Spatial Proximity by Electrophilic Addition to the Tricyclo[4.2.2.0^{2,5}]deca-3,7-diene System. Structures and Some Comments on the Feature of π Participation

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Reactions of tricyclo[4.2.2.0^{2,5}]deca-3,7-diene derivatives with halogens and sulfur-containing electrophiles have been examined. The transannular halo lactone products were fully identified by x-ray crystallographic techniques. Mechanisms for their addition reactions are also discussed.

Rigid molecules containing two isolated double bonds in spatial proximity are known to undergo facile chemical reaction involving π participation between these two double bonds.[2] The transannular reaction of these molecules has provided a simple synthetic route to new highly strained polycyclic hydrocarbons and information about the participation between these two double bonds.

In the first part of this series,[3] it was reported that the reaction of tricyclo[4.2.2.0^{2,5}]deca-3,7-diene derivatives with electrophiles such as bromine and iodine chloride proceeds by transannular cross bonding of the proximal π bonds. In contrast with our results, Farnum et al.[4] reported that 1,2-addition of bromine to the cyclobutene moiety of this system occurred in addition to the transannular reaction. On the other hand, the preferential cross bridging was explained based on the orbital mixing of the HOMO and LUMO of the double bond system with the LUMO of the electrophiles by Inagaki et al.[5]

To provide some additional data for understanding these reaction modes, we have reexamined the reactions of dimethyl tricyclo[4.2.2.0^{2,5}]deca-3,7-diene-9,10-dicarboxylate (**1**) with bromine and iodine. Moreover, the structure of the products has been determined by x-ray crystallographic techniques. We have also investigated the reaction of **1** with sulfur-containing electrophiles.

Results

Addition of Halogen. Reaction of **1** with bromine in acetic acid at room temperature gave transannular bromo lactone compound **2.** Similar bromination at 80 °C gave not only **2a** (63%) but also **3a** (38%). In the case of **1** with bromine in chloroform at room temperature, **2a** was obtained. In contrast, a similar reaction at refluxing temperature gave **2a** (28%) and **3a** (68%). In addition, reaction of **1** with bromine in carbon tetrachloride at room temperature gave **2a** (84%) and **3a** (14%). Similar reaction at refluxing temperature gave only **3a** (93%). These results of the bromination of **1** under various conditions are summarized in Table I and Scheme I.

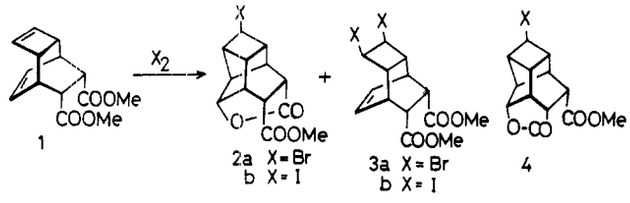
Previously, structure elucidation of the halogenated compounds was accomplished by their spectral analyses and chemical transformations. Compound **2a** was assigned as a cross-type compound with the five-membered lactone moiety **4,** since **2a** shows carbonyl absorption at 1770 and 1735 cm^{-1}. In spite of the characteristic carbonyl absorption of the five-membered lactone moiety,[6] it was proved that **2a** has a six-membered ring lactone moiety by an x-ray crystallographic technique as described below.

Compound **3a** shows carbonyl absorption at 1740 cm^{-1}. Elemental analysis shows the product to be $C_{14}H_{16}O_4Br_2$. The NMR spectrum of **3a** exhibits equivalent hydrogens α to the bromine at δ 4.22 and two equivalent vinyl hydrogens as a clean triplet centered at δ 6.48.[5] On the basis of the above data, the structure of **3a** was established as a cis dibromide as shown in Scheme I. Another support for the assignment has been furnished by x-ray studies as described below.

Owing to the difficulty of iodination of **1** with iodine and potassium iodide in aqueous solvent, iodine chloride and iodine azide were used for these compounds.[3,7] For comparison with the bromination of **1,** reaction of **1** with iodine in organic solvents was investigated. Reaction of **1** with iodine in benzene at room temperature gave **2b** (94%). Treatment of **2b** with n-Bu_3SnH gave deiodinated compound **5,** which was also given both by reduction of **2a** with n-Bu_3SnH and by acetolysis of tricyclo[4.2.2.0^{2,5}]deca-7-enyl-3-tosylate (**6**).[8] These results indicate that the structures of **2b** and **5** have the same skeleton as **2a,** a transannular cross-bonding compound with the six-membered lactone moiety. Reaction of **1** with iodine in refluxing cyclohexane gave **3b.** Compound **3b** was easily assigned as a cis diiodide on the basis of its IR spectrum, NMR spectrum, and elemental analysis.

