THE REACTION OF SULFUR DICHLORIDE WITH *cis,cis*-1,5-CYCLOOCTADIENE

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ABSTRACT

Transannular additions of sulfur dichloride to various cyclic and bicyclic di- and poly-olefins have been disclosed recently. Our observations on the reaction product from *cis,cis*-cyclooctadiene are reported inasmuch as they supplement the previous findings.

INTRODUCTION

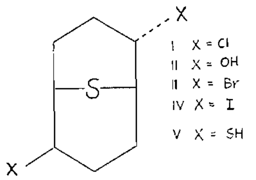
Attempts to synthesize novel sulfur-containing heterocyclic compounds have led us to the observation of the transannular addition of sulfur dichloride to bicycloheptadiene (2). This addition reaction of sulfur dichloride provides a convenient synthesis for a large number of novel cyclic β,β'-dichlorosulfides (1–4). The versatility of that reaction and unusual features of the reaction products were reported recently (4).

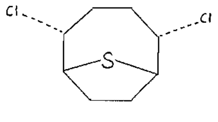
RESULTS AND DISCUSSION

One of the first questions in the structural evaluation of the products from the intramolecular addition reaction of a diolefin with sulfur dichloride is to ascertain which of the possible ring systems is formed. For this, a simple approach was considered, which is of general validity for the resulting ring systems and is of particular value if the reaction products cannot be converted into a known sulfide.

Addition to a cyclic diolefin can lead to a dichlorosulfide with both chlorine atoms either on one side (I*a*) or on both sides (I) of the sulfur atom. Two sulfoxides should be obtained in the first case, but only one in the latter, provided a symmetric diolefin such as *cis,cis*-cyclooctadiene-1,5 is considered. The sulfoxides are interconvertible with triethyloxonium fluoroborate in the first case, but no isomer is obtained in the second case. In the nuclear magnetic resonance spectrum, shielding by the sulfoxide oxygen affects either both CHCl groups or none in the first type, but only one CHCl group should be affected in the second. An example of the first type is the reaction product from bicycloheptadiene (2). The product obtained from cyclooctadiene-1,5, the structure of which was demonstrated by a sequence of unambiguous reactions (1, 3), provides an example of the second type.

The nuclear magnetic resonance spectrum of I at 70 °C on a Varian A-60 spectrophotometer shows a multiplet for the —CHCl— proton at 4.62 p.p.m., whereas its sulfone IX (1) exhibits that proton at 4.43 p.p.m. In contrast, the nuclear magnetic resonance spectrum of its sulfoxide VIII (1) at 70 °C in hexachlorobutadiene shows two resonances for the —CHCl— groups, of equal intensity, at 4.63 p.p.m. and 4.06 p.p.m., respectively. The chemical shifts are independent of temperature (20 and 150 °C) and remain unchanged on dilution (5 and 10 mole %). The magnitude of the observed shielding effect of the sulfoxide oxygen on the —CHCl— group ($\Delta = 0.57$ p.p.m.) is in very good agreement with that effect observed on *exo,exo*-4,8-dichloro-2-thiatricyclo[3.2.1.0^{3,7}]octane 2-oxide (VII) ($\Delta = 0.53$ p.p.m.) (2), suggesting the similar proximity of the sulfoxide oxygen to the hydrogen of the —CHCl— group in both ring systems, and therefore identical configuration of the chlorine atoms with respect to the sulfur atom and identical conformation. In contrast, in the hypothetical sulfoxides of I*a*, the proton of both —CHCl— groups is symmetrically oriented with respect to the sulfoxide oxygen in all conformations, provided the chlorine groups are *cis* to each other. The significant shielding of only one —CHCl— group cannot therefore be explained on the basis of the [4.2.1] ring system.





