooctadiene.[3] 9-Thiabicyclo[3.3.1]-nonan-3-one was indicated to be the reaction product of pseudopelletierine methiodide with sodium sulfide.[4] However, a convenient synthetic entry into this ring system from readily available starting materials has not hitherto been reported.

The isomeric ring system 9-thiabicyclo[4.2.1]nonane (II) seems not to have been described in the literature, although Birch and co-workers considered the possibility of it occurring in the sulfide fraction of Middle East petroleum.[2]

I

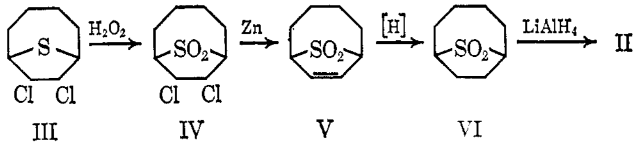


II

We have found that both ring systems can easily be produced by transannular addition of sulfur dichloride to the commercially available 1,5- and 1,3-cyclooctadienes. In the case of 1,5-cyclooctadiene, the adduct was obtained directly from the reaction mixture as a crystalline solid in good yield and purity, whereas in the case of 1,3-cyclooctadiene the desired 1:1 adduct was accompanied by a major quantity of higher molecular weight material but was separable by vacuum sublimation.

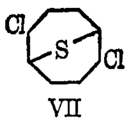
The structure of the 1:1 adduct of sulfur dichloride and 1,3-cyclooctadiene was readily established to be that of 7,8-dichloro-9-thiabicyclo[4.2.1]nonane (III). An alternative structure having a three-membered sulfide ring was disproved by oxidation of the product in good yield to a stable high-melting sulfone (IV)[5] and also by the unreactivity of III toward various nucleophilic reagents (*vide infra*). Another alternative structure having a four-membered sulfur ring with nonvicinal chlorines was disproved by dechlorination of the sulfone by zinc to form a monoolefin (V). In order to produce the parent 9-thiabicyclo[4.2.1]-nonane (II) the olefin sulfone V was hydrogenated to the saturated sulfone VI which was then reduced by lithium aluminum hydride to the sulfide II, mp 127–128° (Scheme I). The direct conversion of III to II by lithium aluminum hydride reduction failed to proceed, unchanged III being recovered.

Scheme I

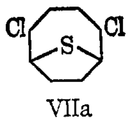


The structure of the 1:1 adduct of sulfur dichloride and 1,5-cyclooctadiene was not reliably predictable on the basis of the known chemistry of 1,5-cyclooctadiene. For example, it was reported that the reaction of formic acid with 1,5-cyclooctadiene yielded both 9-oxabicyclo-[3.3.1]nonane and 9-oxabicyclo[4.2.1]nonane.[6]

Two plausible structures were considered for the 1:1 adduct of sulfur dichloride and 1,5-cyclooctadiene, namely 2,6-dichloro-9-thiacyclo[3.3.1]nonane (VII) and 2,5-dichloro-9-thiabicyclo[4.2.1]nonane (VIIa).



VII



VIIa

Lithium aluminum hydride reduction of the dichloro sulfide yielded a saturated chlorine-free sulfide, $C_8H_{14}S$, mp 172–173°. The presence of the eight-membered ring in the reduction product was confirmed by Raney nickel desulfurization to cyclooctane. Since 9-thiabicyclo-[4.2.1]nonane (II) had already been shown to have a melting point of 127–128°, the reduction product

---

[1] To whom inquiries should be addressed: Stauffer Chemical Co., Eastern Research Center, Dobbs Ferry, N. Y.

[2] S. F. Birch, T. V. Cullum, and R. A. Dean, *Ind. Eng. Chem.* (*Chem. Eng. Data Series*), **3**, 359 (1958).

[3] A. H. Frazer and W. P. O'Neill, *J. Am. Chem. Soc.*, **85**, 2613 (1963).

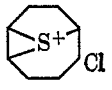
[4] V. Horák, J. Závada, and A. Pískala, *Acta Chim. Hung.*, **21**, 97 (1959); *Chem. Ind.* (London), 1113 (1958).

[5] With the exception of the unusual dibenzoylstilbene episulfide recently reported by D. C. Dittmer and G. C. Levy [*J. Org. Chem.*, **30**, 636 (1965)] episulfides appear not to undergo oxidation to sulfoxides and sulfones: see, for example, H. Staudinger and J. Siegwart, *Helv. Chim. Acta*, **3**, 833 (1920); C. C. J. Culvenor, W. Davies, and N. S. Heath, *J. Chem. Soc.*, 282 (1949). Where episulfones have been made by other means, they have been found to be thermally unstable: L. vonVargha and E. Kovács, *Chem. Ber.*, **75**, 794 (1942); G. Hesse, E. Reichold, and S. Mayundar, *ibid.*, **90**, 2106 (1957); G. P. Hager and R. M. Burgison, *J. Am. Pharm. Assoc.*, **39**, 7 (1950); N. P. Neureiter and F. G. Bordwell, *J. Am. Chem. Soc.*, **85**, 1209 (1963).

[6] A. C. Cope and P. E. Peterson, *ibid.*, **81**, 1643 (1959). Several other products were also obtained.

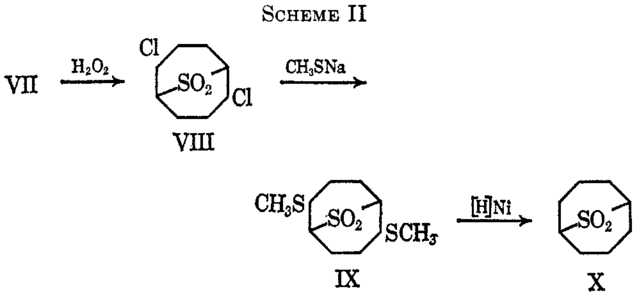
$C_8H_{14}S$ of mp 172–173° must have the alternative structure, 9-thiabicyclo[3.3.1]nonane (I).[7]

However, there remained the possibility that the structure of the sulfur dichloride–1,5-cyclooctadiene adduct was VIIa and that a skeletal rearrangement *via* an episulfonium intermediate (A) had taken place during the reduction reaction, in view of the many known examples of β-chloro sulfide rearrangement *via* episulfonium intermediates.[8] This possibility was eliminated by utilizing a route for removal of the chlorine atoms of VII under conditions where the sulfonium ion intermediate was precluded. Thus, the dichloro sulfide VII was first oxidized to the dichlorosulfone VIII (Scheme II). Although this compound resisted attempts to remove chlorine atoms by various dissolving metal reductions, it was successfully converted to the bis(methylthio) derivative IX by sodium methylmercaptide. Finally IX upon treatment with Raney nickel underwent selective removal of the divalent sulfur to yield 9-thiabicyclo[3.3.1]nonane 9,9-dioxide (X) identical with the sulfone obtained by oxidation of I. Thus, the adduct of sulfur dichloride and 1,5-cyclooctadiene was proved to be 2,6-dichloro-9-thiabicyclo[3.3.1]nonane (VII).



A

SCHEME II



The facile synthesis of VII and the lability of its chlorine atoms toward displacement encouraged us to investigate the preparation of a series of bifunctional compounds containing the 9-thiabicyclononane ring system. However, in the replacement of the chlorine atoms of VII by nucleophilic reagents, there was some uncertainty as to whether the 3.3.1 or the 4.2.1 ring system would be obtained, since these reactions were expected to proceed *via* a bridged sulfonium ion (as mentioned above in connection with the hydride reduction). Thus it appeared desirable to have a convenient and general spectroscopic method for assigning the derivatives to either the 3.3.1 or the 4.2.1 ring system.

Frazer and O'Neill[3] had suggested that the 9-thiabicyclo[3.3.1]nonane 9,9-dioxide structure could be distinguished from its 4.2.1 isomer by means of a correlation between ring size and the positions of the $-SO_2-$ infrared bands, using tetramethylene sulfone and pentamethylene sulfone as model compounds. However, the data given by these authors for the sulfone bands of tetramethylene sulfone appeared to be at variance with that reported elsewhere.[9] Our reinvestigation (Table I) shows that bicyclic five- and six-membered ring sulfones cannot be reliabily distinguished by correlation of their $-SO_2-$ bands with those of monocyclic model compounds.

TABLE I

INFRARED SPECTRA OF VARIOUS CYCLIC SULFONES IN $-SO_2-$ STRETCHING REGIONS[a]

Compound	Observed bands, cm^{-1}
Tetramethylene sulfone (solid)	1107 (s), 1149 (s), 1260 (m), 1281 (m), 1297.5 (vs)
Tetramethylene sulfone (liquid)[b]	1112.5 (s), 1146 (s), 1262 (m), 1274 (m), 1301 (vs)
Pentamethylene sulfone (solid)[c]	1130 (vs), 1277 (vs), 1319 (m)
IV	1117 (vs), 1300 (strong sh), 1308 (vs)
VI	1112 (vs), 1290 (vs), 1311 (sh)
VIII	1136 (vs), 1302 (s), 1308 (vs)
X	1110 (vs), 1119 (sh), 1126 (sh), 1131 (sh), 1278 (s), 1290 (vs)

[a] Not all of the bands in the regions examined (1090–1190 and 1250–1350) are attributable to $-SO_2-$. Frequencies are believed correct to ±3 cm^{-1}, based on calibration using polystyrene. [b] Feairheller, *et al.*,[9] give 1143 and 1298 cm^{-1} as asymmetric and symmetric stretching frequencies. Frazer and O'Neill[3] give 1100 and 1270 cm^{-1} (physical state unspecified). [c] Frazer and O'Neill[3] give 1120 and 1300 cm^{-1}.

A suitable spectroscopic method for distinguishing the 3.3.1 and 4.2.1 ring systems was found, based on the work of Brown, *et al.*, who showed that the bicyclo[3.3.1]nonane ring system exhibits "anomalous" C–H stretching and bending bands near 2990 and 1490 cm^{-1}.[10] Such "anomalous" bands were found in the spectra of I, VII, and the various nucleophilic displacement and oxidation products derived (*vide infra*) from VII (Table II). These bands were attributed (as did Brown, *et al.*,[10] in relation to the corresponding hydrocarbon) to nonbonded interactions between the inner hydrogens of the 3 and 7 methylene groups. Thus, the presence of these bands established not only that I, VII, and derivatives of VII have the 3.3.1 skeleton, but also that these compounds exist in the twin-chair conformation.[11,12]

---

[7] Birch and co-workers[2] had reported a melting point of 155.5–158° for the material which they tentatively identified as 9-thiabicyclo[3.3.1]nonane. Through the kindness of Drs. R. A. Dean and E. V. Whitehead of the British Petroleum Co. Ltd., a specimen of the substance described by Birch, *et al.*, was obtained. Infrared examination showed it to be principally 9-thiabicyclo[3.3.1]nonane with impurity bands corresponding to the strong bands of 9-thiabicyclo[4.2.1]nonane.

[8] Reviewed by K. D. Gundermann, *Angew. Chem.*, **75**, 1194 (1963); see also C. S. Marvel and E. D. Weil, *J. Am. Chem. Soc.*, **76**, 61 (1954), for additional examples. It should be noted that formation of an episulfonium intermediate of this type *permits* but does not *require* rearrangement.

(9) W. R. Feairheller, Jr., and J. E. Katon, *Spectrochim. Acta*, **20**, 1099 (1964), refer to a liquid-state spectrum. In view of the significant effect of physical state on the positions of sulfone bands (L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p 361) we examined the spectrum of tetramethylene sulfone chilled well below its melting point of 27–28°.

(10) W. A. C. Brown, G. Eglinton, J. Martin, W. Parker, and G. A. Sim, *Proc. Chem. Soc.*, 57 (1964); G. Eglinton, J. Martin, and W. Parker, *J. Chem. Soc.*, 1243 (1965).