In connection with the halogenation of **1,** we have previously reported that acid-catalyzed epoxide cleavage of 3,4-epoxytricyclo[4.2.2.0^{2,5}]deca-7-ene (**7**) gave **8a.**[9] Although compound **8a** had been assigned as a five-membered lactone on the basis of its IR spectrum, compound **8a** was proved to be a six-membered lactone by its correlation with the bromo lactone compound **2a;** acetolysis of **8b** gave **9** and **10** in a 1:1 ratio.[10] The reaction of **2a** with equimolar silver acetate in acetic acid at reflux temperature gave **9** and **10.** Furthermore, from the reaction of **2b** with silver acetate, chemical transformations

Scheme I



Scheme II

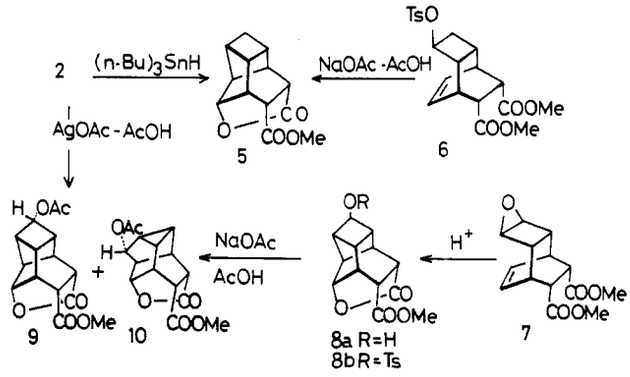


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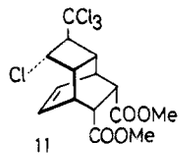
Table I. Reaction of 1 to Halogen under Various Conditions

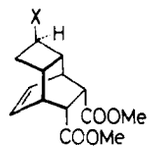
Reagents	Solvent	Temp, °C	Reaction products (yield, %)
Br_2	AcOH	20	**2a** (quant); **3a**
Br_2	AcOH	80	**2a** (63); **3a** (37)
Br_2	$CHCl_3$	20	**2a** (quant); **3a**
Br_2	$CHCl_3$	61	**2a** (28); **3a** (68)
Br_2	CCl_4	20	**2a** (84); **3a** (14)
Br_2	CCl_4	77	**2a; 3a** (93)
I_2	Benzene	20	**2b;** (94); **3b**
I_2	Cyclohexane	81	**2b; 3b** (44)

as previously reported[10] confirmed that **8a,b, 9,** and **10** have exactly a six-membered lactone moiety. These results are summarized in Scheme II.

Addition of Free Radicals. Fray et al.[11] reported that the free-radical addition of bromotrichloromethane and carbon tetrachloride to the 1:1 adduct of cyclooctatetraene and maleic anhydride results in trans addition to the cyclobutene double bond. In accordance with these results, reaction of **1** with carbon tetrachloride in the presence of AIBN gave **11,** a trans



11



12 X = Br
13 X = -S-C6H4-Cl
14 X = -SO-C6H4-Cl

adduct to the cyclobutene double bond. Reaction of **1** with hydrogen bromide in the presence of AIBN at 80 °C gave **12.** The configuration of the bromine moiety in **12** was determined to be exo on the basis of a chemical shift of a proton adjacent to bromine (multiple centered at δ 4.0). Similar reaction in the absence of a radical initiator resulted in the recovery of **1.** In order to compare these results with a reaction under milder conditions, we carried out the addition of *p*-chlorobenzenethiol to **1** in a cyclohexane solution with an access of oxygen at room temperature, which afforded **13** and **14,** and none of the transannular products by free-radical addition were detected.[12]

Additions of Methanesulfenyl Chloride and Thiocyanogen. Reaction of methanesulfenyl chloride with a methylene chloride solution of the diester **1** at −30 °C gave the trans adduct **15** in 85% yield. The NMR spectrum of **15** exhibits a hydrogen adjacent to the chlorine as a double doublet centered at δ 4.35. This chemical shift corresponded to that of the trans adduct of benzenesulfenyl chloride to the diester **1** (δ 4.42).[13] Similar treatment of **1** with thiocyanogen in acetic acid at room temperature in the presence of a radical inhibitor gave **16** (44%) and **17** (27%). The IR spectrum of **16** shows thiocyanate absorption at 2160 cm^{-1} together with carbonyl absorptions at 1780 and 1755 cm^{-1}. The NMR spectrum of **16** exhibits a methine proton signal adjacent to a lactone moiety at δ 4.85 (dd), one methyl group at δ 3.72, and a methine proton signal adjacent to a thiocyanate at δ 3.60 (s), but no olefinic proton signals were observed. The final structural determination of the compound was accomplished by chemical transformation. Reduction of **16** with sodium borohydride and nickel chloride[14] gave **5.** The IR spectrum of **17** shows thiocyanate absorption at 2160 cm^{-1}. The NMR spectrum of **17** exhibits two olefinic proton signals as a multiplet centered at δ 6.50, two methine proton signals adjacent to thiocyanate at δ 4.25 and 3.60, and two methyl groups at δ 3.60. The presence of nonequivalent vinyl hydrogens and methine proton signals adjacent to the thiocyanate suggested **17** to be trans dithiocyanate. These results are summarized in Scheme III.

