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Facile Skeletal Rearrangement by Reaction of Polycyclic Olefins with Lead(IV) and Thallium(III) Salts[1]

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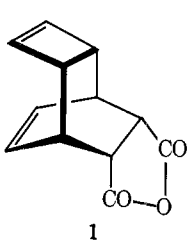
Reaction of tricyclo[4.2.2.0^{2,5}]deca-3,7-diene derivatives with lead tetraacetate, thallium triacetate, and thallium trinitrate has been studied. The structures of the products were determined by spectral means and chemical transformations. Skeletal rearrangement of the polycyclic hydrocarbons was examined. Some mechanisms for the formation of the products are discussed.

Rigid molecules such as the norbornadiene skeleton containing two isolated double bonds in spatial proximity are known to undergo facile chemical reactions involving π-participation between two double bonds.[2,3] The transannular reactions of these molecules have provided a simple synthetic route to new highly strained polycyclic hydrocarbons and information about the participation between two double bonds. Little is known concerning the relationship among the reactivity, regioselectivity, and stereoselectivity of the transannular reaction, and the nature of the double bond participation.

We have previously reported the reaction of tricyclo[4.2.2.0^{2,5}]deca-3,7-diene derivatives **1** and **2** with electrophiles.[3-6] These results are summarized on the basis of common intermediate **3** which divided into two groups according to the nature of the bridged ion atom "X": (1) transannular cross cyclization via the intermediacy of a bridged cation with more electronegative atoms such as oxygen, chlorine, and bromine;[3,5] (2) syn addition via an organomercuric intermediate to the strained double bond.[4] An iodine cation intermediate is situated in the intermediate position.[6]



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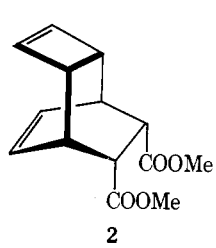

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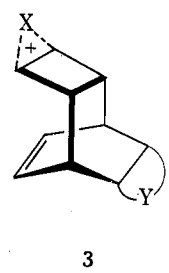

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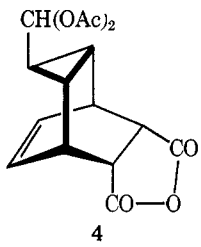
Oxidation of **1** and **2** with mercury(II) acetate has revealed the exo-cis addition to a strained double bond controlled by the twist strain of the transition state.[4] In this connection, it is well known that mercury(II), thallium(III), and lead(IV) salts are isoelectronic and the oxidation potentials of the ions are in the order Hg < Tl < Pb.[7]

In the hope of providing some additional data for understanding the reaction of type 2, we have investigated the reactions of **1** and **2** with lead tetraacetate, thallium triacetate, and thallium trinitrate, respectively, and have also examined the skeletal rearrangement of the related compounds leading to novel strained bridged polycyclic hydrocarbons.

Results

Reaction of Lead Tetraacetate with 1 and 2. The reaction of **1** with equimolar lead tetraacetate in acetic acid at 70 °C gave product **4** in about 10% yield with recovery of the starting material (90%). Similar reaction at 100 °C gave a complex mixture as evidenced by TLC inspection, but compounds **4** and **5** were obtained in 25 and 3% yields, respectively. On the other hand, the reaction of **2** with lead tetraacetate gave **6** in a moderate yield. The reaction of **2** with lead tetraacetate in the presence of boron trifluoride–acetic acid complex at 70 °C gave **7** in 67% yield, but at 100 °C the yield of **7** decreased considerably.