(11) The twin-chair conformation of the bicyclo[3.3.1]nonane ring system and certain of its aza analogs has recently been established by various infrared, nmr, dipole moment, and X-ray methods: see, besides Brown, *et al.*,[10] N. W. J. Pumphrey and M. J. T. Robinson, IUPAC Congress, London, 1963, Abstracts A 3-19, p 135; J. Dale, I. Laszlo, and W. Ruland, *Proc. Chem. Soc.*, 190 (1964); M. Dobler and J. D. Dunitz, *Helv. Chim. Acta*, **47**, 695 (1964); J. M. Eckert and R. J. W. Lefevre, *J. Chem. Soc.*, 358 (1964). It had earlier been thought that steric compression would perhaps disfavor the twin-chair relative to a boat–chair conformation (see, for example, E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 295).

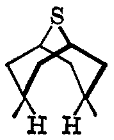
(12) Since yields of isolated products in displacement reactions of VII were not quantitative, the formation of a minor amount of rearrangement (*i.e.*, 4.2.1) products is not precluded.

TABLE II

"ANOMALOUS" CARBON–HYDROGEN BENDING AND STRETCHING BANDS IN 1475–1505- AND 2970–3010-CM^{-1} REGIONS[a]

Compound	Bending	Stretching
9-Thiabicyclo[3.3.1]nonanes		
I	1491	2995
I, 9-oxide	1485[b]	2985
VII	1485	2992
VIII	1481	3002
IX	1478	2982
X	1490	2995
XI	1485	2981, 3000
XII	1488	2988
XIII	1489	2974, 2980 sh
XIV	1491	2995
XV	1491	3001
XVI	1485	2990
XVII	1481	2981
XVIII	1487	2990
XX	1486	2990
XXI	1487	2990
XXII	1482	2990 w
XXIV	1500	2985 sh
XXV	1482, 1497.5[c]	2979, 3001
XXVIII	1488	3000
XXXIII	1490	2990
XXXVII	1487	2997
9-Thiabicyclo[4.2.1]nonanes		
II, III, IV, VI	None	None
9-Thiabicyclo[3.3.1]-2-nonenes		
XXVI, XXIX, XXX, XXXI, XXXIX, XLV, XLVI	None	None
XXVII	None	2976 vw
XXXIV	None	2970 w
XXXV	None	2980 w sh
XXXVI	None	2971, 3000
XXXVIII	(1485, 1497)[c]	None
XLI	(1483 sh, 1497 sh, 1505)[c]	None
XLIII	None	2970 vw
XLIV	None	2985 vw sh
XLVIII	None	3000 w sh

[a] Measured in Fluorolube mull unless otherwise indicated, using Beckman IR-9 or IR-12 grating spectrophotometer, calibrated to ±2 cm^{-1} using polystyrene standard. [b] In CCl_4 solution. [c] These bands may be associated with the aromatic ring.

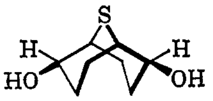


Examination of a Dreiding model of 9-thiabicyclo-[3.3.1]nonane indicated that, if the bond angles were normal, the nuclei of the inner hydrogens would be about 1 A apart (obviously some distortion of the bond angles would be expected in this situation). On the other hand the 9-thiabicyclo[4.2.1]nonane system has no plausible conformation wherein extremely close H–H oppositions occur[13] and these "anomalous" bands would therefore not be expected to occur. Consistently with this expectation, the 9-thiabicyclo[4.2.1]-nonanes II, III, IV, and VI were found to lack bands in the 2990- and 1490-cm^{-1} regions. Further validation of these bands as criteria for the 3.3.1 chair–chair ring system was afforded by the absence of these bands in the spectra of 9-thiabicyclo[3.3.1]-2-nonenes (*vide infra*) wherein such close H–H oppositions cannot occur.[14]

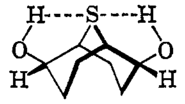
The very high reactivity of the chlorine atoms in VII suggests that both are equatorial and *trans* to the sulfide bridge thus permitting the sulfur to participate anchimerically in their release. A strong band at 737 cm^{-1} occurs in the spectrum of the dichlorosulfide and close to this position (747 cm^{-1}) in its sulfone (VIII) but does not occur in the chlorine-free sulfide I and/or its sulfone (X); therefore, this band is assigned to C–Cl stretching. This band is near the characteristic frequency of equatorial chlorocyclohexanes.[15]

The displacement of both chlorine atoms of VII occurred readily. Thus the following 2,6-disubstituted 9-thiabicyclo[3.3.1]nonanes were prepared by using the reagents indicated in parentheses: dimethoxy (XII) (by sodium methoxide or methanol); diethoxy (XIII) (by sodium ethoxide or ethanol); diacetoxy (XIV) (by sodium acetate or acetic acid); dihydroxy (XV) (by aqueous sodium hydroxide or water); dibromo (XVI) (by hydrogen bromide in acetic acid); diiodo (XVII) (by sodium iodide in acetone); diisothiocyano (XVIII)[16] (by ammonium thiocyanate); dicyano (XX) (by sodium cyanide), also hydrolyzed by aqueous acid to the dicarboxylic acid (XXI); bis(O,O-dimethyl phosphorodithioate) (XXII) (by dimethyl phosphorodithiolate as free acid or sodium salt); bis(O,O-diethyl phosphorodithioate) (XXIII) (by diethyl phosphorodithiolate as free acid or sodium salt); bis(N,N-dimethyldithiocarbamate) (XXIV) (by sodium dimethyldithiocarbamate); diphenoxy (XXV) (by sodium phenolate).

The diol XV was shown to have both hydroxy groups *trans* to the sulfide bridge by the absence of an infrared band in the vinicity of 3524 cm^{-1} which, according to Lüttringhaus, *et al.*, is characteristic of intramolecular hydrogen bonding in 3-hydroxythiacyclohexanes[17] and which would have been expected in the hypothetical diaxial diol XVa or in the monoaxial monoequatorial diol.



XV



XVa

In each of the displacement products of VII, the presence of the "anomalous" carbon–hydrogen stretching and bending bands in the infrared indicates that the 3.3.1 skeleton has been retained. The ease of reaction of VII with even the weaker nucleophiles and the formation of the same isomer with pairs of weak and strong nucleophiles capable of introducing the same group (such as methanol and sodium methoxide)

---

(13) One conformation of the 4.2.1 ring system can be found wherein close H–H oppositions occur; however, this conformation is unlikely since it requires most of the hydrogens to be eclipsed.

(14) Weak bands or shoulders at one or the other region, but never both, were found in certain of the 9-thiabicyclo[3.3.1]-2-nonenes (see Table II) but could not be mistaken for the generally well-resolved and moderately strong bands of the thiabicyclo[3.3.1]nonanes.

(15) L. J. Bellamy, ref 9, p 331.

(16) Identified as the isothiocyanate by characteristic broad infrared bands at 2080 and 2160 cm^{-1}: G. L. Caldow and H. W. Thompson, *Spectrochim. Acta*, **13**, 212 (1958); L. Lieber, C. N. R. Rao, and J. Ramanchandran, *ibid.*, 296 (1958); also by reaction with ethanol to form the bis(ethylthionocarbamate) derivative (XIX).

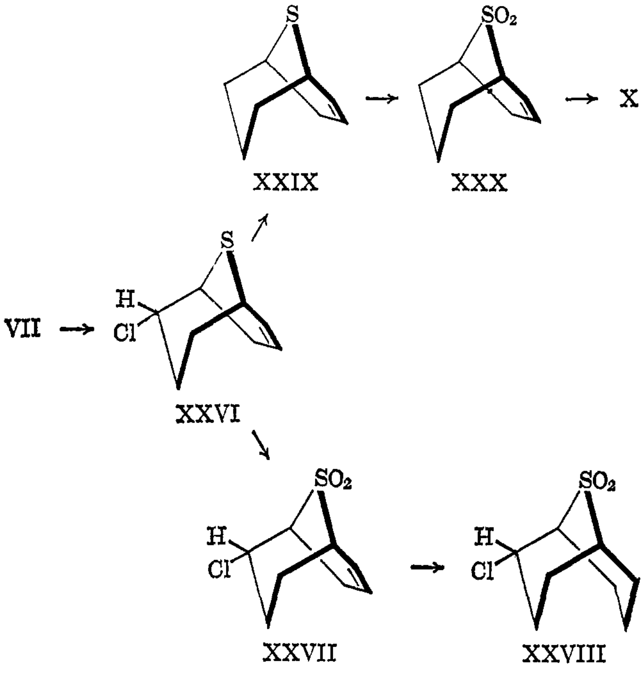
(17) A. Lüttringhaus, S. Kabuss, H. Prinzbach, and F. Langenbucher, *Ann.*, **653**, 195 (1952).

suggest that all of these displacements proceed *via* an episulfonium intermediate which must reopen primarily to restore the 3.3.1 skeleton. It would appear that the 3.3.1 skeleton, despite the nonbonded interactions of the 3- and 7-methylene groups, is less strained than the 4.2.1 skeleton.

The lability of substituents in the 2 and 6 positions of the 9-thiabicyclo[3.3.1]nonane ring system was not limited to the dichloro compound, but was found to extend to the diethers prepared therefrom. Reaction of 2,6-dimethoxy-9-thiabicyclo[3.3.1]nonane, for example, with O,O-dimethyl phosphorodithiolate yielded the 2,6-bis(dimethoxyphosphinodithioyl) derivative XXII identical with that obtained as described above from the dichloro compound VII. The lability of these ethers toward phosphorothiolates is explainable by assuming initial protonation of the ether oxygen, followed by displacement of alcohol by anchimeric attack by the sulfide sulfur forming a cyclic sulfonium ion which is then opened by phosphorodithiolate.

Thermal dehydrochlorination of VII was found to proceed readily above about 130° to yield a monoolefin with release of 1 mole of hydrogen chloride. The monodehydrochlorination product of VII was shown to be 6-chloro-9-thiabicyclo[3.3.1]-2-nonene (XXVI) (rather than a skeletal rearrangement product) by oxidation to its sulfone (XXVII) followed by catalytic hydrogenation of the sulfone to 2-chloro-9-thiabicyclo-[3.3.1]nonane 9,9-dioxide (XXVIII) which exhibited the characteristic C–H stretching and bending bands indicative of the 3.3.1 system (Scheme III). Reduction of the unsaturated chloro sulfide XXVI by lithium aluminum hydride yielded 9-thiabicyclo[3.3.1]-2-nonene (XXIX), the structure of which was proved by oxidation to the sulfone (XXX) followed by catalytic hydrogenation to 9-thiabicyclo[3.3.1]nonane 9,9-dioxide (X) identical with that prepared as described above from I. Thus, no skeletal rearrangement from the 3.3.1 to the 4.2.1 ring system had occurred during the replacement of chlorine by hydrogen.

Scheme III



The infrared spectrum of XXVI showed a strong band at 748 cm^{-1} indicative of equatorial chlorine.[15] The chlorine-free sulfide XXIX showed no bands within 40 cm^{-1} of this position. However, XXVI also showed a band of medium strength at 660 cm^{-1} which may indicate the presence of some axial chlorine. In the chlorine-free sulfide XXIX there is a band of lesser strength at 635 cm^{-1} (probable C–S) not observed in XXVI, so that possibly the 660-cm^{-1} band of XXVI is a C–S stretching band of abnormally high strength, or a coincidental superposition of C–S and axial C–Cl. The infrared spectrum of the chloro sulfone XXVII indicated less ambiguously that the C–Cl bond is equatorial (band at 754 cm^{-1}, not present in the spectrum of XXX). The only band of XXVII in the 600–700-cm^{-1} region is a weak band at 653 cm^{-1} assigned to C–S stretching; the chlorine-free sulfone XXX has a similarly assigned weak band at 639 cm^{-1}.