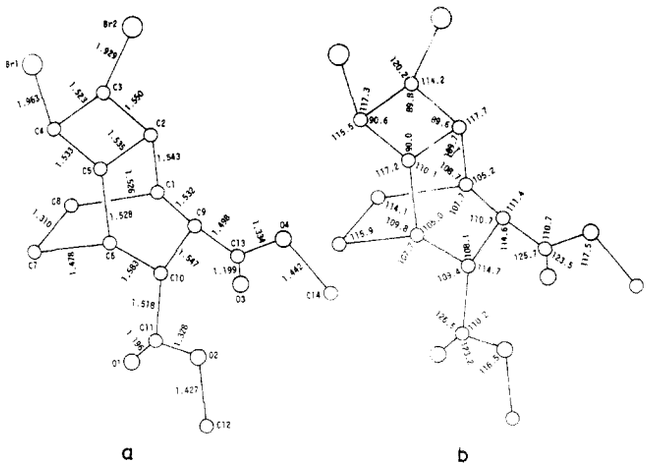
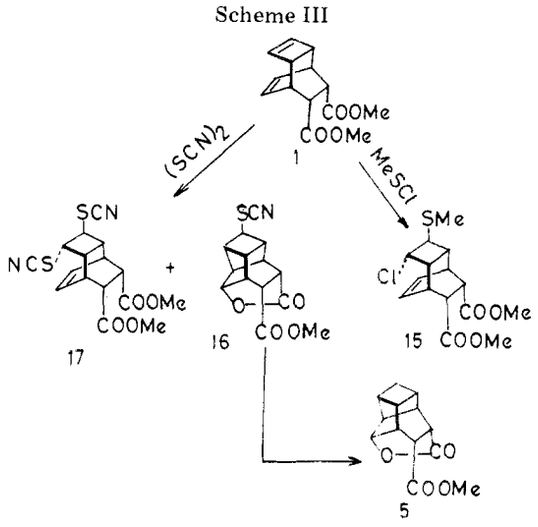


Figure 1. (a) Bond Lengths (Å) of **3a.** (b) Bond angles (deg) of **3a.**

Scheme III



Description of Structures. Compound 3a. The atomic parameters are given in Tables II and III. The bond lengths and angles are shown in Figure 1, together with the atom numbering system. The estimated standard deviations of the bond lengths are 0.011–0.016 Å, while those of the bond angles are 0.7–1.0°. The stereoscopic view obtained by the program ORTEP[15] is shown in Figure 2. The four-membered ring is planar. All four bond lengths and angles in the ring are nearly equivalent. The C(7)–C(8) double bond length is slightly shorter than the usual value. The distance of the nonbonded contact between C(1) and C(6) is 2.580 Å. The molecule consists of six planar fragments. They are a four-membered ring, three four-atom systems each containing both C(1) and C(6), and two ester groups. The planarity is excellent in each group. The equations of the least-squares planes are listed in Table IV. The framework of tricyclo[4.2.2.0^{2,5}]deca-3,7-diene has a pseudomirror plane bisecting the bonds of C(3)–C(4), C(2)–C(5), C(7)–C(8), and C(9)–C(10). The view of the molecule projected along the C(1) to C(6) direction on the dihedral angles between the three planes of the four-atom systems. Among the three dihedral angles, both the ones between the planes C(1) and C(2) and between C(2) and C(3) are enlarged to decrease the steric repulsions between the C(7)–C(8) group and the four-membered ring and those between the C(7)–C(8) and the two C=O groups in the ester groups. The distances of the nonbonded C(7)···C(4) and C(8)···C(3) contacts are 2.950 and 2.976 Å, respectively. Taking this molecular skeleton into consideration, it is clear that only an exo-cis adduct of halo-

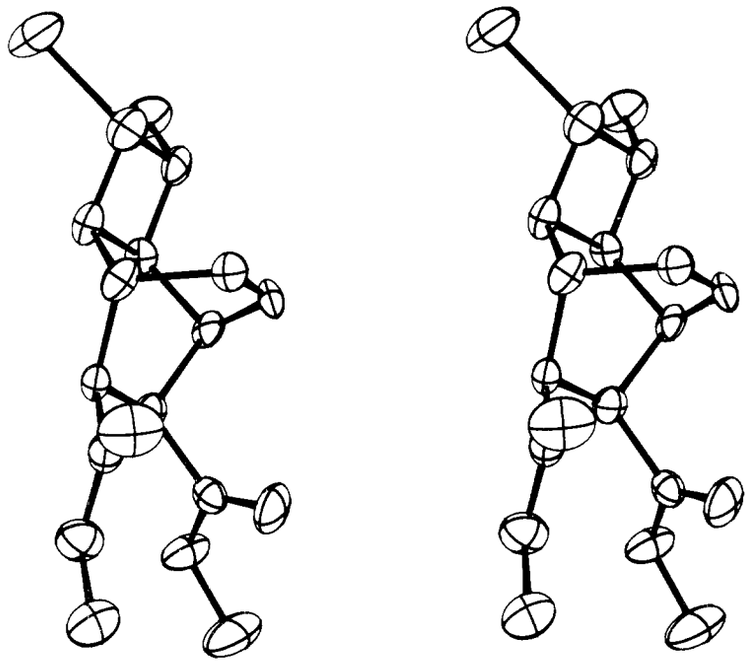


Figure 2. Stereodrawing of **3a** with thermal ellipsoids drawn to enclose 50% probability.

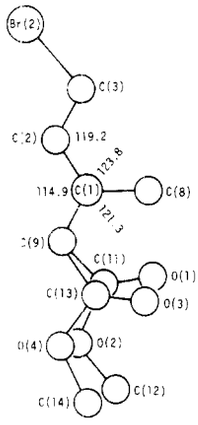


Figure 3. A view of **3a** projected along the C(1) to C(6) direction.