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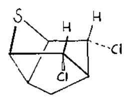

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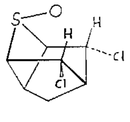

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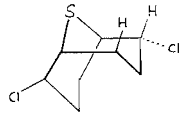

XI

As expected, attempted inversion of the sulfoxide to an isomer by its reaction with triethyloxonium fluoroborate failed (5). The successful inversion of a tricyclic β,β-dichlorosulfoxide under identical conditions was reported previously (2).

Although a dipole moment determination is not expected to distinguish between the [4.2.1] and [3.3.1] ring systems, conclusions about the conformation and configuration of the dichlorosulfide can be drawn from the observed moment if the [3.3.1] system is accepted. The twin-chair conformation for I has been suggested on the basis of the coupling constants between the proton of the —CHCl— group and the adjacent methylenic protons (3), and on the basis of the 'abnormal' infrared band at 1 485 ± 5 cm^{-1} (1) which results from non-bonding interaction between the two methylenic groups in that conformation. This conclusion is supported by the observed dipole moment.

A moment of 0.85 D for I in benzene at 20 °C is very close to the value of 0.8 D for VI (1). The thiane ring in the latter compound has a rigid chair conformation, with both chlorine atoms equatorial (2). Inspection of molecular models of I and VI shows that the resultant moment of both chlorine groups forms an angle of 180° with the moment angle of C—S—C in the twin-chair conformation XI and in the rigid system VI. The observed moment is therefore best explained by the assumption of a twin-chair conformation for I. The moment is lower than calculated (1.4 D), assuming group moments of 1.8 D for C—Cl (6) and 1.6 D for C—S—C (7). Moments of 1.6 D and 1.9 D are calculated for the chair–boat and boat–boat conformations of I, respectively. For a configuration with the chlorine groups *trans* to each other, a moment of 2.6 D is calculated for the chair–boat conformation, 2.1 D for the chair–chair conformation, and 1.3 D for the boat–boat conformation. The isomer with both chlorine atoms *cis* to each other and *cis* with respect to the sulfur atom would show moments of 3.7 D for the chair–chair, 3.8 D for the chair–boat, and 1.6 D for the boat–boat conformations.

The dichlorosulfide I was shown to exhibit the characteristic reactivity of β,β'-dichlorosulfides towards nucleophilic substitution (1). The diol II can be obtained in polymorphic forms with melting points from 188 to 256 °C. The low-melting polymorph melts with decomposition by elimination of water. A sample melting close to that reported by Weil (1) was obtained by hydrolysis with aqueous sodium carbonate. Recrystallization of the low- and high-melting species from toluene did not affect their melting points. Whereas the high-melting polymorph is unaffected by crystallization from methanol or water, the melting point of the low-melting polymorph is increased to 248–250 °C on a single crystallization from methanol and to 215–220 °C on crystallization from water. Both diols show identical infrared absorption in potassium bromide, although in Nujol small differences in the relative intensities of several peaks appear, particularly those of the three unidentified peaks at 865, 880, and 895 cm^{-1}. Both the higher and lower melting polymorphs show a single peak for the OH stretching frequency at 3 443 ± 2 cm^{-1} in dioxane and at 3 620 ± 2 cm^{-1} in carbon tetrachloride. The diol was oxidized to its sulfone X with hydrogen peroxide in glacial acetic acid. The nuclear magnetic resonance spectrum of the sulfone X shows a single resonance at 4.45 p.p.m. in pyridine for the proton alpha to the hydroxy group, which is 0.13 p.p.m. downfield from the resonance of that proton in the diol II.

The dimercaptan V was obtained from the dichlorosulfide I via its thiouronium salt in a yield of 41%.