The nucleophilic displacement and solvolysis of the chlorine atom of XXVI occurs readily, as in the case of VII. In a number of such products it was possible to show that the replacement of chlorine had occurred without 3.3.1 to 4.2.1 rearrangement. Thus, treatment of XXVI with aqueous sodium hydroxide yielded 9-thiabicyclo[3.3.1]-6-nonen-2-ol (XXXI). This alcohol was oxidized to its sulfone (XXXII) which was then hydrogenated to obtain 2-hydroxy-9-thiabicyclo-[3.3.1]nonane 9,9-dioxide (XXXIII), having the characteristic C–H infrared bands indicative of the 3.3.1 twin-chair structure and conformation. The sulfide alcohol was shown to have its hydroxy group in the equatorial position (*trans* to the sulfide bridge) since its infrared spectrum lacked the internally hydrogen-bonded hydroxy group which would have been evident[17] in the hypothetical axial isomer.

Displacement of the chlorine atom in 6-chloro-9-thiabicyclo[3.3.1]-2-nonene by acetate was shown also to proceed without rearrangement to yield the acetate (XXXIV) of the alcohol XXXI. The same acetate was obtained by solvolysis of the chloro compound in acetic acid with evolution of hydrogen chloride. Saponification of the acetate yielded the alcohol XXXI.

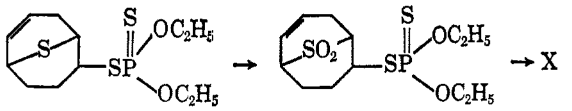
Nucleophilic displacement of the chlorine of XXVI by sodium methoxide or by solvolysis in methanol yielded the methyl ether XXXV. Oxidation to the sulfone XXXVI followed by hydrogenation yielded 2-methoxy-9-thiabicyclo[3.3.1]nonane 9,9-dioxide (XXXVII), having the infrared bands characteristic of the saturated 3.3.1 system.

The reaction of XXVI with other nucleophiles such as sodium phenoxide, sodium cyanide, sodium dimethyldithiocarbamate, aniline, and sodium cyanate proceeded readily to yield the expected products (XXVIII–XLII), which were assigned the 3.3.1 structure by analogy with the previously discussed products. The 6-cyano-9-thiabicyclo[3.3.1]-2-nonene (XXXIX) was further characterized by hydrolysis to the amide (XLIII) and the acid (XLIV). The 6-isocyanato-9-thiabicyclo-[3.3.1]-2-nonene (XLII) was not purified but was converted to the N,N-dimethylurea (XLV) by addition of dimethylamine. As in the case of VII, nucleophilic displacement of the chlorine of XXVI by thiocyanate yielded the isothiocyanate (XLVI) characterized by the presence of the characteristic –N═C═S bands in the infrared spectrum.

Especially because of their potential value as insecticides and acaricides of the anticholinesterase type, the reaction products of XXVI and O,O-dialkyl phosphorodithiolates were investigated in greater detail. As expected, the salts of the latter readily displaced the chlorine atom of 6-chloro-9-thiabicyclo[3.3.1]-2-nonene; also it was found that the free O,O-dialkyl phosphorodithiolic acids readily displaced the chlorine atom with evolution of hydrogen chloride. The same O,O-dialkyl S-(9-thiabicyclo[3.3.1]-6-nonen-2-yl) phosphorodithioates were obtained by either method.

The structure of the O,O-diethyl S-(9-thiabicyclo-[3.3.1]-6-nonen-2-yl) phosphorodithioate (XLVIII) thus produced was proved by permanganate oxidation to the corresponding sulfone (XLIX) followed by partial Raney nickel desulfurization and hydrogenation of the double bond to obtain 9-thiabicyclo[3.3.1]nonane 9,9-dioxide (X) (Scheme IV).

SCHEME IV

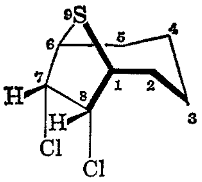


XLVIII XLIX

Surprisingly, it was found that O,O-dimethyl phosphorodithiolate failed to add to the double bond of O,O-dimethyl S-(9-thiabicyclo[3.3.1]-2-nonen-2-yl) phosphorodithioate (XLVII) although this reagent is known to add readily to many olefins. Also, it was found that 6-methoxy-9-thiabicyclo[3.3.1]-2-nonene (XXXV) or 6-phenoxy-9-thiabicyclo[3.3.1]-2-nonene (XXXVIII) failed to add O,O-dimethyl phosphorothiolate to the double bond but rather suffered loss of the methoxy or phenoxy groups yielding in each case XLVII, identical with that prepared directly from XXVI.

In contrast to the extreme lability of the chlorine atoms in 2,6-dichloro-9-thiabicyclo[3.3.1]nonane (VII), the chlorine atoms in 7,8-dichloro-9-thiabicyclo[4.2.1]-nonane (III) were found to be extremely unreactive compared to typical β-chloro sulfides. They were practically inert to lithium aluminum hydride reduction, and sodium iodide in acetone failed to effect replacement or removal of chlorine. Whereas both chlorine atoms of VII were removed within 15 min by methanolic potassium hydroxide, only 2.2% of the available chloride was released from III under the same conditions. Solvolysis of III by 20 M aqueous dioxane at 100° released less than 0.3% of its chlorine as chloride in 100 hr, whereas VII suffered loss of 90% of its chlorine as chloride in 0.5 hr under the same conditions.[18]

The unreactivity of the chlorine atoms in III was thought to have two possible explanations. Either both chlorine atoms are *cis* to the sulfur bridge, in which case the unshared electron pairs on the sulfur cannot readily assist in chloride release, or, if the chlorine atoms are *trans* to the sulfur bridge, the ring strain involved in the formation of a episulfonium ring (or approximation thereto in the transition state) is excessive because of the bond-angle distortion necessary to form such a ring. Since sulfenyl chlorides are believed to add *trans* to a double bond[19] and in the present study the *trans* addition of sulfur dichloride to 1,5-cyclooctadiene was established, it seems more probable that the chlorine atoms in III are also *trans* to the sulfur and the unreactivity of III must be explained on the basis of the excessive bond-angle distortion required for the sulfur to participate in chloride release.



III

The belief that both chlorine atoms of III are *trans* to the sulfide bridge was further supported by the nmr spectrum of III and its sulfone IV, which showed several interesting features. The spectrum of III exhibited a two-proton pattern consisting of four equal peaks (separation, 2.4, 2.5, 2.5 cps) centered at 4.84, a two-proton poorly resolved heptuplet centered at 3.65, a two-proton unresolved multiplet at 2.35, and a six-proton unresolved multiplet at 1.68 ppm.[20] On the basis of its furthest downfield chemical shift and the relative simplicity of its splitting pattern, the peaks at 4.84 were assigned to protons 7 and 8 geminal to chlorine, and the heptuplet at 3.65 was assigned to the bridgehead protons 1 and 6. It was noted that quartets (or "unsymmetrical triplets") have been observed for the *exo*-5,6 protons of *endo*-5,6-dihalo-2-norbornenes.[21] The approximate value of $J_{6,7}$ ($= J_{1,8}$) was estimated using the approach employed under similar circumstances in the norbornene series.[21] The observed separation ($S = 7.4$ cps) between the outside pair of peaks in the four-line pattern was set equal to $J_{6,7} + J_{1,7}$. Since the long-range proton coupling $J_{1,7}$ would be small (most likely $\cong 0$ cps as in the norbornene series), $J_{6,7}$ must have a value in the vicinity of 7 cps. This value is consistent only with an *exo* configuration of the 7 and 8 protons, since in the norbornane and norbornene series J (*exo* bridgehead) = 3–5 cps and J (*endo* bridgehead) $\cong$ 0. Comparison of Dreiding models showed that the dihedral angle between protons 6 and 7 (or 1 and 8) in III is considerably smaller than the angle between the bridgehead and the *exo* protons in the *endo*-5,6-dihalonorbornenes, thus affording a reasonable explanation for the enhanced magnitude of $J_{6,7}$ (or $J_{1,8}$) in III relative to J (*exo* bridgehead) in the norbornenes.

Further support for the proposed configuration of III was afforded by the nmr spectrum of the corresponding sulfone IV, wherein the quartet assigned to the 7 and 8 protons had been shifted downfield by 0.32 ppm. (without appreciable change in the splitting pattern, thus confirming that protons 7 and 8 are substantially iso-

---

[18] These conditions were employed by H. Böhme and K. Sell, *Chem. Ber.*, **81**, 123 (1948), for determination of solvolysis rates of various chlorosulfides. It had been our desire to measure the first-order rate constants for these solvolyses, but that of VII was so rapid and that of III so slow that first-order kinetics could not readily be established for either reaction under these conditions.

[19] N. Kharasch, "Organic Sulfur Compounds," Vol. I, Pergamon Press Inc., New York, N. Y., 1961, p 383.

[20] Given in δ units relative to tetramethylsilane. The nmr spectra were determined using Varian A-60 and H-100 spectrometers.

[21] (a) P. Laszlo and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1171 (1960); (b) P. M. Subramanian, M. T. Emerson, and N. A. LeBel, *J. Org. Chem.*, **30**, 2624 (1965).

chronous), whereas the peak assigned to the bridgehead protons 1 and 6 had shifted scarcely at all (3.65 ppm in III, 3.60 ppm in IV). The relative size of these shifts is consistent with data reported for tetrahydrothiophene (α proton at 2.82, β proton at 1.93) and tetrahydrothiophene 1,1-dioxide (α proton at 3.00, β proton at 2.23).[22] The relatively large shift of the 7 and 8 protons resulting from the oxidation of the sulfur atom to a sulfone group is most satisfactorily explained on the basis that these protons are *cis* to the sulfur bridge and are in a deshielding zone of the sulfur-to-oxygen bond.[23]

Experimental Section

7,8-Dichloro-9-thiabicyclo[4.2.1]nonane (III).—From separate funnels 108 g (1 mole) of 1,3-cyclooctadiene (Columbian Carbon Co.) and 103 g (1 mole) of commercial sulfur dichloride were added with stirring to 5 l. of benzene at 25–26° (water-bath cooling) over 7 hr. The reaction mixture was allowed to stand for 10 hr, then the benzene was removed by distillation leaving 200 g of brown syrup which was subjected to short-path distillation at 7 μ to obtain 28 g of volatile liquid (collected in the Dry Ice cooled trap and found by infrared to contain 1,3-cyclooctadiene), and 50 g of waxy solid distillate, the residue being a tar undistillable up to a stillpot temperature of 130°. The solid distillate melted at 155–168° and was found by infrared to contain more than 90% III by comparison to the purified sample obtained by recrystallization from hexane (50% recovery); the purified product was a colorless crystalline solid, mp 185.5–186.5°. The infrared spectrum (Nujol mull) showed bands at 1286 (w), 1258 (m), 1242 (m), 1166 (m), 1123 (mw), 1111 (mw), 1079 (m), 1070 (m), 982 (ms), 972 (ms), 955 (m), 861 (vs), 823 (m), 776 (s), 749 (s), 718 (s), 692 (w), 656 (ms), 622 (ms), 602 (s), 514 (w), and 420 cm^{-1} (m).

Anal. Calcd for $C_8H_{12}Cl_2S$: C, 45.50; H, 5.73; Cl, 33.58; S, 15.18; mol wt, 211.1. Found: C, 45.36; H, 5.85; Cl, 33.59; S, 15.02; mol wt, 217 (±5%).

A solution of 0.1433 g (0.68 mmole) of 7,8-dichloro-9-thiabicyclo[4.2.1]nonane in 20 ml of 1 *N* methanolic potassium hydroxide was refluxed for 15 min and then subjected to Volhard titration, which indicated that 0.03 mequiv of chloride had been released (2.2% yield for complete dechlorination).

Under the hydrolytic conditions of Böhme and Sell[18] in 20 *M* aqueous dioxane at 100°, less than 0.0015 mequiv of chloride (Volhard titration) was released per millimole of III in 100 hr.

7,8-Dichloro-9-thiabicyclo[4.2.1]nonane 9,9-Dioxide (IV).—A solution of 18 g (0.085 mole) of the dichlorosulfide III and 30 ml of 30% hydrogen peroxide in 100 ml of glacial acetic acid was heated for 4 hr on the steam bath, 30 ml more hydrogen peroxide was added, then heated overnight on the steam bath, cooled, and filtered to obtain 17.5 g (84% yield) of colorless crystals, mp 264° dec. The infrared $-SO_2-$ bands of IV are listed in Table I.

