dithiolate 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}_{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.

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

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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

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[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. Scherer, *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).

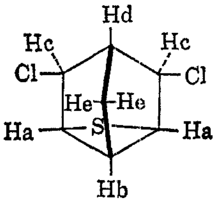
TABLE I
CHEMICAL SHIFTS OF DICHLOROTRICYCLOTHIAOCTANE AND DERIVATIVES[a]

Compd	H_a	H_b	H_c	H_d	H_e
Sulfide 1[b]	3.09	3.76	4.43	...[c]	2.01
Sulfide 1[d]	2.95	3.67	4.25	...[c]	1.93
Sulfoxide 2[d]	3.00	4.26	3.72	2.74	2.04
Sulfoxide 3[d]	3.38	2.67	4.23	2.87	2.15
Sulfone 4[d]	3.57	2.87	3.91	2.65	2.07

[a] Values are in parts per million downfield from tetramethylsilane, recorded on a Varian A-60 spectrophotometer (δ, ±0.01 ppm). [b] Hexachlorobutadiene, 35° (10 mole %). [c] Overlapping with H_a. [d] Hexachlorobutadiene, 100° (10 mole %).

4.5 cps and by H_e and H_d to 2 cps. A pair of doublets at 3.23 ppm arises from H_a, which is split by H_b and H_d but is not coupled to H_c, indicating a dihedral angle of nearly 90° between H_a and H_c and supporting the *exo* position of the chlorine groups. The expanded spectrum in chloroform-d_3 shows the signal for H_e at 2.03 ppm split by H_d and H_c to 2 and 0.5 cps, respectively.

The dipole moment of the dichloro sulfide in benzene at 20° was found to be 0.8 D. The value calculated for **1** is 1.4 D., assuming a group moment of 1.8 D. for each chlorine atom[4] and a moment of 1.6 D. for the group C–S–C.[5] The observed value is sufficiently different from the value of 4.1 D. calculated for the isomer of **1** with *endo* chlorine atoms and from the value of 2.6 D. calculated for an isomer with chlorine atoms in *exo* and *endo* position.



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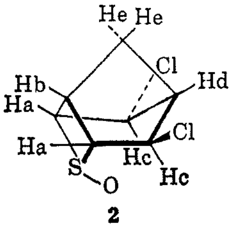

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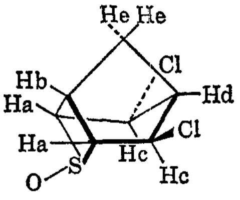

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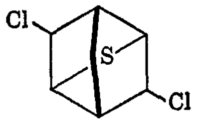

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The thietane ring is indicated by the characteristic ultraviolet absorption of three- and four-membered sulfur heterocyclic rings at 267 mμ (log ϵ 1.0). This value is in good agreement with the absorption of thietane itself, 267 mμ (log ϵ 1.2).[6] The thietane ring is assumed to be nonplanar and of high rigidity. The infrared spectrum of **1** shows a single peak in the region of the methylene bending frequencies at 1449 cm^{-1} (±3 cm^{-1}) and a carbon–sulfur stretching mode at 688 cm^{-1}. The position of the carbon–chlorine stretching frequency at 763 cm^{-1} is in good agreement with the corresponding absorption of *exo*-2-chloronorbornane at 761 cm^{-1}.

The dichloro sulfide was oxidized to the sulfone **4** with hydrogen peroxide in glacial acetic acid. Oxidation of the sulfide with a slight deficiency of hydrogen peroxide in glacial acetic acid leads to the two isomeric sulfoxides **2** and **3** in a proportion of 2:3. The isolation of two sulfoxides excludes the symmetrical structure **5** for the sulfide. In view of the *cis* and *trans* ratio of 2.5:1 obtained by Johnson[7] on oxidation of 4-substituted thianes, the large proportion of the thiane oxide **3** obtained under identical conditions is remarkable. The sulfide **1** represents a 4-substituted thiane in which its substituent, the methylene bridge, locks the thiane ring into a chair conformation. The preponderance of the sulfoxide **3** can be best explained on the basis of a preferred approach of the oxidizing agent to the sulfide from the *exo* side of the tricyclic sulfide which leads to a thiane oxide with an equatorial sulfur–oxygen bond.