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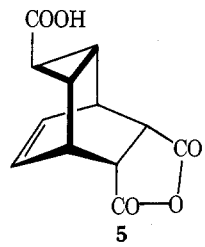

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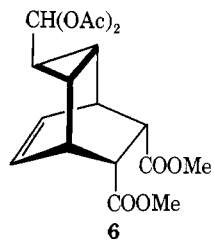

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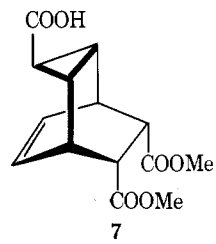

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Table I. Reactions of 1 and 2 with Lead Tetraacetate under Various Conditions

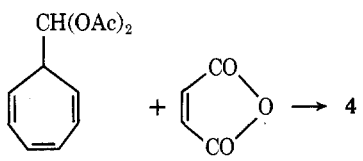
Compd	Reaction conditions: Solvent	Temp, °C	Products (%)	
1	AcOH	70	4 (10)	
	AcOH	100	4 (25)	5 (3)
2	AcOH	70	6 (67)	
		100	6 (63)	
	$AcOH-BF_3$	70	7 (67)	
	$AcOH-BF_3$	100	7 (20)	

These results are summarized in Table I.

Structural elucidation of 4 and 5 was accomplished on the basis of spectral data and chemical transformations.

The ir spectrum of 4 shows carbonyl absorption at 1860, 1840, 1790 (anhydride), and 1770 cm^{-1} (acetoxy). The NMR spectrum of 4 exhibits two characteristic olefinic proton signals at δ 5.93 (t), three methine proton signals of the cyclopropane at δ 1.47–0.84 (m), two methyl groups at δ 2.05 (6 H, s, 2 OAc), a methine proton signal at δ 6.39 (d), and four methine proton signals at δ 3.2–3.5 (m). Furthermore, the structure 4 was established by unequivocal independent synthesis; the Diels–Alder reaction of the diacetoxy acetal of 2,4,6-cycloheptatriene-1-carboxaldehyde[8] with maleic anhydride gave compound 4 as shown in Scheme I.

Scheme I



Compound 5 shows carbonyl absorption at 1860 and 1800 (anhydride) and 1690 cm^{-1} (carboxylic acid) by ir. Moreover, compound 5 was derived from compound 4; heating of 4 with acetic acid in the presence of boron trifluoride in a sealed tube gave a formyl compound 9, which was oxidized to 5 spontaneously at room temperature as shown in Scheme II.

Compound 6 was easily assigned as a ring contracted product, since the NMR spectrum is grossly similar to that of 4 except for the signal of two methoxy groups at δ 3.52 (6 H, s). This assignment was supported by the fact that both 4 and 6 gave 8 by treatment with methanol in the presence of sulfuric acid.

Table II. Reaction of 2 with Thallium Salts under Various Conditions

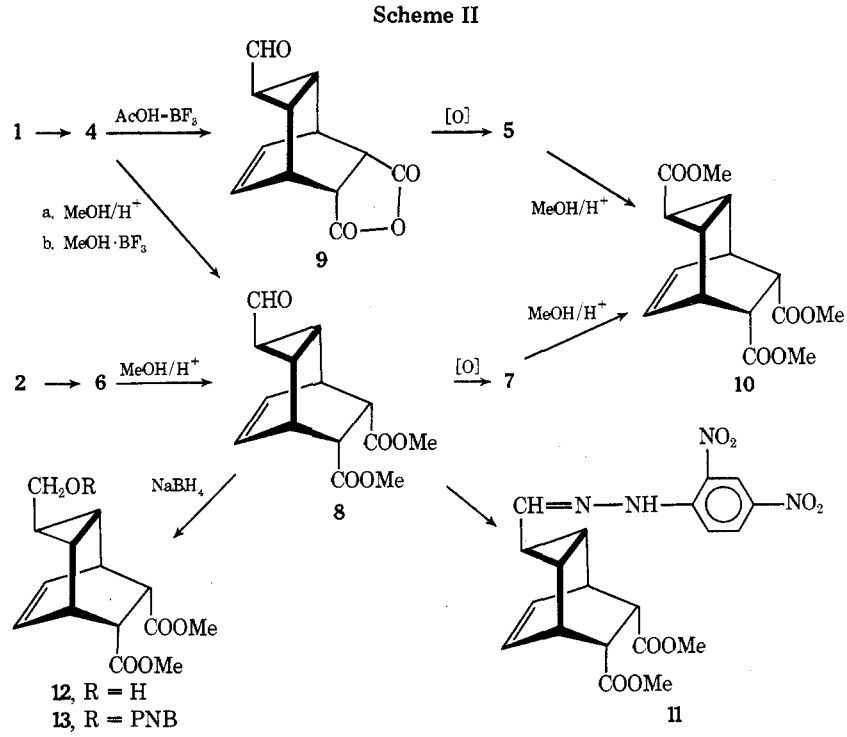
Compd	Reagent	Reaction conditions: Solvent	Temp, °C	Products (%)	
2	$Tl(OAc)_3$	AcOH	25	6 (61)	14 (5)
2	$Tl(OAc)_3$	AcOH	118	8 (59)	7 (31)
2	$Tl(NO_3)_3$	MeOH	25	8 (8)	15 (11)
2	$Tl(NO_3)_3$	MeOH	65	8 (24)	15 (10)