Anal. Calcd for $C_8H_{12}Cl_2O_2S$: C, 39.52; H, 4.97; Cl, 29.15; S, 13.19. Found: C, 39.96; H, 5.05; Cl, 28.9; S, 13.26.

9-Thiabicyclo[4.2.1]-7-nonene 9,9-Dioxide (V).—A mixture of 15 g (0.062 mole) of the dichlorosulfone IV, 12.5 g of zinc dust, and 120 ml of 2B anhydrous ethanol was vigorously refluxed for 4 days. The mixture was then filtered, the filtrate was stripped free of ethanol, and the residual oil was crystallized twice from aqueous methanol (employing a small amount of magnesia and fullers' earth to remove zinc chloride which was a tenacious impurity) to obtain 8 g (75%) of colorless platelets, mp 190–191°. The product gave a positive Baeyer test for unsaturation. The infrared spectrum (Nujol mull) showed $-SO_2-$ bands at 1130 and 1295 cm^{-1}, but no detectable band in the C═C stretching region. The nmr spectrum confirmed the presence of two olefinic protons (closely spaced four-line pattern, S = 4 cps) at 6.2 ppm (in deuteriochloroform).

Anal. Calcd for $C_8H_{12}O_2S$: C, 55.78; H, 7.02; S, 18.61. Found: C, 55.68; H, 7.00; S, 18.81.

9-Thiabicyclo[4.2.1]nonane 9,9-Dioxide (VI).—A solution of 2.5 g (14.5 mmoles) of the sulfone V in 150 ml of 2-propanol plus 0.5 ml of 1 *N* alcoholic potassium hydroxide[25] and 0.4 g of Raney nickel was hydrogenated in a Parr shaker apparatus at 60 psig for 24 hr. The mixture was filtered, the filtrate was stripped free of solvent under aspirator vacuum, the residue was taken up in ether, a small amount (0.2 g) of insolubles was filtered off, and the ether was chilled to obtain 1.7 g of crystals, mp 199–215°. By twice-repeated sublimation at 110° and 0.5 mm and recrystallization from ether, there was obtained 1.3 g (52%) of colorless crystalline product, mp 235–237°, giving a negative Baeyer test for unsaturation. The infrared spectrum (Nujol mull) showed no C═C or olefinic CH stretching bands. The $-SO_2-$ bands of VI are listed in Table I.

Anal. Calcd for $C_8H_{14}O_2S$: C, 55.14; H, 8.10; S, 18.40; mol wt, 174. Found: C, 55.26; H, 8.00; S, 18.67; mol wt (Rast), 176.

9-Thiabicyclo[4.2.1]nonane (II).—A mixture of 12 g (0.069 mole) of the sulfone VI, 15 g (0.38 mole) of lithium aluminum hydride, and 250 ml of ethyl ether was refluxed for 5 days, then filtered, and the ether was removed by distillation through a fractionating column leaving as residue 3.5 g of colorless camphorlike volatile solid, mp 106–118°. Repeated recrystallization from methanol and sublimation at 100° ultimately yielded a product of constant mp 127–128°. Losses in purification were substantial because of the high camphorlike volatility of the compound. The infrared spectrum (solid deposited from carbon disulfide solution) showed bands at 2920 (vs), 2860 (s), 2690 (w), 1520 (s), 1466 (s), 1446 (vs), 1435 (sh), 1384 (m), 1355 (mw), 1342 (w), 1305–1318 (w, broad), 1270 (m), 1220 (w), 1168 (m), 1098 (ms), 1002 (w), 972 (w), 952 (w), 930 (s), 840 (m), 820 (w), 798 (w), 770 (w), 748 (m), 692 (w), 612 (w), 580 (m, broad), 485 cm^{-1} (w).

Anal. Calcd for $C_8H_{14}S$: C, 67.54; H, 9.92; S, 22.54. Found: C, 67.31; H, 9.76; S, 22.44.

Attempted Dechlorination of 7,8-Dichloro-9-thiabicyclo[4.2.1]nonane (III) by Lithium Aluminum Hydride.—A solution of 5.8 g (27.5 mmoles) of the dichloro sulfide III and 1.8 g (8.5 mmoles) of lithium aluminum hydride in 80 ml of tetrahydrofuran was refluxed for 15 hr. The excess hydride was then decomposed with a small amount of ethyl acetate, and the reaction mixture was then admixed with ether and water, the insolubles filtered out and dissolved in dilute nitric acid, and the combined aqueous solutions found by Volhard titration to contain 4.0 mequiv of chloride ion (7.3% yield). The ether layer was evaporated and the residue recrystallized from hexane to obtain 5.5 g of recovered III.

2,6-Dichloro-9-thiabicyclo[3.3.1]nonane (VII).—From separate funnels, 8880 ml (72 moles) of 1,5-cyclooctadiene (Columbian Carbon Co.) and 4596 ml (72 moles, calculated on an assumed 100% purity) of commercial sulfur dichloride[26] were added at constant 2:1 volume ratio to 9 l. of methylene chloride stirred at −5 to 0° (Dry Ice bath cooling) over 5 hr. The reaction mixture was allowed to warm to room temperature over 12 hr, warmed to 50° to dissolve all solids, then chilled, and filtered. The solids thus obtained were washed with hexane and dried in air to obtain 7531 g (50% yield) of nearly colorless solid, mp 100–101°. A further recovery of 2093 g of the same product could be obtained by further concentrating the filtrate, collecting the solids, and recrystallizing these from methylene chloride, to obtain a total yield of 63%. By further concentrating the mother liquors, less pure crops were obtained which were worked up by addition to the reaction mixture of subsequent runs; in this way, an over-all yield of 68% product, mp 100–101°, was obtained over a series of three similar runs. The analytical sample, purified by repeated recrystallizations from benzene, melted at 101–102°. The infrared spectrum (Nujol mull) showed bands at 1378 (s), 1354 (w), 1337 (m), 1280 (w), 1266 (m), 1239 (ms),

---

[22] "High Resolution NMR Spectra Catalog," Vol. I, Varian Associates, Inc., Palo Alto, Calif., Spectrum No. 80; Vol. II, Spectrum No. 416.

[23] A similar downfield shift of protons *cis* to the S═O group in cyclic ethylene sulfites and sulfates has been explained on the basis of the electric field effect and S═O bond anisotropy by J. G. Pritchard and P. C. Lauterbur, *J. Am. Chem. Soc.*, **83**, 2105 (1961).

[24] Infrared data determined using Beckman IR-4 or IR-10 spectrophotometers. Fluorolube mull data in the carbon-hydrogen stretching and bending regions is given in Table II. Microanalyses were done by Galbraith Laboratories, Inc., Knoxville, Tenn., and by the Hooker Research analytical laboratory.

[25] R. C. Morris and N. C. Melchior (to Shell Development Co.), U. S. Patent 2,451,298 (1948); *Chem. Abstr.*, **43**, 1065*e* (1949).

[26] Commercial sulfur dichloride contains 71–85% actual SCl_2, the remainder being mainly S_2Cl_2. A yield of 92.8% VII was obtained by using sulfur dichloride of 99.3% purity, freshly distilled and stabilized by the method of J. H. Schmadebeck (to Hooker Chemical Corp.), U. S. Patents 3,071,441, 3,071,442 (1963); *Chem. Abstr.*, **58**, 7640*h*, 7641*a* (1963).

1202 (m), 1162 (s), 1092 (m), 1080 (m), 1073 (m), 1000 (m), 953 (m), 887 (m), 859 (ms), 816 (vs), 757 (m), 737 (vs), 712 (mw), 686 (s), 624 (s), and 468 cm^{-1} (m).

Anal. Calcd for $C_8H_{12}Cl_2S$: C, 45.50; H, 5.73; Cl, 33.58; S, 15.18; mol wt, 211. Found: C, 45.62; H, 5.67; Cl, 33.6; S, 15.05; mol wt, 226 (±10%, cryoscopic in benzene).

Both chlorine atoms of III were released as chloride (Volhard determination) by 15-min refluxing with excess 1 *N* KOH in methanol. Hydrolysis of III (0.2990 g) in 20 *M* aqueous dioxane (50 ml) at 100° for 0.5 hr released 1.8 mequiv of chloride/mmole of III. The first equivalent of chloride was released in less than 6 min.

9-Thiabicyclo[3.3.1]nonane (I).—To 125 g (0.6 mole) of the dichlorosulfide VII in 1500 ml of ether was added 11.4 g (0.3 mole) of lithium aluminum hydride in 600 ml of ether over 1.5 hr, allowing the ether to reflux. After standing overnight, the mixture was cautiously treated with water to decompose excess hydride. The mixture was then filtered with fullers' earth, and the filtrate was dried over magnesium sulfate and evaporated on the steam bath to obtain 74 g (87% crude yield) of colorless crystalline solid, mp 170–171°. The product was recrystallized from aqueous methanol to obtain 45 g (53% yield) of colorless crystals, mp 172–173°.

Anal. Calcd for $C_8H_{14}S$: C, 67.54; H, 9.92; S, 22.54. Found: C, 67.72; H, 10.21; S, 22.45.

The infrared spectrum (Nujol mull) showed bands at 1350 (w), 1312 (w), 1265 (ms), 1228 (s), 1113 (s), 999 (m), 927 (vs), 868 (s), 822 (w), 807 (mw), 787 (s), 778 (mw), 730 (m, broad), 702 (w), 690 (w), 667 (mw), 618 (s), 575 (mw), 508 (mw), and 482 cm^{-1} (w). The compound also shows bands in CCl_4 at 2985 (m), 2940 (strong shoulder), 2922 (vs), 2900 (s), 2880 (sh), 1485 (ms), 1469 (w), 1448 (m), 1437 (s), and 1429 cm^{-1} (m).

9-Thiabicyclo[3.3.1]nonane 9,9-Dioxide (X).—To 20 g (0.14 mole) of the sulfide I in 200 ml of glacial acetic acid at 20–35° was added 43 ml (0.4 mole) of 30% hydrogen peroxide, and the mixture heated for 25 min on the steam bath. A sample obtained by evaporation showed by infrared a mixture of sulfoxide and sulfone to be present; therefore the oxidation was continued with 30 ml more 30% hydrogen peroxide for 3.5 hr. Upon evaporation and recrystallization of the residue from benzene there was obtained 15 g (66%) of colorless crystals, mp 298–299°. The infrared $-SO_2-$ bands of X are listed in Table I.

Anal. Calcd for $C_8H_{14}O_2S$: C, 55.14; H, 8.10; S, 18.40. Found: C, 55.30; H, 8.08; S, 18.60.

Raney Nickel Desulfurization of 9-Thiabicyclo[3.3.1]nonane (I).—A solution of 10 g of the sulfide I in 600 ml of 2B ethanol was refluxed and stirred for 7 days with 100 g of alcohol-washed Raney nickel (W. R. Grace Co. No. 28). The mixture was then filtered, the filtrate was diluted with 3500 ml of water and extracted with 250 ml of hexane, and the hexane solution was washed, dried over calcium chloride, and fractionally distilled. The fraction distilling over in the C_8 range (120–165°) was found to be cyclooctane by nmr (single peak at δ 1.56) and by infrared comparison with an authentic sample. The undistilled pot residue (bp above 200°) material appeared to be undesulfurized starting material.

2,6-Dichloro-9-thiabicyclo[3.3.1]nonane 9,9-Dioxide (VIII).—To a solution of 211 g (1 mole) of the dichloro sulfide VII in 1000 ml of glacial acetic acid was added 272 g (2.4 moles) of 30% hydrogen peroxide, the temperature was then slowly raised to 93° for 2.5 hr, then cooled to room temperature, and the mixture was filtered. The colorless crystalline solid thus obtained (134 g, 55% yield) after vacuum drying at 85° melted at 175–176°. The infrared $-SO_2-$ bands of VIII are listed in Table I.