Attempts to isolate the isomeric [4.2.1] ring system were unsuccessful. The absence of the isomeric dichlorosulfide I*a* in the reaction product of sulfur dichloride and cyclooctadiene was indicated by gas chromatographic analysis, which shows a single peak for I. Also, no evidence for the [4.2.1] ring system was found in products resulting from heterolytic substitution reactions in which isomerization via an intermediate episulfonium ion was expected (8). The diol II was recovered from its solution in 97% sulfuric acid in a yield of 68% by neutralization with aqueous sodium bicarbonate. Treatment of II with concentrated hydrochloric acid leads to I in a yield of 97%. The crude product shows a melting point of 99–101 °C, compared with 101–102 °C for I. Similarly, the bromide III and the iodide IV (1) were obtained from II in yields of 80 and 64%, respectively, by use of the corresponding acids. The iodide IV is identical with the product obtained from the chloride I with sodium iodide in acetone. Hydrolysis of the iodide IV with aqueous sodium bicarbonate leads to II in a yield of 60%.

The participation of the free electrons on sulfur in the stabilization of the carbonium ion is demonstrated by comparison of the reactivity in nucleophilic reactions of sulfide versus sulfoxide and sulfone. In contrast to the dihydroxysulfide II, the dihydroxysulfone X can be recovered unchanged from its solution in concentrated hydrochloric acid. Also, the dichlorosulfoxide VIII is not hydrolyzed in hot aqueous sodium carbonate, although rapid hydrolysis of I to II proceeds under these conditions.

The absence of the [4.2.1] ring system is surprising if an episulfonium ion is involved in the addition of sulfur dichloride to the diene and in substitution reactions. Both the [4.2.1] and [3.3.1] ring systems of bicyclononane were isolated in the acetolysis of 4-cyclooctene-1-methylbrosylate (9), and a bridged intermediate was suggested on the basis of the observed products. Analogous to the reaction of sulfur dichloride with bicycloheptadiene, an *endo* approach of the chlorosulfenium ion (10) is suggested in the addition step. The flexibility of the bicyclic ring system obtained from cyclooctadiene allows the formation of a configuration and conformation of the most favorable staggering of the carbon–hydrogen bonds, which could be the deciding factor in the observed formation of the [3.3.1] ring system in preference to the [4.2.1] ring system, and which distinguishes between the reaction of sulfur dichloride with cyclooctadiene and that with bicycloheptadiene.

EXPERIMENTAL

The dielectric constants were determined with the instruments described earlier (11). The melting points were determined in a Hallenkamp block and are uncorrected. Gas chromatographic analysis was carried out on a Perkin–Elmer 800 chromatograph at 175 °C, with Apiezon as the stationary phase and helium as the carrier gas.

2,6-Dichloro-9-thiabicyclo[3.3.1]nonane (I)

A suspension of 1.75 g (0.01 mole) of the diol II (m.p. 188 °C) in 50 ml of concentrated hydrochloric acid was stirred for 8 h at room temperature, and the product was filtered off and air-dried to give 2.05 g (97%) of I, m.p. 99–101 °C. The product was identified as I by mixed melting point with a sample obtained from the reaction of cyclooctadiene-1,5 and sulfur dichloride, and by its infrared absorption in potassium bromide. Gas chromatographic analysis of that product and a crude reaction product of sulfur dichloride and cyclooctadiene showed a single peak for I.

This agrees with the result of the thin-layer chromatography reported by Corey and Block (3).

9-Thiabicyclo[3.3.1]nonane-2,6-diol (II)

(*a*) To a refluxing solution of 6.2 g (0.05 mole) of sodium carbonate in 100 ml of water was added 10.5 g (0.05 mole) of I, with high-speed stirring, over a period of 10 min. A clear solution formed, from which colorless crystals separated when it was cooled, yield 7 g (80%), m.p. 189 °C (decomp.). The aqueous solution was continuously extracted with diethyl ether to give another 1.1 g (13%) of the dihydroxy compound, m.p. 205 °C (decomp.).

Anal. Calcd. for $C_8H_{14}O_2S$: C, 55.13; H, 8.10; S, 18.40. Found (for the fraction with m.p. 189 °C): C, 55.36; H, 8.02; S, 18.52.