The configurations **2** and **3** for the sulfoxides were assigned on the basis of their nmr spectra. In hexachlorobutadiene at 100° the sulfoxide **2** shows a diamagnetic shift of 0.53 ppm for the proton H_c from the position of that proton in the sulfide **1**, whereas the chemical shift of H_c in the isomeric sulfoxide **3** is identical with that of the sulfide (Table I). This deshielding arises from both the anisotropy and the field effect of the sulfoxide group.[8] Only isomer **2** provides a favorable steric arrangement for that effect. The position of the resonance for H_c in the sulfone **4** is between that of the sulfide and the sulfoxide **2**.

The proton H_a in the sulfide is insignificantly different from that proton in the sulfoxide **2**; its chemical shift is 0.43 ppm downfield in the sulfoxide **3** and 0.62 ppm downfield in the sulfone **4**. The bridgehead hydrogen H_d is only little affected by the oxygen atoms on the sulfur, but the resonance position of the bridgehead proton H_b is strongly influenced. The chemical shift for H_b is 0.59 ppm downfield from the sulfide in the sulfoxide **2** and 1.00 and 0.80 ppm upfield in the sulfoxide **3** and sulfone **4**, respectively. The chemical shifts are unchanged at 135° and in 5% dilutions at 100 and 135°.

The identical shielding of both protons H_c in the sulfoxide **2** excludes a structure with *trans* arrangements of the chlorine atoms and also the symmetrical isomer **5**. The marked effect of the sulfoxide oxygen on the chemical shift of the β hydrogen and the smaller magnitude of this effect in the corresponding sulfone reflects the relative ease of the thermal abstraction of the hydrogen in sulfoxides[9] and the more polar character of sulfoxide oxygen compared with sulfone oxygen.[10]

On an Apiezon gas chromatography column at 200° using helium as carrier gas, isomer **2** is completely decomposed but no decomposition of **3** was observed. Complete decomposition occurs if isomer **2** is heated to 190° at a rate of 10°/min. Under the same conditions isomer **3** is recovered unchanged. The thermal decomposition of sulfoxide isomer **2** under conditions which do not affect isomer **3** suggest the closer proximity and increased availability of the *cis* β-hydrogen atoms in that isomer. Only the bridgehead *cis* β hydrogen is available in isomer **3** and its orientation with respect to the sulfoxide oxygen does not allow the formation

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of a five-membered cyclic transition state necessary for that elimination.[9]

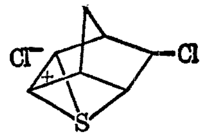
The sulfoxide **3** was converted to its isomer **2** with triethyloxonium fluoroborate in methylene chloride and subsequent treatment of the resulting alkylation product with dilute aqueous sodium hydroxide.[7] Both sulfoxides were oxidized to the identical sulfone **4**. In the infrared, the carbon–chlorine stretching frequency is observed at 777 for sulfoxide **2**, at 756 for sulfoxide **3**, and at 798 cm^{-1} for the sulfone **4**, compared with 763 cm^{-1} for the sulfide **1**.

The dichloro sulfide **1** fails to react with methyl iodide. Desulfurization of **1** with Raney nickel leads to *exo*-2-chloronorbornane, norbornadiene, norbornene, and norbornane. Formation of norbornadiene as the major product can be best accounted for on the basis of a 2,3,5,6-substituted norbornane derivative such as **1** or **5**.

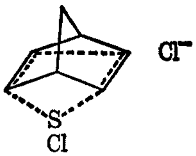
The formation of the product **1** requires an *endo* approach of the sulfur chloride cation to norbornadiene. This is in contrast to the generally accepted rule whereby the first moiety of a reagent adds *exo* to the double bonds of that bicyclic molecule. There is insufficient reason to assume that the *endo* side of norbornadiene offers more steric hinderance than the *exo* side to an approaching electrophile. An increasing number of *endo* additions to norbornadiene are currently reported. Chloroplatinic acid catalyzed addition of trimethylgermane to norbornadiene and hydrosilation of norbornadiene were shown to proceed by initial *endo* attack, suggesting a coordination control of the addition step.[11] Methyl phosphonous dichloride was found to add *endo* to norbornadiene.[12] The addition of sulfur dichloride provides another example of this type of addition.