Anal. Calcd for $C_8H_{12}Cl_2O_2S$: C, 39.52; H, 4.97; Cl, 29.15; S, 13.19. Found: C, 39.60; H, 4.92; Cl, 29.1; S, 13.25.

2,6-Bis(methylthio)-9-thiabicyclo[3.3.1]nonane 9,9-Dioxide (IX).—To a solution of 8 g (0.17 mole) of methyl mercaptan in 75 ml of dimethylformamide was added 4.5 g (0.083 mole) of sodium methylate, then 10 g (0.041 mole) of the dichloro sulfone VIII, and the mixture was heated in a sealed tube for 8 hr at 150°. The mixture was cooled and filtered, and the filtrate was evaporated to dryness. The residue was recrystallized twice from benzene to obtain 5 g (46%) of a colorless solid, mp 176.5–177°.

Anal. Calcd for $C_{10}H_{18}O_2S_3$: C, 45.08; H, 6.81; Cl, 0.0; S, 36.10. Found: C, 44.87; H, 6.73; Cl, 0.5; S, 35.63.

Partial Desulfurization of 2,6-Bis(methylthio)-9-thiabicyclo[3.3.1]nonane 9,9-Dioxide (IX).—A mixture of 5 g (0.019 mole) of IX, 100 g of Raney nickel (W. R. Grace No. 28), and 600 ml of ethanol was refluxed for 1 day, then filtered, and the filtrate was evaporated to dryness on the steam bath under aspirator vacuum, leaving a solid residue which upon recrystallization twice from ethanol yielded 1.5 g (46%) of colorless crystalline solid, mp 297–298°. The product was shown by mixture melting point and infrared spectrum to be 9-thiabicyclo[3.3.1]nonane 9,9-dioxide (X).

2,6-Dichloro-9-thiabicyclo[3.3.1]nonane 9-Oxide (XI).—To 21.1 g (0.1 mole) of the dichloro sulfide VII in 300 ml of acetone at 15° was added 11.3 g of 30% hydrogen peroxide. To initiate the reaction, 0.1 g of vanadyl sulfate was added, causing the temperature to rise to 37°. After 2 hr, the reaction mixture was diluted with 600 ml of water, causing precipitation of 16 g (70% yield) of colorless solid, mp 121–122°. Recrystallization from benzene–heptane mixture did not raise the melting point.

Anal. Calcd for $C_8H_{12}Cl_2OS$: C, 42.30; H, 5.33; Cl, 31.22; S, 14.11. Found: C, 42.53; H, 5.41; Cl, 30.7; S, 14.29.

2,6-Dimethoxy-9-thiabicyclo[3.3.1]nonane (XII).—A solution of 106.5 g (0.5 mole) of VII and 108 g (2 moles) of sodium methylate in 700 ml of methanol was heated briefly on the steam bath after the reaction ceased to be exothermic, diluted with water, and extracted with hexane. The hexane solution was washed with water and fractionally distilled to obtain 54 g (53%) of product as a pale yellow oil, bp 145–147° (11 mm), $n^{25}D$ 1.5195.

Anal. Calcd for $C_{10}H_{18}O_2S$: C, 59.37; H, 8.97; S, 15.85. Found: C, 59.10; H, 8.97; S, 15.52.

2,6-Diethoxy-9-thiabicyclo[3.3.1]nonane (XIII). A. By Ethanolysis.—A solution of 10 g (0.047 mole) of VII in 200 ml of ethanol was refluxed for 17 days, then evaporated to obtain 10.8 g of crystalline residue, mp 40–42°; this was recrystallized from hexane to obtain 5 g (46% yield) of colorless crystals, mp 44–45°.

Anal. Calcd for $C_{12}H_{22}O_2S$: C, 62.60; H, 9.63; S, 13.92. Found: C, 62.63; H, 9.57; S, 14.05.

B. By Displacement Using Sodium Ethoxide.—A solution of 5 g of sodium in 200 ml of ethanol and 100 ml of tetrahydrofuran was stirred at 25–33° with 21.1 g (0.1 mole) of the dichloro sulfide VII for 8 hr, then 100 ml of hexane and 100 ml of water were added. The hexane layer was washed with water, dried over magnesium sulfate, and evaporated on the steam bath to obtain 22 g (96% yield) of 2,6-diethoxy-9-thiabicyclo[3.3.1]-nonane, shown by infrared to be the same product as obtained by method A.

2,6-Diacetoxy-9-thiabicyclo[3.3.1]nonane (XIV). A. By Solvolysis in Acetic Acid.—A mixture of 42.2 g (0.2 mole) of the dichloro sulfide VII and 150 ml of glacial acetic acid was stirred and refluxed. Evolution of hydrogen chloride proceeded vigorously at first, and was substantially complete in 14 hr. The dark solution was poured into 1 l. of water and ice, yielding an oil which solidified. The solids were removed by filtration and recrystallized from aqueous methanol, using clay and decolorizing charcoal, to obtain 23 g (45% yield) of colorless crystals, mp 100–101°.

B. By Displacement Using Sodium Acetate.—A mixture of 105 g (0.5 mole) of the dichloro sulfide VII and 98 g (1.2 moles) of anhydrous sodium acetate in 500 ml of glacial acetic acid was stirred and heated on the steam bath for 2 hr, then cooled, and filtered to remove inorganic salts, and the filtrate then was poured into 2 l. of water; the precipitated solids were removed by filtration and washed. The product consisted of 103 g (80% yield) of colorless crystals, mp 100–101°. A further 4.5 g, mp 99°, was obtained by diluting the filtrate with water.

Anal. Calcd for $C_{12}H_{18}O_4S$: C, 55.80; H, 7.02; S, 12.39. Found: C, 56.07; H, 7.01; S, 12.49.

9-Thiabicyclo[3.3.1]nonane-2,6-diol (XV). A. By Hydrolysis with Aqueous Sodium Hydroxide.—A mixture of 21.1 g (0.1 mole) of the dichloro sulfide VII, 100 ml of 10% aqueous sodium hydroxide, and 100 ml of ethylene glycol dimethyl ether was refluxed for 19 hr under nitrogen. Upon cooling, two layers were observed. Volhard titration of aliquots indicated 53 mequiv of chloride in the upper (organic) layer and 131 mequiv of chloride in the lower (aqueous) layer. The mixture was evaporated to dryness under aspirator vacuum on the steam bath, and the resultant cake was extracted with two 250-ml portions of hot benzene. On cooling, 2 g of colorless solid, mp 250.5–251.5°, was deposited. The undissolved solids were then leached with 200 ml of water which left undissolved 13 g of microcrystalline colorless solid, mp 249–250.5°. Infrared spectra showed both solids were identical: total yield, 86%. The infrared spectrum of a saturated solution in carbon tetrachloride (less than 10^{-2} *M*) showed only a single sharp band at 3622 cm^{-1} in the OH stretching region.

Anal. Calcd for $C_8H_{14}O_2S$: C, 55.14; H, 8.10; S, 18.40. Found: C, 55.28; H, 7.92; S, 18.20.

B. By Solvolysis in Water.—A suspension of 22 g (0.1 mole) of VII in 1 l. of water containing 5 drops of Triton X100 wetting agent (Rohm and Haas Co.) was agitated at 35° for 1 day. The nearly clear solution was found by titration to contain 0.195 mole of hydrogen chloride. The solution was evaporated to 100 ml and chilled to obtain 6 g of solid product identified as XV by infrared. The filtrate on evaporation yielded a colorless, brittle resin which, by infrared, was found to contain little or no XV, a weaker OH band than shown by XV, and a strong band at 1054 cm^{-1} not possessed by XV. This product was not further investigated.

2,6-Dibromo-9-thiabicyclo[3.3.1]nonane (XVI).—A solution of 21.1 g (0.1 mole) of the dichloro sulfide VII in 100 ml of glacial acetic acid was saturated with hydrogen bromide gas, then allowed to stand overnight in a closed container. The solution was then poured into water, and the precipitate was filtered, washed, dried in vacuum, and recrystallized from benzene–heptane to obtain 20 g (67%) colorless prisms, mp 134.5–135.5°.

Anal. Calcd for $C_8H_{12}Br_2S$: C, 32.02; H, 4.03; Br, 53.27; S, 10.68. Found: C, 32.90; H, 4.04; Br, 53.1; S, 10.86.

2,6-Diiodo-9-thiabicyclo[3.3.1]nonane (XVII).—A mixture of 10 g (0.05 mole) of the dichloro sulfide VII and 25 g (0.20 mole) of sodium iodide in 300 ml of acetone was stirred for 3 hr at room temperature and filtered to remove salt, and the filtrate was evaporated to dryness. The residue was digested with hot heptane and filtered, and the filtrate on cooling gave 14 g (71%) colorless crystals, mp 139.5–140°. Recrystallization from heptane–benzene (90% recovery) raised the melting point to 145–146°.

Anal. Calcd for $C_8H_{12}I_2S$: C, 24.38; H, 3.07; I, 64.4; S, 8.14. Found: C, 24.54; H, 2.87; I, 63.8; S, 8.07.

2,6-Diisothiocyano-9-thiabicyclo[3.3.1]nonane (XVIII).—A mixture of 1330 g (17.5 moles) of ammonium thiocyanate, 1477 g (7 moles) of the dichloro sulfide VII, and 8 l of methyl ethyl ketone was refluxed and stirred for 19 hr, then, while warm, the mixture was extracted several times with 1.5-l. portions of water until a negligible chloride test with silver nitrate was obtained on the washings. The solution was cooled, and the precipitated solids were removed by filtration, washed with methyl ethyl ketone, and dried in air to obtain 1040 g of slightly yellowish crystals, mp 145–148°. A second crop of 267 g of product of the same melting point was obtained by concentrating the filtrate to 3 l. and cooling: total yield, 73%. Recrystallization of the analytical sample from methyl ethyl ketone raised the melting point to 149–150°.

Anal. Calcd for $C_{10}H_{12}N_2S_3$: C, 46.84; H, 4.72; N, 10.93; S, 37.51. Found: C, 46.71; H, 4.54; N, 11.00; S, 37.59.

9-Thiabicyclo[3.3.1]nonane-2,6-bis(thionocarbamic acid) Diethyl Ester (XIX).—A mixture of 20 g (0.078 mole) of the diisothiocyanate XVIII and 1 l. of ethanol was refluxed for 40 hr, then evaporated; the residue was taken up in carbon disulfide, cooled, and filtered to obtain 14 g (51%) of solid product, mp 229° dec; after recrystallization from methyl isobutyl ketone, the melting point was 243–244° dec. The infrared spectrum indicated that the isothiocyanate structure was no longer present and an -NH- band at 3.03 μ was evident.

Anal. Calcd for $C_{14}H_{24}N_2O_2S_3$: C, 48.24; H, 6.94; N,8.04; S, 27.60. Found: C, 48.77; H, 7.10; N, 7.72; S, 27.58.

2,6-Dicyano-9-thiabicyclo[3.3.1]nonane (XX).—To a solution of 84.4 g (0.4 mole) of the dichloro sulfide VII in 200 ml of N-methylpyrrolidone was added a solution of 59.0 g (1.2 moles) of sodium cyanide in 200 ml of N-methylpyrrolidone at such a rate that the temperature did not exceed 70°. The mixture was allowed to cool and stirred overnight, then poured into 3 l. of water, and the solids were removed by filtration. Recrystallization to constant melting point from benzene–hexane then from ethanol yielded 25 g (33%) of tan crystalline solid, mp 157–158°. The infrared spectrum showed bands at 2128 and 2222 cm^{-1} ($C \equiv N$), and no bands in the carbonyl or double-bond regions.

Anal. Calcd for $C_{10}H_{12}N_2S$: C, 62.46; H, 6.29; N, 14.57; S, 16.67. Found: C, 62.30; H, 6.11; N, 14.23; S, 16.46.