(*b*) Hydrolysis under the same conditions in a repeat experiment led, with a yield of 87%, to a diol having m.p. 252–253 °C.

Anal. Found: C, 55.20; H, 8.15; S, 18.3.

(*c*) To a solution of 5.3 g (0.025 mole) of I in 100 ml of tetrahydrofuran were added 10 ml of water and 2 g of sodium bicarbonate. The suspension was refluxed, with stirring, for 64 h, and evaporated to dryness on a rotary evaporator; the residue was ground and exhaustively extracted with 400 ml of benzene. After evaporation of the benzene solutions, 1.6 g of II was obtained, m.p. 188 °C (decomp.). The benzene-insoluble residue was extracted three times with 50 ml of acetone. On evaporation, another 2.35 g of II was obtained, m.p. 254–256 °C. When a solution of the high-melting product in boiling methanol or water was allowed to evaporate, the melting point of the recovered material was unchanged. Similar solutions of the low-melting material led to a product with a melting point of 248–250 °C after recovery from methanol, and 215–220 °C after recovery from water.

(*d*) A suspension of 12 g (0.03 mole) of IV in 100 ml of water containing 16.8 g (0.2 mole) of sodium bicarbonate was stirred under reflux for 10 min. The solution was filtered to remove traces of undissolved material, and continuously extracted with diethyl ether. The ether solution was dried with magnesium sulfate and evaporated to give 3.4 g (65%) of II, m.p. 255–257 °C, shown by its infrared absorption in potassium bromide and by mixed melting point to be identical with the product described under method *c*.

II (2 g) was dissolved in 10 g of 97% sulfuric acid at room temperature. The clear, colorless solution was allowed to drop into 50 ml of a saturated sodium bicarbonate solution with rapid stirring, the internal temperature being kept at 5–10 °C. The resulting suspension was continuously extracted with diethyl ether, and the extract was dried and evaporated to give 1.6 g (80%) of a product which, on exhaustive sublimation, yielded 1.28 g (64%) of diol, m.p. 196–203 °C (decomp.). The diol was identified as II by its infrared spectrum in potassium bromide and Nujol.

2,6-Dibromo-9-thiabicyclo[3.3.1]nonane (III) from II with Hydrobromic Acid

In 50 ml of fuming hydrobromic acid was dissolved 3.5 g (0.02 mole) of II (m.p. 255–257 °C). The suspension was stirred for 2 h and filtered, and the residue was washed with water and dried over calcium chloride to yield 5.8 g (97%) of product, m.p. 124 °C (decomp.). By sublimation, 1.2 g of polymeric material was separated. An analytical sample was obtained by recrystallization of 2.5 g from 25 ml of hexane, m.p. 136–137.5 °C.

Anal. Calcd. for $C_8H_{12}SBr_2$: C, 32.02; H, 4.03; Br, 53.27; S, 10.68. Found: C, 32.21; H, 3.89; Br, 53.05; S, 10.60.

2,6-Diiodo-9-thiabicyclo[3.3.1]nonane (IV) from II with Hydriodic Acid

Into 50 ml of 47% hydriodic acid was stirred 3.5 g (0.02 mole) of II (m.p. 255–257 °C). After the solution was stirred for 2 h at room temperature, the colorless product was filtered off, washed with water, and dried over calcium chloride to yield 7.8 g (99%), m.p. 128 °C (decomp.). Sublimation (an initial colored fraction was discarded) produced a colorless sample, yield 5 g (64%), m.p. 143–145 °C.

The product was shown to be identical by mixed melting point and infrared absorption with the product obtained from I with potassium iodide (1).

9-Thiabicyclo[3.3.1]nonane-2,6-thiouronium Chloride

To a solution of 4.22 g (0.02 mole) of I in 100 ml of ethanol was added 6.1 g (0.08 mole) of thiourea; the suspension was refluxed for 14 h, allowed to cool to room temperature, and filtered; the residue was washed with ethanol and air-dried to give 4.8 g (61%), m.p. 232 °C (decomp.) (A). The solvent was evaporated from the combined ethanol solutions, and the crystalline residue was extracted with 50 ml of tetrahydrofuran and 50 ml of hot ethyl acetate to leave another 2.4 g (30%) of product, m.p. 200–212 °C (decomp.) (B).