The assumption of a classical episulfonium intermediate such as **6** is not satisfactory. A mixture of two isomers is expected to result from this intermediate by attack of the chloride ion. Although thermodynamic control may lead to one isomer preferentially, the absent isomer **5** can be assumed to be the thermodynamically more stable because of the better staggering of its bonds and the involvement of the sulfur in the five-membered ring in preference to the four-membered ring.

The postulation of an intermediate ion **7** agrees best with the observed product. The ion would be resonance stabilized and may therefore be the preferred intermediate in the addition.



6



7

The reaction of norbornadiene with sulfur dichloride is the only reported reaction in which predominantly addition to both double bonds occurs. The only similar example of an intramolecular addition of sulfur dichloride is its reaction with 2,3-dimethylbutadiene from which about 1% of 3,4-dichloro-3,4-dimethyldihydrothiophene was obtained.[13]

Experimental Section

Reagents.—Commercial grade norbornadiene was twice distilled through an 18-in. Vigreux column: bp 88–89.5° (760 mm).

Sulfur dichloride was obtained from Hooker Chemical Corp. Chlorine was removed from the sulfur dichloride by distillation under reduced pressure (250 mm) and collecting the crude sulfur chloride in traps at −20°. The product was three times fractionated with 0.1% phosphorous pentachloride in the distillation pot, column, and receiver. The fraction boiling at 59–60° (760 mm) was used for the reactions. The infrared spectrum showed the absence of sulfur monochloride.

Unstabilized sulfur dichloride was fractionated under normal pressure prior to each reaction. Melting points were determined in a Gallenkamp block and are uncorrected.

Dichlorotricyclothiaoctane (1, *exo,exo*-3,5-Dichloro-8-thiatricyclo[2.2.1.1^{2,6}]octane).—A solution of 322 g (3.5 moles) of norbornadiene in hexane and a solution of 360 g (3.5 moles) of sulfur dichloride in hexane (both made up to 2000 ml with hexane) were added dropwise at an equivalent rate to 500 ml of rapidly stirred anhydrous hexane over a period of 12 hr with cooling, maintaining the internal temperature at 0°. The hexane solution was evaporated to 500 ml and cooled to −20° to give 327 g (48%) of a crystalline product, mp 39–42°. The mother liquor was distilled to give another 184 g (27%) of a product, bp 89–91° (0.5 mm), mp 43.5–45°.

Anal. Calcd for $C_7H_8Cl_2S$: C, 43.1; H, 4.13; Cl, 36.36; S, 16.45. Found: C, 42.9; H, 4.04; Cl, 36.26; S, 16.13.

When the reaction was carried out with unstabilized sulfur dichloride, 81% of **1** was obtained.

The infrared spectrum in carbon disulfide shows three absorption bands in the C–H stretching region at 2976, 2950, 2865 cm^{-1} (Beckman IR4); absorption bands at 478, 450, and 328 cm^{-1} characterize the region from 650 to 310 cm^{-1}.

Dichlorotricyclothiaoctane Dioxide (4, *exo,exo*-3,5-Dichloro-8-thiatricyclo[2.2.1.1^{2,6}]octane-8,8-Dioxide.—To a solution of 0.98 g (0.005 mole) of **1** in 25 ml of glacial acetic acid was added 2 g (0.03 mole) of 50% aqueous hydrogen peroxide. The solution was evaporated at room temperature, yield 1.15 g (99%). The product was recrystallized from 12 ml of ethanol: 0.7 g. of needles, mp 139–141.5°. On evaporation of the mother liquor a cubic polymorph was obtained.

Anal. Calcd for $C_7H_8Cl_2O_2S$; C, 37.34; H, 3.58; Cl, 31.51; S, 14.2. Found: C, 37.24; H, 3.44; Cl, 31.22; S, 14.14.

The infrared spectrum in potassium bromide shows characteristic absorption at 1467 cm^{-1} for the CH_2 bending, at 1320, 1309, and 1297 cm^{-1} for the asymmetric sulfone stretching, and strong peaks at 1203, 1186, and 1104 cm^{-1} in the region of the symmetric sulfone stretching frequency.