9-Thiabicyclo[3.3.1]nonane-2,6-dicarboxylic Acid (XXI).—A mixture of 15 g (0.078 mole) of the dinitrile XX, 60 g of concentrated sulfuric acid, and 60 g of water was refluxed for 1.5 hr and poured into water, and the solids were removed by filtration and dried to obtain 10 g (56% yield) of crystalline solid, mp 219–223°, neut equiv 119 (calcd 115). Recrystallization to constant melting point from acetic acid afforded 5 g, mp 237.5–238°, neut equiv 115.

Anal. Calcd for $C_{10}H_{14}O_4S$: C, 52.16; H, 6.13; S, 13.92. Found: C, 52.42; H, 6.14; S, 13.95.

2,6-Bis(dimethoxyphosphinodithioyl)-9-thiabicyclo[3.3.1]nonane (XXII). A. By Displacement with Sodium Dimethyl Phosphorodithiolate.[27]—To a solution of 10.45 g (0.05 mole) of the dichloro sulfide VII in 300 ml of toluene was added a mixture of 38.3 ml of 2.72 *N* dimethyl phosphorodithiolate and 100 ml of 1 *M* sodium methoxide in methanol over 0.5 hr at 20–25° with stirring, then the mixture was refluxed 0.5 hr and filtered, the filtrate was evaporated, the residue was taken up in benzene, washed with water, dried over magnesium sulfate, and evaporated, and the residue was recrystallized from alcohol to obtain 17 g (96% yield), mp 126–128°. The analytical specimen recrystallized further from benzene–heptane melted at 128-129°.

Anal. Calcd for $C_{12}H_{24}O_4P_2S_5$: C, 31.70; H, 5.32; P, 13.63; S, 35.26. Found: C, 31.83; H, 5.30; P, 13.6; S, 35.76.

B. By Displacement of Chloride by Dimethyl Phosphorodithiolate.—A solution of 100 g (0.47 mole) of the dichloro sulfide VII in 360 ml of 2.83 *N* dimethyl phosphorodithiolate in toluene was heated on the steam bath for 6 hr, during which time 0.92 mole of hydrogen chloride was evolved. On cooling and standing, solids precipitated and were removed by filtration and recrystallized from benzene-heptane to obtain 180 g of colorless crystals, mp 125–128°, found by infrared to be the same as the product of method A.

C. By Displacement of Methoxy Groups from XII.—A solution of 4.0 g (0.02 mole) of XII and 6.3 g (0.04 mole) of dimethyl phosphorodithiolate in 40 ml of toluene was refluxed for 12 hr, then evaporated on the steam bath under aspirator vacuum to obtain a nearly quantitative yield of colorless solid, identified by infrared as the same compound as made by methods A and B.

2,6-Bis(diethoxyphosphinodithioyl)-9-thiabicyclo[3.3.1]nonane (XXIII). A. By Displacement with Sodium Diethyl Phosphorodithiolate.[27]—The procedure and reactant quantities were similar to method A employed for the methyl ester, giving 22.6 g (88% yield) of nearly colorless product, mp 54–57° (from alcohol). Recrystallization from heptane raised the melting point to 60–61°.

Anal. Calcd for $C_{16}H_{32}O_4P_2S_5$: C, 37.62; H, 6.32; P, 12.13; S, 31.39. Found: C, 37.53; H, 6.31; P, 12.2; S, 31.4.

Methods B and C as described above for the methyl homolog were employed for the reaction of diethyl phosphorodithiolate with VII and XIII to obtain 76 and 50% yields of XXIII (after recrystallization).

9-Thiabicyclo[3.3.1]nonane-2,6-dithiol Bis(N,N-dimethyldithiocarbamate) (XXIV).—A mixture of 21.1 g (0.1 mole) of the dichloro sulfide VII, 70.6 g of 40.97% aqueous solution of sodium dimethyldithiocarbamate, and 50 ml of water was stirred on the steam bath for 1 hr, then cooled, and filtered to obtain 38 g of crude product which was recrystallized from benzene–heptane to obtain 19 g of yellowish crystals, mp 210–211°.

Anal. Calcd for $C_{14}H_{24}N_2S_5$: C, 44.17; H, 6.35; N, 7.36; S, 42.11. Found: C, 44.25; H, 6.26; N, 6.9; S, 41.93.

2,6-Diphenoxy-9-thiabicyclo[3.3.1]nonane (XXV).—A solution of 20.7 g (0.22 mole) of phenol and 8.8 g (0.22 mole) of sodium hydroxide in 200 ml of water and a solution of 21.1 g (0.1 mole) of VII in 100 ml of methylene chloride were stirred together at reflux for 2 days. Volhard titration of the aqueous layer showed 2 molar equiv of chloride to have been released. The mixture was diluted with 150 ml of methylene chloride, and the organic layer was separated, dried over magnesium sulfate, and partially evaporated. The resultant solids were removed by filtration, washed with hexane, and dried to obtain 17 g (52%) of colorless crystals, mp 161–162°.

Anal. Calcd for $C_{20}H_{22}O_2S$: C, 73.58; H, 6.79; S, 9.82. Found: C, 73.52; H, 6.79; S, 9.81.

6-Chloro-9-thiabicyclo[3.3.1]-2-nonene (XXVI).—2,6-Dichloro-9-thiabicyclo[3.3.1]nonane (211 g, 1 mole) was melted and held at 166–184° with a slow nitrogen purge until 1 mole of hydrogen chloride had been collected in a water-filled trap attached to the reactor outlet, this requiring 20 hr. The residual liquid was then

---

[27] This experiment was conducted by Dr. Sheldon B. Greenbaum of this laboratory.

distilled through a short packed column to obtain 148 g (85%) of colorless liquid, bp 64–69° (0.3 mm), n^{25}D 1.5713.

Anal. Calcd for $C_8H_{11}ClS$: C, 55.01; H, 6.35; Cl, 20.3; S, 18.35; mol wt, 174.7. Found: C, 55.05; H, 6.43; Cl, 20.1; S, 18.29; mol wt, 179 (by boiling point elevation in tetrahydrofuran). These data were obtained on a redistilled specimen.

The infrared spectrum of XXVI (neat) exhibited bands at 3015 (m), 2950 (sh), 2927 (s), 2895 (s), 2835 (mw), 2810 (w), 1647 (m), 1470 (w), 1447 (m), 1432 (m), 1415 (m), 1384 (w), 1355 (w), 1342 (w), 1336 (w), 1323 (mw), 1276 (w), 1256 (w), 1246 (mw), 1206 (ms), 1180 (w), 1160 (w), 1146 (w), 1103 (w), 1076 (mw), 1043 (w), 1001 (mw), 976 (mw), 962 (mw), 951 (w), 924 (mw), 876 (m), 849 (m), 832 (m), 803 (mw), 743 (vs), 714 (ms), 690 (ms), 660 (s), 579 (mw), 553 (s), and 483 cm^{-1} (w).

6-Chloro-9-thiabicyclo[3.3.1]-2-nonene 9,9-Dioxide (XXVII).—To a solution of 52.5 g (0.3 mole) of XXVI in 300 ml of glacial acetic acid was added 85.2 g (0.75 mole) of 30% hydrogen peroxide over 20 min, with stirring, allowing the temperature to rise to the boiling point. The mixture was then heated on the steam bath for 20 min, added to 3 l. of water, and extracted with 400 ml of chloroform. The extract was dried over magnesium sulfate, filtered, and evaporated to remove the chloroform, and the residue was recrystallized from acetic acid to obtain 38 g of colorless crystals, mp 114–116°. Recrystallization from acetic acid afforded 34 g (55% yield), mp 119–120°; from methanol, 120.5–121.5°. The infrared spectrum (Nujol mull) showed a C=C band at 1646 and $-SO_2-$ bands at 1119 and 1297 cm^{-1}.

Anal. Calcd for $C_8H_{11}ClO_2S$: C, 46.48; H, 5.36; Cl, 17.16; S, 15.51. Found: C, 46.52; H, 5.33; Cl, 17.20; S, 15.47.

The infrared spectrum (Nujol mull) exhibited bands at 3036 (w), 1644 (w), 1296 (vs), 1221 (w), 1182 (mw), 1118 (vs), 1071 (w), 1039 (w), 990 (mw), 960 (w), 924 (mw), 872 (m), 846 (m), 821 (s), 754 (s), 694 (s), 653 (w), 577 (s), 560 (m), 516 (m), 441 (m), 410 cm^{-1} (m sh).

2-Chloro-9-thiabicyclo[3.3.1]nonane 9,9-Dioxide (XXVIII).—A solution of 8 g (0.039 mole) of XXVII in 150 ml of 2-propanol plus 20 ml of dioxane was hydrogenated over 1 g of Raney nickel in a Parr shaker apparatus for 24 hr at 70-psig initial pressure. The catalyst was removed by filtration, the solvent was evaporated, and the residue was recrystallized from benzene–cyclohexane, then twice from aqueous methanol to obtain colorless crystals, mp 186–187.5°, giving a negative Baeyer test for unsaturation.

Anal. Calcd for $C_8H_{13}ClO_2S$: C, 46.04; H, 6.28; Cl, 16.99; S, 15.36. Found: C, 45.90; H, 6.29; Cl, 16.80; S, 15.31.

Volhard titration of an aliquot of the reaction mixture prior to work-up showed no chloride ion to be present, indicating that no hydrogenolysis had occurred.

9-Thiabicyclo[3.3.1]-2-nonene (XXIX).—To 175 g (1 mole) of XXVI in 1 l. of ether was slowly added 19 g (0.49 mole) of lithium aluminum hydride in 500 ml of ether, allowing the solvent to reflux. The mixture was stirred for 1 hr, then 40 ml of ethyl acetate was added cautiously to destroy excess hydride. The mixture was filtered, and the filtrate was evaporated to a pot temperature of 110° under aspirator vacuum to obtain a residue of colorless solid, mp 133–138°. Three recrystallizations from aqueous methanol raised the melting point to 143–143.5°.

Anal. Calcd for $C_8H_{12}S$: C, 68.51; H, 8.63; S, 22.86. Found: C, 68.50; H, 8.62; S, 22.4.

The infrared spectrum of XXIX (Nujol mull) exhibited bands at 3019 (m), 1652 (m), 1438 (m), 1417 (m), 1342 (w), 1329 (w), 1304 (w), 1265 (m), 1248 (w), 1235 (w), 1209 (m), 1174 (w), 1150 (m), 1098 (ms), 1044 (m), 1000 (w), 971 (ms), 951 (w), 940 (m), 883 (m), 847 (mw), 835 (ms), 824 (w), 798 (s), 702 (s), 689 (s), 635 (m), 561 (s), and 452 cm^{-1} (mw).

9-Thiabicyclo[3.3.1]-2-nonene 9,9-Dioxide (XXX).—To a solution of 7.5 g (0.053 mole) of XXIX in 50 ml of glacial acetic acid was slowly added 11 ml of 30% hydrogen peroxide, allowing the temperature to rise to 60°, then the mixture was heated on the steam bath for 1 hr. The acetic acid was removed by distillation, and the residual solid was recrystallized from benzene to obtain 7.0 g of colorless crystals, mp 253–255°, and a second crop of 1.5 g, mp 246–250° (total yield, 92%). Recrystallization from benzene or 2-propanol did not raise the melting point above 253–255°.

Anal. Calcd for $C_8H_{12}O_2S$: C, 55.78; H, 7.02; S, 18.61. Found: C, 55.22; H, 6.74; S, 18.50.

The infrared spectrum (Nujol mull) exhibited bands at 3030 (w), 1651 (w), 1352 (w), 1330 (w), 1288 (vs), 1244 (m), 1211 (ms), 1118 (vs), 1097 (sh), 1085 (w), 1048 (w), 998 (w), 945 (w), 897 (w), 850 (w), 840 (mw), 827 (w), 812 (m), 782 (ms), 704 (s), 638 (mw), 583 (ms), 552 (m), 518 (ms), 461 (w), 412 cm^{-1} (m).