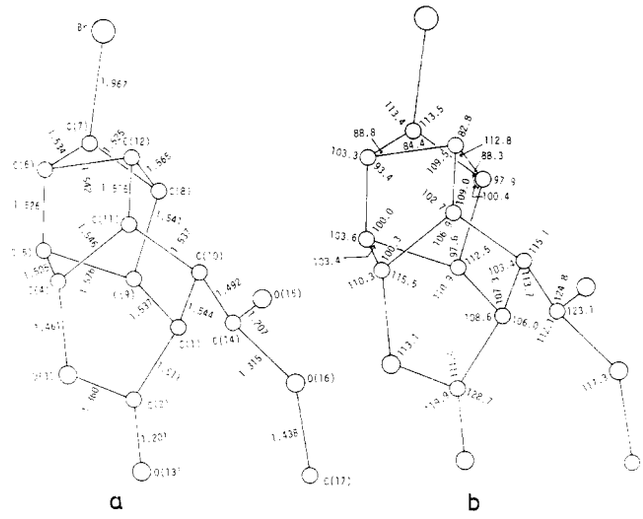


Figure 4. (a) Bond lengths (Å) of **2a.** (b) Bond angles (deg) of **2a.**

gens can be obtained to avoid the steric repulsion between halogens and the C(7)–C(8) bond. The torsion angle Br(1)–C(4)–C(3)–Br(2) is 0.3°. The carbonyl oxygen atoms of the ester groups are the nearest atoms to the C(7)–C(8) double bond, and the disposition is in favor with the lactone ring formation. The distances of the nonbonded contacts are: C(7)···O(1), 3.028; C(7)···O(3), 3.955; C(8)···O(1), 3.480; and C(8)···O(3), 3.117 Å. The dihedral angles between the plane C(3) and the ester groups are 88.7° between C(3) and C(6), and 50.6° between C(3) and C(5).

Compound 2a. The atomic parameters are given in Tables V and VI. The bond lengths and angles are shown in Figure 4, together with the atom numbering system. The estimated standard deviations of the bond lengths are 0.009–0.014 Å, while those of the bond angles are 0.6–0.9°. The stereoscopic view is shown in Figure 5. This molecule is expected to have large strains imposed by a cage formation. The strains are mainly found on the distortions of the bond angles from the ideal tetrahedral value. Each atom in the fused ring system has one or two small bond angles, while most of the bond lengths are normal. The puckering of the four-membered ring is severe; the dihedral angles in the ring are 138.8° between the C(6)C(7)C(8) plane and the C(6)C(8)C(12) plane and 136.6° between C(6)C(7)C(12) and C(7)C(8)C(12). The values in this ring are close to the value of 135° found in photooxidized dimer of plastoquinone-1.[16] Both of the two five-membered rings are in the so-called "envelope" form; C(7) is puckered out in the C(5)C(6)C(7)C(8)C(9) ring, and C(5) is puckered out in the C(4)C(5)C(6)C(11)C(12) ring. Most of the bond angles in the six-membered lactone rings are normal. Each of the four-atom systems, C(1)C(2)O(3)C(4), C(1)-C(9)C(5)C(4), and C(1)C(10)C(11)C(4), is nearly planar. Fairly short nonbonded contacts are found between C(2) and C(14), 2.800 Å, and between C(11) and O(15), 2.878 Å.

Discussion

With respect to halogenation, it is very interesting that 1,2-addition occurs only in the sterically unhindered olefins on the cyclobutene moiety by a cis fashion. It is apparent that the reaction of **1** with halogen is dependent on reaction temperatures and solvents. At elevated reaction temperature, 1,2-addition was superior to transannular reaction, although the effect of temperature was small in a protic solvent such as acetic acid. A convenient explanation of these facts and that of the regiospecific reaction, predominant cis addition, and

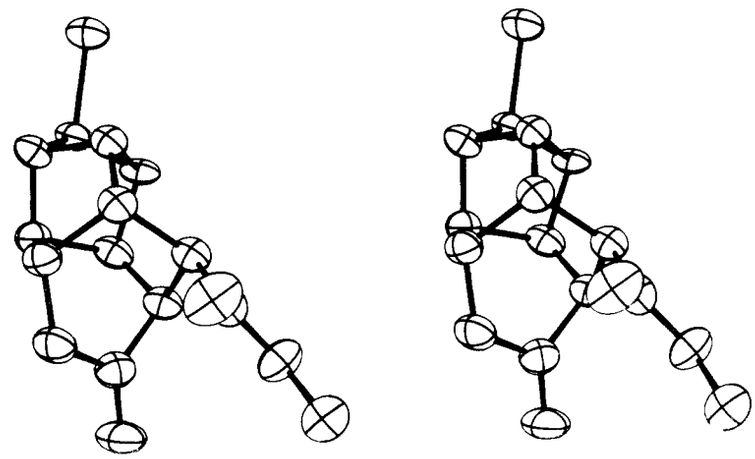


Figure 5. Stereodrawing of **2a** with thermal ellipsoids drawn to enclose 50% probability.

cross-bonding at transannular reaction is provided by the following hypothesis. It seems that the reaction pathway in the halogenation of **1** might involve the initial attack of the reagent at the cyclobutene double bond and participation by cyclohexene double bond as shown in Scheme IV.