Compound 8, which contains a cyclopropyl aldehyde moiety, was gradually oxidized to give 7, and treated with 2,4-dinitrophenylhydrazine to afford red crystals of 11. Reduction of 8 by sodium borohydride gave 12, which reacted with *p*-nitrobenzoyl chloride in the presence of pyridine to give 13. Further treatment of 5 or 7 with methanol in sulfuric acid gave a trimethyl ester 10. Heating of 6 in acetic acid in the presence of boron trifluoride at 80 °C gave 7. These results indicate that the formyl compound 8 is too labile to exist and readily autoxidized to 7 under these conditions. Thus, it is concluded that the reaction of 2 with lead tetraacetate in the presence of boron trifluoride gave compound 6 as the primary product. These reactions are summarized in Scheme II.

Reaction of 2 with Thallium(III) Salts. The reaction of 2 with equimolar thallium triacetate in acetic acid at room temperature gave 6 (61%) together with 14 (5%). However, similar reaction at reflux temperature gave 8 (59%) and 7 (31%), and compound 14 could not be detected. Compound 7 was also derived from 6 in acetic acid at reflux temperature in almost quantitative yield.

On the other hand, the reaction of 2 with equimolar thallium trinitrate in methanol at room temperature afforded a mixture of 8 and 15. These results are summarized in Table II.

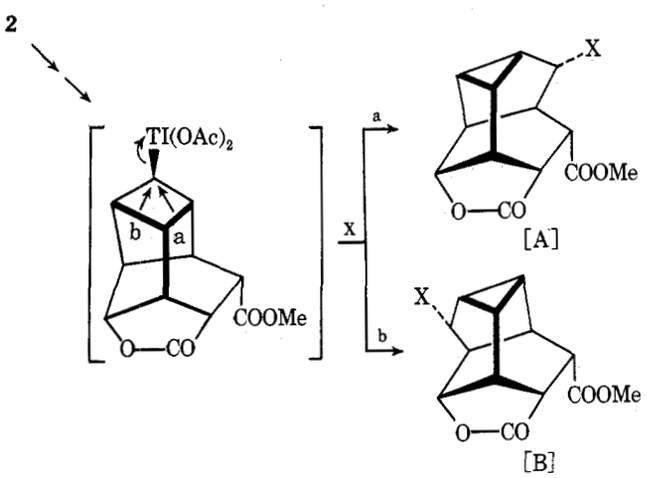
Scheme II



The ir spectrum of **14** shows carbonyl absorption at 1790 and 1730 cm^{-1} suggesting the presence of a five-membered lactone moiety, and acetoxy and ester groups. The NMR spectrum of **14** exhibits a methine proton signal adjacent to an acetoxy group at δ 5.00 (s), a methine proton signal adjacent to a lactone moiety at δ 4.20 (d), one methoxy group at δ 3.57 (3 H, s), one methyl group at δ 2.07 (3 H, s) and three methine proton signals of a cyclopropane ring at δ 1.1–1.7 (m), but no olefinic proton signals were observed.

On the basis of the above data, the structure of the product **14** is assumed to be either A or B via a plausible pathway as shown in Scheme III.