Hydrogenation of 9-Thiabicyclo[3.3.1]-2-nonene 9,9-Dioxide (XXX) to 9-Thiabicyclo[3.3.1]nonane 9,9-Dioxide (X).—A solution of 6.5 g (0.038 mole) of XXX in 250 ml of 2-propanol was hydrogenated over 1 g of Raney nickel at an initial pressure of 70 psig for 24 hr. A sample of the product still gave a positive Baeyer test for unsaturation so the hydrogenation was continued for 3 days at 95 psig. After removing the catalyst by filtration and concentrating the filtrate, the product crystallized out and was removed by filtration: yield 3.3 g (50%) of colorless crystals, mp 296–297°, giving a negative test for unsaturation. The identity of this product with that produced from 9-thiabicyclo-[3.3.1]nonane by oxidation was established by infrared and mixture melting point.

9-Thiabicyclo[3.3.1]-6-nonen-2-ol (XXXI).—To a mixture of 52.5 g (0.3 mole) of XXVI (0.3 mole) in 100 ml of ethylene glycol dimethyl ether was added 120 g of 10% aqueous sodium hydroxide (0.3 mole), then the mixture was stirred and heated at reflux for 24 hr. The mixture was then evaporated on the steam bath until the upper (organic layer) had disappeared, and the precipitated solids were then removed by filtration to obtain 44 g of crude product. This product was recrystallized from hot water (discarding insoluble material) to obtain 32 g (68% yield) of colorless microcrystalline product, mp 176–177°. The infrared spectrum of a 0.003 *M* solution in carbon tetrachloride showed a single sharp band at 3621 cm^{-1} in the OH stretching region.

Anal. Calcd for $C_8H_{12}OS$: C, 61.50; H, 7.74; S, 20.52. Found: C, 61.65; H, 7.68; S, 20.49.

The same product was obtained by saponification of the acetate (XXXIV) using aqueous sodium hydroxide at 90–100°.

9-Thiabicyclo[3.3.1]-6-nonen-2-ol 9,9-Dioxide (XXXII).—To 1.60 g (0.0103 mole) of XXXI in 30 ml of glacial acetic acid at 10° was added 2.7 g of 30% hydrogen peroxide. After 2 hr at 10–25°, the mixture was warmed at 80° for 40 min, then evaporated to dryness, and the residue was recrystallized from ethyl acetate to obtain 0.9 g (47% yield) of colorless solid, mp 261–262°. The infrared spectrum showed $-SO_2-$ bands at 1120 and 1280 (broad), a C=C stretching band at 1648, and unsaturated C–H stretching band at 3030 cm^{-1}.

Anal. Calcd for $C_8H_{12}O_3S$: C, 51.04; H, 6.43; S, 17.03. Found: C, 51.29; H, 6.46; S, 16.91.

9-Thiabicyclo[3.3.1]nonan-2-ol 9,9-Dioxide (XXXIII).—A solution of 0.48 g (2.5 mmoles) of XXXII in 20 ml of 2-propanol was hydrogenated at 40 psig over 1.6 g of Raney nickel catalyst (charged in two portions over 2 days), the mixture was filtered and evaporated to dryness, and the residue was recrystallized from ethyl acetate–hexane mixture to obtain 0.22 g (46% yield) of colorless solid, mp 329–330°. The infrared spectrum showed the absence of C=C or olefinic C–H absorption.

Anal. Calcd for $C_8H_{14}O_3S$: C, 50.51; H, 7.42. Found: C, 50.24; H, 7.47.

9-Thiabicyclo[3.3.1]-6-nonen-2-yl Acetate (XXXIV). A. By Use of Sodium Acetate.—A mixture of 174.5 g (1.0 mole) of XXVI, 98.4 g (1.2 moles) of sodium acetate, and 225 ml of glacial acetic acid was stirred and heated on the steam bath for 1 day, then cooled, filtered, diluted with water to precipitate the product, and refiltered to obtain 184 g (93% yield) of solid, mp 50–52°. Recrystallization from hexane yielded 122 g of colorless crystalline product, mp 51–52°.

Anal. Calcd for $C_{10}H_{14}O_2S$: C, 60.57; H, 7.12; S, 16.17. Found: C, 60.19; H, 7.10; S, 16.17.

B. By Use of Glacial Acetic Acid.—A mixture of 21.1 g (0.1 mole) of XXVI and 50 ml of glacial acetic acid was refluxed until the theoretical amount of hydrogen chloride was evolved and collected in a water-filled trap (12 hr). The solution was cooled and poured into water, the organic product (oil) was extracted with methylene chloride and washed with water and sodium bicarbonate solution, and the solvent was evaporated to obtain 20 g of colorless semisolid product. The infrared spectrum showed this was mainly the acetate as prepared by method A. Recrystallization from acetic acid and sublimation at 100° (0.6 mm) yielded 13.2 g of the crystalline product, mp 52–53°, found by infrared and mixture melting point to be identical with the product of method A.

The infrared spectrum of XXXIV in the C=O stretching region exhibited a doublet at 1730 and 1750 cm^{-1}. In KBr disk or Nujol mull the 1730-cm^{-1} band was stronger, whereas in CS_2, or in CCl_4 the 1750-cm^{-1} band was stronger, with the 1730-cm^{-1} band occurring as a strong shoulder. Recrystallization of the sample did not affect these bands; the substance behaved as a single compound in thin layer chromatography on silica gel using methanol, hexane, or benzene as developing solvents, and iodine vapor as detecting reagent; therefore, the splitting was attributed to some sort of conformational effect.

6-Methoxy-9-thiabicyclo[3.3.1]-2-nonene (XXXV). A. By Use of Sodium Methoxide.—A solution of 120 g (0.7 mole) of XXVI and 41.3 g (0.76 mole) of sodium methylate in 200 ml of methanol was heated under reflux for 15 min, cooled, and filtered to remove salt, the alcohol was removed by distillation, and the residual oil was distilled through a 6-in. Vigreux column to obtain 80 g (67% yield) of colorless liquid, bp 133–137° (13 mm), $n^{24.5}_D$ 1.5379.

Anal. Calcd for $C_9H_{14}OS$: C, 63.48; H, 8.29; S, 18.83. Found: C, 62.84; H, 8.31; S, 18.53.

B. By Methanolysis in the Absence of Base.—A solution of 21.1 g (0.1 mole) of XXVI and 100 ml of methanol was refluxed for 12 hr, then partitioned between 100 ml of hexane and 100 ml of water, and the hexane layer was washed with water, dried over magnesium sulfate, and evaporated on the steam bath to obtain as residue 16 g of colorless oil, shown by infrared to be almost pure 6-methoxy-9-thiabicyclo[3.3.1]-2-nonene.

6-Methoxy-9-thiabicyclo[3.3.1]-2-nonene 9,9-Dioxide (XXXVI).—To a solution of XXXV (17 g, 0.1 mole) in 50 ml of glacial acetic acid was added 0.22 mole of 30% hydrogen peroxide over 0.5 hr with cooling at 20–35°. After 2 hr, the temperature was raised to 95–100° and held for 2 hr, and the solution was evaporated on the steam bath under aspirator vacuum to obtain 19.6 g of waxy residue which upon recrystallization from benzene–hexane mixture gave 14 g of colorless solid, mp 81.5–82.5°.

Anal. Calcd for $C_9H_{14}O_3S$: C, 53.44; H, 6.98; S, 15.85. Found: C, 53.50; H, 6.83; S, 15.95.

2-Methoxy-9-thiabicyclo[3.3.1]nonane 9,9-Dioxide (XXXVII).—A solution of 140 mg of XXXVI in 11 ml of 2-propanol was hydrogenated at 35 psig over 0.3 g of Raney nickel catalyst for 48 hr, the mixture was centrifuged to remove catalyst, and the solvent was evaporated to obtain 140 mg of colorless solid, mp 106–106.5°.

Anal. Calcd for $C_9H_{16}O_3S$: C, 52.91; H, 7.90; S, 15.69. Found: C, 52.78; H, 7.93; S, 15.89.

6-Phenoxy-9-thiabicyclo[3.3.1]-2-nonene (XXXVIII).—To a solution of sodium phenate, prepared from 48 g (0.51 mole) of phenol and 12.6 g (0.55 mole) of sodium in 300 ml of tetrahydrofuran, was added 90 g (0.51 mole) of XXVI, the solution was refluxed for 0.5 hr, cooled, and filtered, the filtrate was evaporated to remove solvent, and the residue was distilled through a 6-in. Vigreux column to obtain 91 g (77% yield) of colorless solid, bp 167–170° (0.3 mm), mp 76–76.5° (recrystallized from aqueous ethanol).

Anal. Calcd for $C_{14}H_{16}OS$: C, 72.37; H, 6.94; S, 13.80. Found: C, 72.59; H, 7.24; S, 13.73.

6-Cyano-9-thiabicyclo[3.3.1]-2-nonene (XXXIX).—To a solution of 10 g (0.20 mole) of sodium cyanide in 10 ml of water and 40 ml of methanol was added 17.4 g (0.1 mole) of XXVI, the mixture was refluxed for 15 min, then diluted with warm water, and the oil was separated off, washed with warm water, and dried at 100° (20 mm). The resultant 11 g of waxy solid after recrystallization from aqueous methanol melted at 59–59.5°.

Anal. Calcd for $C_9H_{11}NS$: C, 65.40; H, 6.71; N, 8.48; S, 19.40. Found: C, 65.11; H, 6.60; N, 8.38; S, 19.58.

9-Thiabicyclo[3.3.1]-6-nonene-2-carboxamide (XLIII) and 9-Thiabicyclo[3.3.1]-6-nonene-2-carboxylic Acid (XLIV).—A solution of 5 g (0.03 mole) of the nitrile XXXIX, 4 g of potassium hydroxide, and 25 ml of ethanol was refluxed for 5 hr and cooled, and the precipitated crystals were filtered out. This product amounted to 3 g (55% yield) of colorless crystalline amide, mp 208–209°.

Anal. Calcd for $C_9H_{13}NOS$: C, 58.98; H, 7.15; N, 7.64; S, 17.49. Found: C, 58.85; H, 7.03; N, 7.69; S, 17.27.

The filtrate containing the potassium salt of the acid was evaporated free of ethanol, and the residue was dissolved in water and acidified with hydrochloric acid. The precipitated solid was extracted with ether and reextracted with sodium hydroxide, the solution was acidified, and the product was filtered out as colorless needles, mp 155–156°. Recrystallization from aqueous ethanol raised the melting point to 157–158°.

Anal. Calcd for $C_9H_{12}O_2S$: C, 58.66; H, 6.56; S, 17.40; neut equiv, 185. Found: C, 58.87; H, 6.72; S, 17.22; neut equiv, 186.

9-Thiabicyclo[3.3.1]-6-nonen-2-yl N,N-Dimethyldithiocarbamate (XL).—A mixture of 35 g (0.2 mole) of XXVI and 70.6 g of a 40.5% aqueous solution of sodium dimethyldithiocarbamate was stirred and heated at 95° for 1 hr, then cooled and filtered. The solids were taken up in hot benzene, the solution was filtered to remove inorganic salts, and the filtrate was diluted with hexane and chilled to obtain 30 g of pale yellow crystals, mp 124–126°. A further 11 g, mp 121–124°, was obtained by concentrating the filtrate.

Anal. Calcd for $C_{11}H_{17}NS_3$: C, 50.92; H, 6.68; N, 5.4; S, 37.1. Found: C, 50.92; H, 6.61; N, 5.24; S, 37.0.

N-(9-Thiabicyclo[3.3.1]-6-nonen-2-yl)aniline (XLI).—A mixture of 8.7 g (0.05 mole) of XXVI and 50 ml of aniline was heated at 100° for 1 hr, then stripped to a pot temperature of 100° at 0.1-mm final pressure. The residue was agitated with an excess of dilute aqueous sodium hydroxide and ether. The insoluble solids were filtered out, washed with water and a small amount of ether, and dried under vacuum to obtain 7 g (60% yield) of tan crystals, mp 112–114°. Recrystallization from aqueous ethanol raised the melting point to 116–116.5°.

Anal. Calcd for $C_{14}H_{17}NS$: C, 72.68; H, 7.41; N, 6.06; S, 13.86. Found: C, 72.98; H, 7.54; N, 6.16; S, 13.53.