When X^+ approached the cyclobutene HOMO from the direction perpendicular to the plane of the molecule, the resulting LUMO of the cyclobutyl cation extended to the opposite direction of the location of X. As a result of this perturbation of orbital, the participation of the HOMO of the cyclohexene double bond to the LUMO of the developing cation became effective. At the first stage of this interaction, an overlap with the p lobe which is located close to the cation center might be predominant. However, on account of the difference of the total strain energy of the resulting polycyclic cation and the relief of van der Waals repulsion among the methine protons in the cyclobutane moiety, the interaction with the p lobe on a remote carbon atom increased its significance with progress of the reaction.

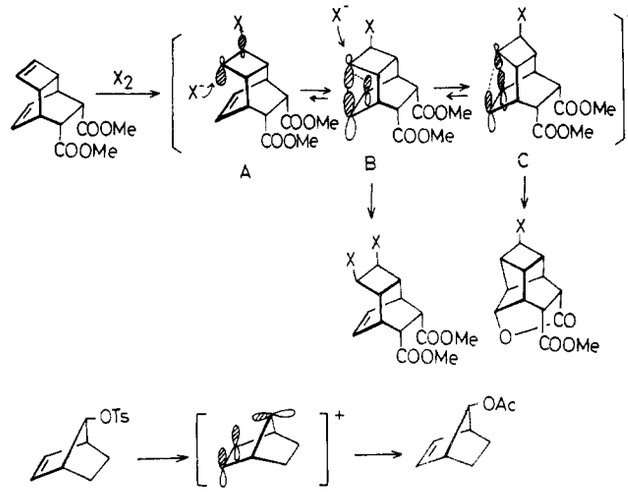
If the reaction was carried out under conditions that stabilized the cation intermediate, electrophilic attack of the reagent at the cyclobutane double bond gave the cation C followed by lactonization affording the cage compound. This explains why the yield of transannular product is high at room temperature or in acetic acid. At elevated temperature, cation B might be trapped by X^- before the formation of cation C. In this connection, solvolysis of 7-norbornadienyl tosylate is reported to give a retention product.[17] This retention of configuration has been rationalized in terms of π participation (Scheme IV).

It seems reasonable to assume that the attack of bromine at an intermediacy of cation B occurs from the less-hindered and electronically favored side to give an exo–cis 1,2-adduct. If the 1,2-adduct was derived from cation A, the product should be a trans dihalide via attack to the most extended site of LUMO.[18]

We have previously reported that cis addition of mercuric acetate and iodine azide on the cyclobutene moiety can be explained by examination on the transition state according to the twist strain theory.[19] Because of the highly strained anti coplanar transition state, the cis addition occurs preferentially via the syn transition state. However, this explanation proved to be in conflict with the results of free-radical addition to this system. As described above, the addition occurred on the cyclobutene double bond by trans fashion.

It was explained that the trans addition was due to the steric hindrance of the *exo*-trichloromethyl group.[11] However the steric effect is not adequate to explain the result. Reaction of **1** with mercuric acetate resulted in the formation of the exo–

Scheme IV



cis adduct in spite of the bulkiness of the reagents.[20,21]

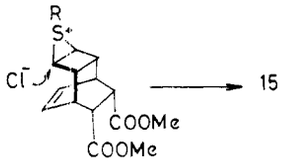
It is probable that the difference between the free-radical addition and the reaction of electrophiles is attributed to the mode of orbital interactions. The orbital interactions between the singly occupied molecular orbital (SOMO) and the lowest unoccupied molecular orbital (LUMO) of the closed-shell molecule were reported to be of importance. In the case of an addition of methyl radical to ethylene,[22] the configuration in which an electron is transferred from the SOMO of methyl to the LUMO of ethylene is calculated to be the most dominant, and the one from the HOMO of ethylene to the SOMO of methyl is the next dominant.

Although we can not ascertain the feature of the interactions between **1** and the radicals, they must differ from that of an electrophilic reaction which is controlled by the HOMO of the cyclobutene double bond. On account of the interaction controlled mainly by LUMO of the cyclobutene double bond, the participation between the resulting cyclobutyl radical and cyclohexene double bond might be uneffective.

As a result, it is to be noted that the free-radical addition to **1** resulted in trans addition to the cyclobutene double bond instead of cis addition and transannular cyclization. On the other hand, the observed trans stereospecific addition of methanesulfenyl chloride to the cyclobutene moiety is consistent with a bridged episulfonium ion with little charge on the carbon atom (Scheme V).

Reaction of thiocyanogen with **1** is also trans stereospecific for the cyclobutene double bond. A two-step heterolytic addition reaction involving initial electrophilic attack on the

Scheme V



alkene by an electron-deficient sulfur atom of the thiocyanogen molecule with the formation of a cyanosulfonium ion followed by a trans-diaxial opening of the sulfonium ring by a thiocyanate anion or a cyclohexene double bond accounts for the observed trans stereospecificity. The electron withdrawing group might enhance the cationic character of the carbon and make an overlap between the back lobe of sulfonium ion and the p lobe of the cyclohexene double bond effective.