Dichlorotricyclothiaoctane Monoxide (3, *exo,exo*-3,5-Dichloro-8-thiatricyclo[2.2.1.1^{2,6}]octane 8-Oxide.—To a solution of 9.75 g (0.05 mole) of **1** in 100 ml of glacial acetic acid was added 3.0 g (0.044 mole) of hydrogen peroxide (50% solution in water). The solvent was allowed to evaporate at room temperature and the residue was vacuum dried: yield 10 g (95%), mp 70–110°. Gas chromatographic analysis showed 5% unchanged sulfide and the absence of sulfone; infrared analysis of 2% solutions in carbon disulfide showed 40% of **2** and 60% of **3**. After repeated recrystallization from cyclohexane, the melting point was 130–131°.

Anal. Calcd for $C_7H_8Cl_2OS$: C, 39.8; H, 3.81; Cl, 33.6; S, 15.2. Found: C, 39.7; H, 3.86; Cl, 33.9; S 15.3.

The purity of the isomer was demonstrated by gas chromatographic and infrared analysis, which also identifies this isomer with the major component in the crude sulfoxide mixture. The sulfur–oxygen stretching frequency in carbon disulfide (2%) was found at 1084 and 1070 cm^{-1}.

Dichlorotricyclothiaoctane Monoxide (2, *exo,exo*-3,5-Dichloro-8-thiatricyclo[2.2.1.1.^{2,6}]octane 8-Oxide.—To a solution of 2.1 g (0.01 mole) of **3** in 25 ml of methylene chloride was added 1.7 g (0.009 mole) of triethyloxonium fluoroborate.[14] After 10 hr at room temperature the alkylation product crystallized out, mp 148° dec. A second crop was obtained on evaporation of the mother liquor, yield 2.9 g (93%). To 20 ml of 5% of aqueous sodium hydroxide was added 2 g (0.006 mole) of the alkylation product, the suspension was stirred for 5 min at 40° and filtered

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to give 1.4 g (100%) of **2**. After recrystallization from cyclohexane, the melting point was 131–134°.

Anal. Calcd for $C_7H_8Cl_2OS$: C, 39.8; H, 3.81; Cl, 33.6; S, 15.2. Found: C, 40.1; H, 3.89; Cl, 33.4; S, 15.1.

The purity of **2** was verified by gas chromatographic and infrared analysis which identifies this sulfoxide with the minor component of the crude sulfoxide mixture. The sulfur–oxygen stretching frequency of **2** in carbon disulfide (2%) is at 1057 cm^{-1}.

To a solution of 97 mg (0.0005 mole) of **2** in 2 ml of glacial acetic acid was added 30 mg of 50% of aqueous hydrogen peroxide. After evaporation and sublimation, 80 mg (75%) of **4** was obtained, identified by mixture melting point and infrared absorption. Similarly, 97 mg of **3** in 2 ml of glacial acetic acid gave 73 mg (70%) of **4**, identified by mixture melting point and infrared absorption.

Reaction of 1 with Methyl Iodide.—A solution of 3.9 g (0.02 mole) of the sulfide **1** in 50 ml of methyl iodide was refluxed for 54 hr after which the excess of methyl iodide was allowed to evaporate. The crystalline residue, 3.7 g, mp 42–44°, was identified by its infrared absorption and mixture melting point as unchanged **1**. The crude product was completely soluble in pentane.

Desulfurization of 1.—To a stirred suspension of 172 g of Raney nickel in 250 ml of ethanol was added 25 g (0.128 mole) of **1**. The mixture warmed up immediately and gas chromatographic analysis indicated the absence of starting material 1 hr after the components had been mixed. The Raney nickel was filtered off and washed with ethanol. The combined alcoholic solution was diluted with 200 ml of water and continuously extracted with pentane, and the pentane solution was washed with water to remove ethanol, dried with magnesium sulfate, and distilled to leave 8 g of crude product. Distillation through a 3-in. Vigreux column gave the following fractions at 760 mm: (a) 3 g, bp 94–102°; (b) 2 g, bp 102–110°; (c) 1 g, bp 110–163°. Redistillation of fraction c gave 2-chloronorbornane with bp 162°, mp −5°,[15,16] and an infrared spectrum identical with that reported.[17]

Preparative-scale chromatography and subsequent identification by infrared and nmr spectroscopy characterized the desulfurization components as norbornene, norbornadiene, and norbornane. Approximate gas chromatographic analysis showed 10% chloronorbornane, 50% norbornadiene, 20% norbornene, and 20% norbornane.