9-Thiabicyclo[3.3.1]-6-nonen-2-yl Isocyanate (XLII) and N-(9-Thiabicyclo[3.3.1]-6-nonen-2-yl)-N′,N′-dimethylurea (XLV).—A mixture of 17.4 g (0.1 mole) of XXVI, 8.5 g (0.105 mole) of potassium cyanate, and 320 ml of dry dimethylformamide was stirred at room temperature. A mild exotherm to 33° occurred. After stirring overnight, the mixture was filtered. The salts were found by Volhard titration to contain 0.09 mole of potassium chloride. One-half of the filtrate was evaporated to dryness under aspirator vacuum on the steam bath, yielding a light yellow semisolid residue having a characteristic isocyanate odor and exhibiting a strong infrared band at 4.42 μ (–N=C=O). The material was contaminated with at least one component exhibiting infrared bands at 3.01 (NH) and 5.96 μ (urea C=O). To the unevaporated half of the filtered reaction mixture, 13.5 ml of a benzene solution of dimethylamine (3.85 mequiv/ml) was added and, after 0.5 hr, the mixture was evaporated under aspirator vacuum to a pot temperature of 100°. The residue was triturated with benzene, and the solids were filtered off to obtain 4.5 g of colorless crystalline solid, mp 215–217°. Recrystallization from benzene or ethanol raised the melting point to 219–220°.

Anal. Calcd for $C_{11}H_{18}N_2OS$: C, 58.37; H, 8.01; N, 12.38; S, 14.17. Found: C, 58.20; H, 8.29; N, 12.06; S, 13.88.

9-Thiabicyclo[3.3.1]-6-nonen-2-yl Isothiocyanate (XLVI).—A mixture of 17.5 g (0.1 mole) of XXVI, 7.6 g of ammonium thiocyanate, and 800 ml of methyl ethyl ketone was stirred and refluxed for 2 hr, cooled, and filtered to remove inorganic salts, the filtrate was evaporated to one-tenth volume, and the crystallized solids were filtered out to obtain 12.5 g (63%) of colorless crystals, mp 93–94°. The infrared spectrum (Nujol mull) showed bands at 2080 and 2175 cm^{-1} (broad, characteristic of –N=C=S).

Anal. Calcd for $C_9H_{11}NS_2$: C, 54.78; H, 5.62; N, 7.10; S, 32.5. Found: C, 54.69; H, 5.59; N, 6.94; S, 32.5.

O,O-Dimethyl S-(9-Thiabicyclo[3.3.1]-6-nonen-2-yl) Phosphorodithioate (XLVII). A.—To a mixture of 8.6 g (0.055 mole) of O,O-dimethyl phosphorodithiolate and 5 g (0.05 mole) of triethylamine in 25 ml of benzene was added 8.7 g (0.05 mole) of XXVI, and the mixture refluxed for 3 hr. It was then cooled and filtered, and the filtrate was washed with sodium bicarbonate solution, dried over magnesium sulfate, and evaporated under vacuum. The residual solids were recrystallized from benzene–heptane mixture to obtain 10 g (68%) of a colorless crystalline solid, mp 85–86°.

Anal. Calcd for $C_{10}H_{17}O_2PS_3$: C, 40.51; H, 5.78; P, 10.45; S, 32.44. Found: C, 40.61; H, 5.60; P, 10.23; S, 32.22.

B.—To 320 ml of a toluene solution of O,O-dimethyl phosphorodithiolate (3.11 mequiv/ml) was added 174 g (1 mole) of XXVI. No exotherm or gas evolution was noted. The mixture was heated on the steam bath and at about 40° a smooth evolution of hydrogen chloride began. The mixture was further heated to 96° and within 0.5 hr gas evolution had substantially ceased. The mixture was then cooled, diluted with an equal volume of hexane, chilled, and filtered to obtain 230 g (78%) of the same product (by mixture melting point and infrared) as obtained in method A.

C.—A solution of 5.5 g (0.032 mole) of 6-methoxy-9-thiabicyclo[3.3.1]-2-nonene and 40 mmoles of O,O-diethyl phosphorodithiolate in 250 ml of toluene was refluxed for 2 days, then worked up as in method A to obtain 3.7 g (38%) of the same product (by mixture melting point and infrared) as obtained by method A.

O,O-Diethyl S-(9-Thiabicyclo[3.3.1]-6-nonen-2-yl) Phosphorodithioate (XLVIII).—The same procedure as B above was used, employing O,O-diethyl phosphorodithiolate. The residual product, upon stripping of the solvent to a pot temperature of 100° (10 mm), was a light brownish oil, $n^{25}\mathrm{D}$ 1.5675, d_{25} 1.2162.

Anal. Calcd for $C_{12}H_{21}O_2PS_3$: C, 44.42; H, 6.52; Cl, 0.0; P, 9.55; S, 29.64. Found: C, 44.26; H, 6.50; Cl, 0.1; P, 9.76; S, 29.45.

O,O-Diethyl S-(9-Thiabicyclo[3.3.1]-6-nonen-2-yl) Phosphorodithioate 9,9-Dioxide (XLIX).—To a solution of 45.4 g (0.14 mole) of XLVIII in 150 ml of acetone was added a mixture of 31.5 g (0.2 mole) of potassium permanganate, 38 g of magnesium sulfate in 100 ml of water, and 100 ml of acetone at 20–25° with stirring. The mixture was stirred for 15 min after addition was complete, then decolorized by addition of sulfur dioxide, and then extracted with chloroform. The chloroform extracts were washed with water and with sodium bicarbonate solution, dried over magnesium sulfate, and stripped free of solvent at 50° under aspirator vacuum, and the residual syrup was filtered with fuller's earth to obtain a clear liquid, found by infrared analysis to contain the sulfone as well as unchanged sulfide. Chromatography on Florisil using the method of Patchett and Batchelder[28] yielded two principal fractions, the first to elute being identified by infrared as mainly unconverted sulfide and the second, well resolved from the first fraction, consisting of the desired sulfone which crystallized on standing and which was recrystallized from benzene–hexane mixture to obtain colorless crystals, mp 70–71°.

Anal. Calcd for $C_{12}H_{21}O_4PS_3$: C, 40.43; H, 5.94; P, 8.69; S, 26.99. Found: C, 40.76; H, 5.93; P, 8.70; S, 27.27.

Partial Desulfurization and Hydrogenation of O,O-Diethyl S-(9-Thiabicyclo[3.3.1]-6-nonen-2-yl) Phosphorodithioate 9,9-Dioxide (XLIX).—A mixture of 5 g (0.014 mole) of the crude phosphorodithioate sulfone (XLIX), 100 g of Raney nickel (alcohol washed), and 500 ml of ethanol was refluxed with stirring for 24 hr, then filtered, and the filtrate was evaporated to dryness. The residue, which upon attempted recrystallization yielded a product melting between 9-thiabicyclo[3.3.1]nonane 9,9-dioxide and 9-thiabicyclo[3.3.1]-2-nonene, was further hydrogenated in 2-propanol over 1.5 g of Raney nickel for 24 hr at 30 psig and room temperature. Upon filtration, evaporation, and recrystallization of the residue, there was obtained 0.8 g (33% yield) of colorless solid, mp 295–297°, identical with 9-thiabicyclo[3.3.1]nonane 9,9-dioxide prepared as previously described.

Attempted Reaction of 7,8-Dichloro-9-thiabicyclo[4.2.1]nonane with Sodium Iodide.—A solution of 2.11 g (0.01 mole) of III was refluxed with 50 ml of 10% sodium iodide in acetone. Only a faint trace of iodine color developed and no sodium chloride precipitated. The addition of water precipitated 1.85 g of unchanged starting material.

9-Thiabicyclo[3.3.1]nonane 9-Oxide.—To a solution of 8 g (0.056 mole) of the sulfide I in 80 ml of glacial acetic acid was added 5.7 ml of 30% hydrogen peroxide (0.056 mole) dropwise, maintaining the temperature at 25–35°. The mixture was allowed to stir 0.5 hr, then warmed on the steam bath for 20 min. The solvent was then stripped under oil pump vacuum to 100° pot temperature. The resultant semisolid residue was found to be water soluble. Recrystallization from ether and then from cyclohexane to constant melting point yielded 1.5 g (17% yield) of colorless crystals, mp 251–252°. Sublimation at 130° (0.5 mm) raised the melting point to 253–254°. The infrared spectrum (in carbon tetrachloride) showed a strong –SO– band at 1050 cm^{-1}.

Anal. Calcd for $C_8H_{14}OS$: C, 60.71; H, 8.91; S, 20.26. Found: C, 60.43; H, 9.04; S, 20.08.

Acknowledgment.—We wish to thank Mr. David Eastman, Mr. John Michalovic, Mr. Helmut Joseph, and Dr. James G. Colson for infrared, gas chromatographic, and nmr data, and for helpful discussions thereof.

---

[28] G. G. Patchett and G. H. Batchelder, *J. Agr. Food Chem.*, **9**, 395 (1961).

The Reaction of Bicyclo[2.2.1]-2,5-heptadiene with Sulfur Dichloride

F. LAUTENSCHLAEGER

Dunlop Research Centre, Sheridan Park, Ontario, Canada

Received November 19, 1965

The reaction of bicyclo[2.2.1]-2,5-heptadiene with sulfur dichloride leads to an intramolecular addition product in a yield of 81%. The reaction is the first reported transannular addition of sulfur dichloride to a cyclic diolefin.

Heteropolar and homopolar additions to bicyclo[2.2.1]-2,5-heptadiene (norbornadiene) proceed by 1,2 addition without skeletal rearrangement[1] or by pathways involving homallylic intermediates and resulting in 1,7 addition products and derivatives of nortricycline.[2] In the past, little attention has been given to the addition of such bifunctional reagents which may lead to 1:1 addition. The addition of sulfur dichloride is therefore of interest.

Results and Discussion

The reaction between sulfur dichloride and norbornadiene leads to a monomeric product in a yield of 81%. Gas chromatographic analysis and fractional distillation failed to indicate the presence of isomers. The mass spectrum confirms the molecular formula $C_7H_8Cl_2S$ with three peaks at *m/e* 194, 196, and 198. The structure **1**, *exo,exo*-3,5-dichloro-8-thiatricyclo[2.2.1.1^{2,6}]octane (dichlorotricyclothiaoctane), was primarily assigned on the basis of its nmr spectrum, recorded on a Varian HA-100 spectrometer. In acetone-d_6 the two protons H_c are a closely spaced five-line multiplet at 4.75 ppm coupled to H_d and H_e with coupling constants of 1.0 and 0.5 cps, respectively. A single line for proton H_c is observed on a Varian A-60 instrument in agreement with the general absence of coupling between *endo* and bridgehead hydrogens on spectra recorded on nmr instruments of lower resolution (see Table I).[3] A multiplet signal from H_d at 3.15 ppm arises from coupling of that proton to H_b, H_a, and H_e. H_b exhibits a ten-line pattern at the surprisingly low field of 4.05 ppm. This is split by H_a to

---

[1] G. Brindell and S. J. Cristol in "Organic Sulfur Compounds," Vol. 1, N. Kharasch, Ed., Pergamon Press Inc., New York, N. Y., p 121; S. J. Cristol, R. P. Arganbright, G. D. Brindell, and R. M. Heitz, *J. Am. Chem. Soc.* **79**, 6035 (1957).

[2] P. de Mayo, "Molecular Rearrangements," Vol. 1, Interscience Publishers, Inc., 1963, p 198.

[3] W. D. Kumler, J. N. Schoolery, and F. V. Brutcher, Jr., *J. Am. Chem. Soc.*, **80**, 2533 (1958); E. J. Corey, M. Ohno, S. W. Chow, and R. A. Scherrer, *ibid.*, **81**, 6305 (1959); H. E. Simmons, *ibid.*, **83**, 1657 (1961); J. Meinwald, Y. C. Meinwald, and T. N. Baker, III, *ibid.*, **85**, 2513 (1963).