Experimental Section

The melting points were measured with a Yanagimoto micromelting point apparatus and are uncorrected. Microanalyses were performed with a Perkin-Elmer 240 elemental analyzer. The NMR spectra were taken with a Jeol C-60-XL spectrometer with tetramethylsilane as an internal standard and the chemical shifts are expressed in δ values. The IR spectra were taken with a Jasco Model IRA-1 grating infrared spectrophotometer.

General Procedure for the Bromination of 1. An excess of bromine was added to a solution of **1** in various solvents. The mixture was stirred for 10 h under these conditions. Evaporation of the solvent followed by silica gel chromatography and recrystallization gave products.

(a) A solution of **1** (500 mg) and bromine (600 mg) in acetic acid (20 mL) was stirred at 20 °C. Workup gave **2a** (540 mg).

(b) Bromine (960 mg) was added to a solution of **1** (800 mg) in acetic acid (20 mL) at 80 °C. The mixture was stirred for 10 h at 80 °C. Workup gave **2a** (680 mg) and **3a** (462 mg).

3a: mp 237–238 °C; IR (KBr) 1740 cm^{-1}; NMR ($CDCl_3$) 6.48 (2 H, t, J = 4.5 Hz), 4.22 (2 H, d, J = 3.25 Hz), 3.58 (6 H, s, COOMe 2), 2.8–3.3 (6 H, m). Anal. Calcd for $C_{14}H_{16}O_4Br_2$: C, 41.21 H, 3.95. Found: C, 41.22; H, 3.86.

(c) A solution of **1** (250 mg) and bromine (300 mg) in chloroform was stirred at 20 °C. Workup gave **2a** (270 mg).

(d) To a solution of **1** (500 mg) in refluxing chloroform (20 mL), bromine (600 mg) was added. Workup gave **2a** (170 mg) and **3a** (520 mg).

(e) A solution of **1** (200 mg) and bromine (250 mg) in carbon tetrachloride was stirred at 20 °C. Workup gave **2a** (110 mg) and **3a** (50 mg).

(f) Bromine (300 mg) was added to a solution of **1** (250 mg) in refluxing carbon tetrachloride. Workup gave **2a** (28 mg) and **3a** (380 mg).

Iodination of 1. (a) A solution of **1** (250 mg) and iodine (260 mg) in benzene (20 ml) was stirred at 20 °C. Workup gave **2b** (350 mg).

(b) To a solution of **1** (500 mg) in refluxing cyclohexane, iodine (510 mg) was added. The mixture was refluxed for 8 h. Workup gave **3b** (432 mg).

3b: mp 220–222 °C; IR (KBr) 1740 cm^{-1}; NMR ($CDCl_3$) 6.52 (2 H, t, J = 4.5 Hz), 4.50 (2 H, d, J = 3.75 Hz), 3.59 (6 H, s, COOMe 2), 3.3–3.0 (4 H, m) 2.78 (2 H, s).

Anal. Calcd for $C_{14}H_{16}O_4I_2$: C, 33.49; H, 3.21. Found: C, 33.63; H, 3.30.

Reduction of 2a. A solution of **2a** (800 mg) and n-Bu_3SnH (1 g) in toluene (30 mL) was stirred for 8 h at 80 °C. Evaporation of the solvent followed by silica gel chromatography gave **2a** (560 mg) and **5** (160 mg).

5: mp 87–88 °C; IR (KBr) 1760, 1740 cm^{-1}; NMR ($CDCl_3$) 4.78 (1 H, dd, J = 3.0 and 6.75 Hz), 3.68 (3 H, s, COOMe), 3.22 (1 H, t, J = 5.25 Hz), 2.8–2.6 (7 H, m), 1.95 (1 H, m), 1.95 (1 H, m), 1.40 (1 H, d, J = 8.25 Hz).

Anal. Calcd for $C_{13}H_{14}O_4$: C, 66.65; H, 6.02. Found: C, 66.40; H, 6.11.

Reduction of 2b. A solution of **2b** (1.1 g) and n-Bu_3SnH (1.5 g) in toluene (30 mL) was stirred for 8 h at 40 °C. Workup gave **5** (450 mg).

Reaction of 2a with Silver Acetate. A mixture of **2a** (380 mg) and silver acetate (380 mg) in acetic acid (30 mL) was refluxed for 15 h. The reaction mixture was filtered for precipitated silver salts, and the solvent was evaporated by reduced pressure. The residue was subjected to silica gel chromatography using chloroform–benzene to give a mixture of **9** and **10** (60 mg) and **2a** (290 mg).

Reaction of 1 with Carbon Tetrachloride. A solution of **1** (1,0 g) and azobis(isobutyronitrile) (100 mg) in carbon tetrachloride (30 mL) was refluxed for 8 h. Evaporation of the solvent followed by silica gel chromatography gave **11**[11] (1.0 g) and **1** (280 mg).

Reaction of 1 with Hydrogen Bromide. To a solution of **1** (700 mg) and azobis(isobutyronitrile) (100 mg) in refluxing benzene (30 mL), hydrogen bromide was bubbled. Evaporation of the solvent followed by chromatography gave **12** (800 mg).