Scheme III



In order to obtain additional information about the structure of **14**, we have attempted the skeletal rearrangement of **16**[3] and **17**.[5] The reaction of **16** with equimolar silver acetate in acetic acid at reflux temperature gave **18** and **19** in a 1:1 ratio. In addition, acetolysis of **17** gave a mixture of **18** and **19** having the same composition. On the other hand, the reaction of **16** with silver acetate in water–acetone gave **20** and **21**, which were converted into the corresponding acetylated compounds **18** and **19** by acetic anhydride in pyridine, respectively. Compound **20** was oxidized by chromic anhydride–acetic acid to give **22**, which was also given from **23** using the same reagent. Compound **25** was derived from **21** by chromic anhydride–pyridine oxidation. These reactions are summarized in Scheme IV.

The NMR spectra of **20** and **18** resemble those of **23** and **24** except for the appearance of a triplet signal instead of a singlet signal of a methine proton adjacent to a hydroxy and an acetoxy moiety, respectively. From these data, the structures of **18, 20,** and **22** were established as depicted in Scheme IV.

The NMR spectrum of **19** exhibits a methine proton signal adjacent to a lactone moiety at δ 4.42 (d), one methoxy group at δ 3.73, one methyl group at δ 2.07, and methine proton signals of a cyclopropane ring at δ 1.5–1.8 (2 H, m) and 1.9–2.0 (1 H, m). Elemental analysis shows the product **19** to be the isomer of **14.** Thus, compound **19** must be either A or B as shown in Scheme III (X = OAc). However, the differences in the chemical shifts of the methine proton signals (H_b) adjacent to the lactone moiety between **19** (δ 4.70) and **25** (δ 4.42) can be accounted for by the carbonyl anisotropy. On the basis of the above results, the structure of **19** was established as B. Consequently, the structure of **14** was assigned as A (X = OAc).

Scheme IV

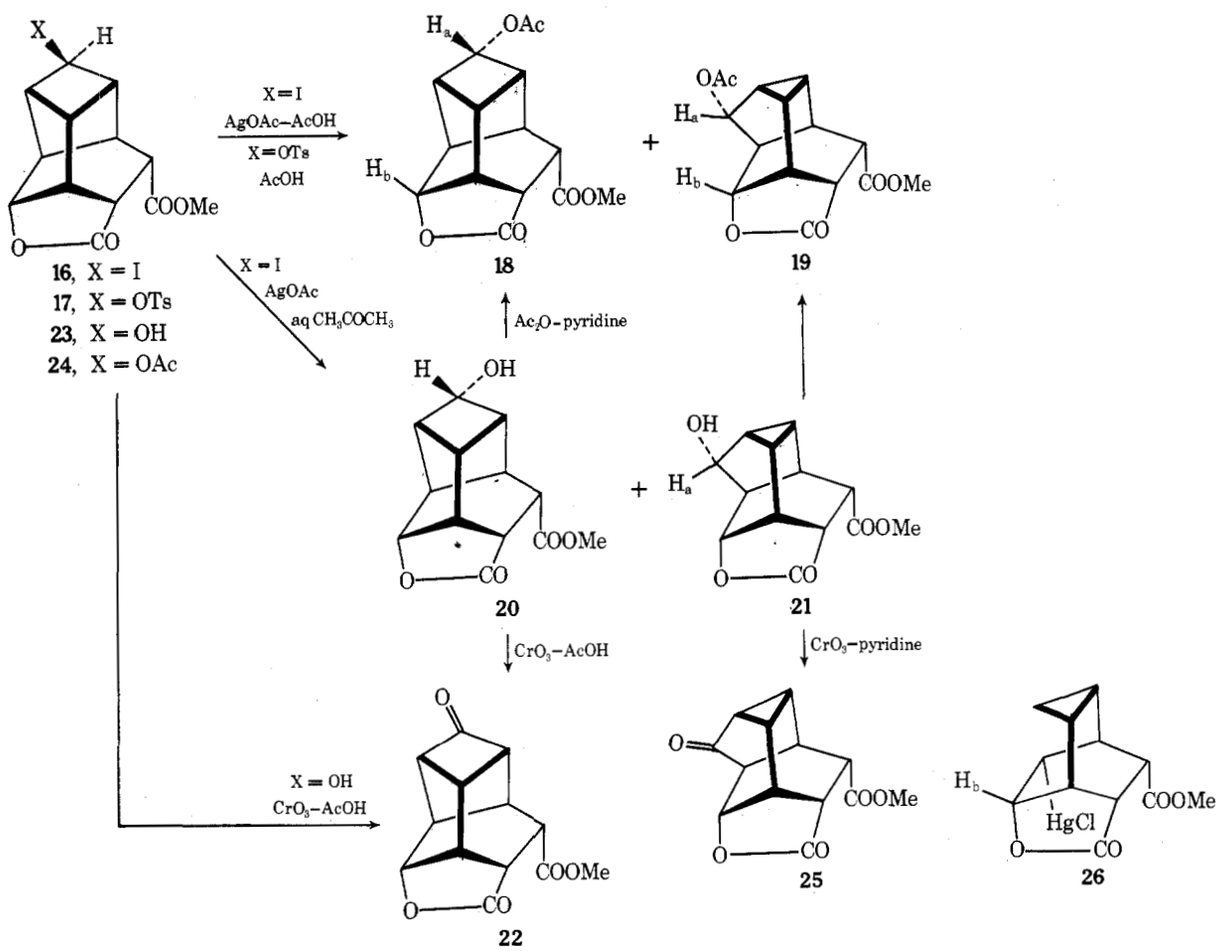
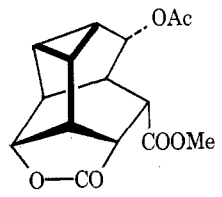