Anal. Calcd. for $C_{10}H_{20}S_2N_4Cl_2$: H, 5.51; S, 26.48. Found: H, 5.30; S, 26.83.

2,6-Dimercapto-9-thiabicyclo[3.3.1]nonane (V)

To a solution of 5.4 g (0.015 mole) of the thiouronium salt A in 25 ml of water was added 25 ml of concentrated ammonium hydroxide. Traces of insoluble material were filtered off and the filtrate was acidified with dilute hydrochloric acid, with cooling, the internal temperature being kept between +5 and +10 °C. The crystalline product was separated with 20 ml of methylene chloride, and the extract was washed with water, dried with magnesium sulfate, and evaporated to give 2.5 g of a crystalline product, m.p. 25–43 °C. Sublimation gave 1.5 g (41%) of V, m.p. 44–46 °C. An analytical sample was obtained by drying over paraffin chips and repeated sublimation.

Anal. Calcd. for $C_8H_{14}S_3$: C, 46.55; H, 6.84; S, 46.61. Found: C, 46.84; H, 6.88; S, 46.86.

Attempted Hydrolysis of VIII

A suspension of 2.27 g (0.01 mole) of VIII in a solution of 10 g of sodium carbonate in 50 ml of water was refluxed, with high-speed stirring, for 30 min. After the solution was cooled, 2.05 g of VIII was recovered, m.p. 121.5–122.5 °C, identified as VIII by mixed melting point and by its infrared absorption.

Attempted Conversion of VIII

To a solution of 3 g (0.013 mole) of VIII in 50 ml of methylene chloride was added 2.85 g (1.5 moles) of triethyloxonium fluoroborate (12). After the solution had stood for 8 h, 1.5 g (26%) of a crystalline adduct was filtered off, m.p. 163 °C (decomp.). On complete evaporation, another 3.2 g of product was obtained.

Anal. Calcd. for $C_{10}H_{17}Cl_2F_4OS$: C, 35.0; H, 5.00. Found: C, 34.8; H, 5.07.

To a solution of 0.2 g of sodium hydroxide (0.05 mole) in 20 ml of water was added 1.1 g (0.0032 mole) of the adduct. After the solution was stirred at 30 °C for 15 min, the crystalline product was filtered off, washed with water, and air-dried to give 0.7 g (96%) of VIII, m.p. 122.5–123.5 °C. The product was identified by mixed melting point and by its infrared and nuclear magnetic resonance spectra in carbon tetrachloride.

2,6-Dihydroxy-9-thiabicyclo[3.3.1]nonane 9,9-Dioxide (X)

To a solution of 17.5 g (0.1 mole) of II (m.p. 255–257 °C) in 500 ml of glacial acetic acid was added 17 g of 50% aqueous hydrogen peroxide. The solution was stirred at room temperature for 48 h and then allowed to evaporate to dryness to give 20 g (100%) of crude X, m.p. 160–190 °C (decomp.); 15 g was recrystallized from 80 ml of dioxane to give a first fraction of 4 g. A second fraction of 4 g was obtained by reducing the volume of the dioxane solution to 40 ml. An analytical sample was obtained by a second recrystallization from dioxane and drying at 60 °C and 0.1 mm for 54 h. The compound is discolored when heated above 250 °C.

Anal. Calcd. for $C_8H_{14}SO_2$: C, 46.57; H, 6.83; S, 15.54. Found: C, 46.87; H, 6.79; S, 15.53.

The dihydroxysulfone X is recovered unchanged from its solution in concentrated hydrochloric acid (0.5 g in 5 ml) after evaporation of the solution.

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