12: mp 98–100 °C; IR (KBr) 1750 cm^{-1}; NMR ($CDCl_3$) 6.45 (2 H, t, J = 3.75 Hz), 3.95 (1 H, m), 3.57 (6 H, s, COOMe 2), 3.2–2.2 (8 H, m).

Anal. Calcd for $C_{14}H_{17}O_4Br$: C, 51.08; H, 5.20. Found: C, 51.08; H, 5.22.

Reaction of 1 with *p*-Chlorobenzenethiol. A solution of **1** (500 mg) and p-chlorobenzenethiol (290 mg) in cyclohexane (20 mg) was stirred for 24 h. After evaporation of the solvent, the residue was dissolved in chloroform. The solution was washed with 4% aqueous sodium hydroxide and then water. Evaporation of the solvent followed by chromatography gave **13** (400 mg) and **14** (44 mg).

13: mp 123–124 °C; IR (KBr) 1740 cm^{-1}; NMR ($CDCl_3$) 7.4–7.0 (4 H, m), 6.50 (2 H, t, J = 3.75 Hz), 3.59 (7 H, s, COOMe 2 and 1 H), 3.40 (1 H, m), 3.1–2.8 (4 H, m), 2.55 (2 H, m), 2.04 (2 H, m).

Anal. Calcd for $C_{20}H_{21}O_4SCl$; C, 61.14; H, 5.39. Found: C, 61.23; H, 5.42.

14: mp 197–199 °C; IR (KBr) 1740 cm^{-1}; NMR ($CDCl_3$) 7.50 (4 H, s), 6.40 (2, H, m), 3.58 (6 H, s), 3.2–1.8 (9 H, m).

Anal. Calcd for $C_{20}H_{21}O_5SCl$: C, 58.75; H, 5.18. Found: C, 58.80; H, 5.18.

Reaction of 1 with Methanesulfenyl Chloride. To a solution of **1** (2.5 g) in dichloromethane (10 mL), methanesulfenyl chloride (1.0 g) was added at −30 °C. The solution was stirred for 4 h. After evaporation of the solvent, the residue was subjected to silica gel chromatography using benzene–chloroform to give **15** (2.72 g): mp 99–100 °C: IR (KBr) 1740 cm^{-1}; NMR ($CDCl_3$) 6.56 (1 H, t, J = 7.5 Hz), 6.38 (1 H, t, J = 7.50 Hz), 4.35 (1 H, dd, J = 6.0, 7.50 Hz), 3.60 (3 H, s, COOMe), 3.4–2.8 (7 H, m), and 2.10 (3 H, s, SMe).

Anal. Calcd for $C_{15}H_{19}O_4SCl$: C, 54.45; H, 5.79. Found: C, 54.51; H, 5.66.

Reaction of 1 with Thiocyanogen. To a solution of thiocyanogen in acetic acid (80 mL) generated in situ from thiocyanate (6.1 g) and bromine (1 mL), 2,6-*tert*-butyl-p-cresol (0.1 g) as a radical inhibitor and **1** (2.0 g) were added. The reaction mixture was stirred for 8 h at room temperature. The reaction mixture was filtered to remove polymeric thiocyanogen, and the product was isolated by dilution of the solution with water followed by extraction with chloroform and removal of solvent under reduced pressure. The resulting residue was subjected to silica gel chromatography (using benzene–chloroform) to give **16** (220 mg) and **17** (450 mg).

16: mp 175–176 °C; IR (KBr) 2160, 1780 and 1755 cm^{-1}; NMR ($CDCl_3$) 4.85 (1 H, J = 3.25, 7.50), 3.75 (3 H, s, COOMe), 3.60 (1 H, s), 3.5–2.5 (8 H, m).

Anal. Calcd for $C_{14}H_{13}O_4SN$: C, 57.72; H, 4.50; N, 4.81. Found: C, 57.50; H, 4.69; N, 4.86.

17: mp 117–118 °C; IR (KBr) 2160, 1740 cm^{-1}; NMR ($CDCl_3$) 6.50 (2 H, m), 4.25 (1 H, m), 3.60 (7 H, s, COOMe 2 and 1 H), 3.5–2.8 (6 H, m).

Anal. Calcd for $C_{16}H_{16}O_4S_2N_2$: C, 52.73; H, 4.43; N, 7.69. Found: C, 52.52; H, 4.41; N, 7.90.

Reduction of 16. To a solution of **3** (200 mg) and $NiCl_2 \cdot 6H_2O$ (2.0 g) in ethanol (20 mL), a solution of sodium borohydride (580 mg) in water (5 mL) was added. The mixture was refluxed under reduced pressure followed by silica gel chromatography to give **5** (100 mg).

Structure Determination. Crystal data are as follows. Compound **3a:** $P2_1/a$, a = 19.097 (3), b = 6.859 (2), c = 12.701 (3) Å, β = 119.15 (3)°, Z = 4, d_{obsd} = 1.77, d_{calcd} = 1.875 g·cm^{-3}, μ = 59.2 cm^{-1} (for Mo Kα).

Compound **2a:** $P\bar{1}$, a = 7.359 (1), b = 12.268 (1), c = 7.240 (1) Å, α = 81.90 (1), β = 108.76 (1), γ = 77.75 (1)°, Z = 2, d_{obsd} = 1.77, d_{calcd} = 1.764 g·cm^{-3}, μ = 34.6 cm^{-1} (for Mo Kα).