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Bridged Ring Compounds. XIII.[1-3] The Reaction of N,N-Dibromobenzenesulfonamide with Bicyclo[2 2.1]heptene, Bicyclo[2.2.2]octene, and *endo*-Bicyclo[2.2.1]-5-heptene-2,3-dicarboxylic Anhydride

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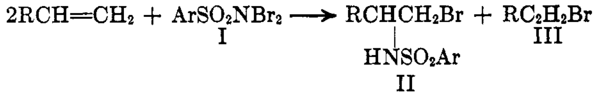
N,N-Dibromobenzenesulfonamide (NNDBS) reacts vigorously with bicyclo[2.2.1]heptene in benzene at room temperature to give 3-bromotricyclo[2.2.1.$0^{2,6}$]heptane, 7-*syn*-bromo-2-exo-benzenesulfonamido- and 7-*anti*-bromo-2-*exo*-benzenesulfonamidobicyclo[2.2.1]heptane, but none of the 2-*exo*-bromo-3-*endo*-benzenesulfonamido isomer could be detected. These results are contrasted with those obtained in the reaction of norbornylene with molecular bromine and the mechanistic implications discussed. Under similar conditions, bicyclo[2.2.2]octene gave 8-*syn*-bromobicyclo[3.2.1]-2-octene, 2-*exo*-bromo-3-*endo*-benzenesulfonamidobicyclo[2.2.2]octane, and 7-*syn*-bromo-2-*exo*-benzenesulfonamidobicyclo[3.2.1]octane. Thus, in the case of bicyclo[2.2.2]octene the halogen-bridged cation is a product forming intermediate, whereas in the case of norbornylene it is not. *endo*-Bicyclo[2.2.1]-5-heptene-2,3-dicarboxylic anhydride was found to react with NNDBS to give 5-*exo*-bromo-6-*exo*-benzenesulfonamido-2,3-*endo*-*cis*-dicarboxybicyclo[2.2.1]heptane anhydride. The solvolysis of 7-*anti*-bromo-2-*exo*-benzenesulfonamidobicyclo[2.2.1]heptane was found to yield the rearranged product 7-*syn*-benzenesulfonamido-2-*endo*-hydroxybicyclo[2.2.1]heptane and the fragmented product 3-cyclopentenylacetaldehyde, whereas the isomeric 7-*syn*-bromo-2-*exo*-benzenesulfonamido derivative was unchanged on solvolysis.

Kharasch and Priestley[6] observed that N,N-dibromoarenesulfonamides (I) added to unsymmetrical alkenes to yield products in which the bromine atom took the position expected in a process involving positive bromine, as in II. The second bromine atom of the N,N-dibromoarenesulfonamide appeared as a vinyl bromide, III.



$$\underset{}{2RCH{=}CH_2} + \underset{\text{I}}{ArSO_2NBr_2} \longrightarrow \underset{\text{II}}{\underset{\substack{|\\ HNSO_2Ar}}{RCHCH_2Br}} + \underset{\text{III}}{RC_2H_2Br}$$

R = alkyl or aryl group

Since a great deal of information on ionic additions to bicyclo[2.2.1]heptene derivatives and to bicyclo[2.2.2]octene has been recorded,[7] we were interested in extending the reaction of N,N-dibromobenzenesulfonamide (NNDBS) to these alkenes. We were particularly interested in comparing the results obtained in this case with the results obtained in the addition of other positive halogen compounds to such compounds.

(1) Part XII: A. C. Oehlschlager and L. H. Zalkow, *Chem. Commun.*, 5 (1966).

(2) For a preliminary account of a part of this work, see L. H. Zalkow and A. C. Oehlschlager, *J. Am. Chem. Soc.*, **86**, 4208 (1964), and ref 3.

(3) A. C. Oehlschlager and L. H. Zalkow, *Tetrahedron Letters*, 2663 (1964).

(4) National Defense Education Act Fellow, 1962–1965. Taken from the Ph.D. Thesis of A. C. Oelschlager, submitted April 1965, Oklahoma State University.

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(6) M. S. Kharasch and H. M. Priestley, *J. Am. Chem. Soc.*, **61**, 3425 (1939).

(7) J. A. Berson in "Molecular Rearrangements," Part One, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, and references therein.