The data collections were carried out on a Rigaku four circle diffractometer, using Zr-filtered Mo Kα radiation. The crystals used for data collection had the dimensions of 0.1 × 0.4 × 0.1 mm (elongated in the b direction) for **3a** and 0.40 × 0.35 × 0.05 mm (elongated in the a direction) for **2a.** Integrated intensities were measured by the $\omega - 2\theta$ scan method, with a speed of 2° (ω) min^{-1} and range of (1.40 ± 0.35 tan θ)° (ω). For **3a,** 2928 independent reflections with $2\theta \leq 52.5°$ were obtained, of which nonzero reflections were 2068; for **2a,** 2244 reflections with $2\theta \leq 50°$ were obtained, of which 1854 were nonzero.

The intensity data were corrected for Lorentz and polarization effects, but no absorption correction was made. The data set of **2a** was corrected for crystal deterioration.

The structures were solved by the heavy-atom method, and the refinement was carried out by the block-diagonal least-squares procedure.[23,24] Temperature factors were anisotropic for the nonhydrogen atoms and isotropic for the hydrogen atoms. In the refinement, the function minimized was $\Sigma\omega(|F_o| - |F_c|)^2$. For **3a** only nonzero reflections were included, and the temperature factors of the hydrogen atoms were held constant ($B = 3.8$ Å^2) in the refinement; the weight was $1/(\sigma^2|F_o| + a|F_o| + b|F_o|^2)$, and the final refinement ($a = -0.1297$, $b = 0.0140$) gave the $R(\Sigma||F_o| - |F_c||/\Sigma|F_o|)$ of 0.104. For **2a** the weighting scheme was $\omega = 1/2$ for $F_o = \theta$, $\omega = 1$ for $\theta < |F_o| < 2\theta$, and $\omega = (2\theta/|F_c|)^2$ for $|F_o| \geq 2\theta$, and the final R is 0.080 for 1854 nonzero reflections. The atomic scattering factors were taken from ref 24. All the calculations were carried out on FACOM 230-60 and 230-75 computers of Nagoya University.

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Registry No.—**1,** 35211-83-7; **2a,** 64682-19-5; **2b,** 51425-75-3; **3a,** 64682-20-8; **3b,** 64682-21-9; **5,** 64682-22-0; **12,** 64682-23-1; **13,** 64682-24-2; **14,** 64682-25-3; **15,** 64682-26-4; **16,** 64728-31-0; **17,** 64682-27-5; bromine, 7726-95-6; iodine, 7553-56-2; Bu_3SnH, 688-73-3; azobis(isobutyronitrile), 764-28-3; *p*-chlorobenzenethiol, 106-54-7; methanesulfenyl chloride, 5813-48-8; thiocyanogen, 505-14-6.

Supplementary Material Available: Tables II–VI, positional and thermal parameters for the structures **2a** and **32** (7 pages). Ordering information is given on any current masthead page.

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(21) A referee pointed out that cis oxymercuration products most likely arise by concerted cycloadditions, as discussed by Professor Cristol in 1976, and thus have nothing to do with the radical additions. However, they discussed the dependence of the reaction mechanisms (mercurinium ion, carbenium ion, and concerted reactions) on the reaction conditions and concluded that a cis concerted addition process intervenes when neither the process via mercurinium ion nor that via carbenium ion occurs readily. In this case, the cis oxymercurations can not explained by the molecular addition as discussed previously.
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Ring Expansion by [2,3]Sigmatropic Shift: Conversion of Five-Membered into Eight-Membered Heterocycles

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Syntheses of α-vinyltetrahydrothiophene and 2-vinyl-*N*-benzylpyrrolidine are described. Conversion of these heterocycles into ylides by an alkylation–deprotonation sequence results in rearrangement to eight-membered heterocycles. In the sulfur series, *cis*-thiacyclooctenes are formed preferentially, but a trans alkene has been isolated in one case. In the nitrogen series, comparable amounts of cis and trans alkenes are formed. The origin of olefin geometry is considered as a function of ylide geometry. In both the sulfur and the nitrogen series, the stereochemistry of ylides is subject to interconversion of diastereomers. Reversible deprotonation α to the vinyl group is a sufficient explanation for diastereomer interconversion in both heterocyclic series, but other mechanisms are not ruled out.

Synthetic approaches to macrocyclic natural products under way in our laboratory require the development of methodology for easily repeatable multicarbon ring expansion ("ring growing reactions"). A solution to this problem has been devised using the [2,3]sigmatropic rearrangement of ylides obtained from α-vinyl heterocycles, as described in a preliminary communication.[1] Assuming that techniques for heteroatom extrusion can be developed, these rearrangements provide rapid access to large rings with varying functionality. In this report we shall describe fundamental aspects of the most difficult ring expansion in terms of ring size, the conversion of five- to eight-membered heterocycles.

Preparation of α-Vinyl Heterocycles. Our synthesis of α-vinyltetrahydrothiophene (**3**) begins with the conversion of thietane into the allylic sulfide **2** via fragmentation of an unstable thietanium bromide (**1**, Scheme I). Similar frag-

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