Table III. NMR Data

Compd	Chemical shift (H_b), δ
24[a]	4.77
26[b]	4.47
19	4.42
14	4.20

[a] Reference 5. [b] Reference 4.



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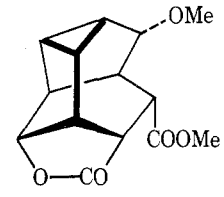

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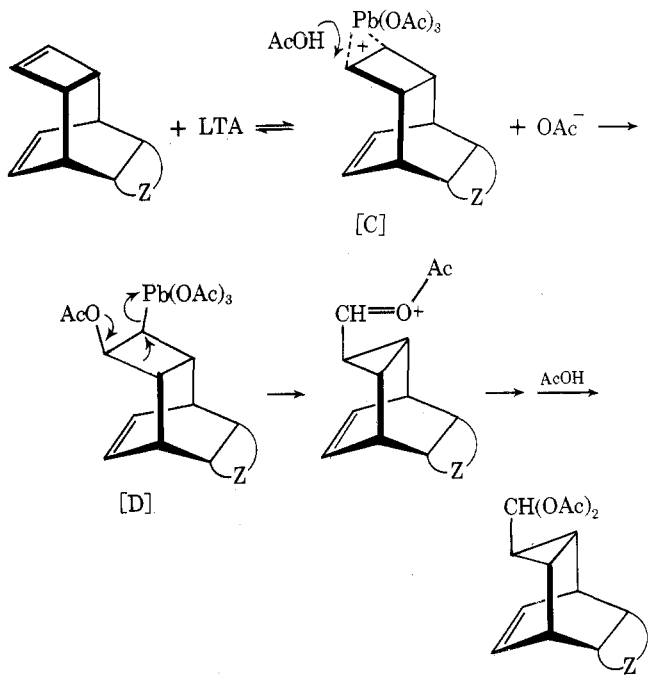
These assignments were also supported by the comparison of the chemical shifts (H_b) of a series of compounds **24**[5] and **26**,[4] which were summarized in Table III. It is also pointed out that the differences in the chemical shifts are dependent on the shielding effect of the cyclopropane ring;[9] the cyclopropyl anisotropy is influenced by the distance between H_b and the cyclopropane ring. The similarity of the value of **26** to that of **19** suggests the similar environment of H_b in both compounds. With respect to **14**, the most upper field displacement of the signal supports the determined structure in which the distance between H_b and the cyclopropane moiety is shorter than that of **19** and **26**.

Compound **15** was easily assigned as type A (X = OMe), since the NMR spectrum of **15** is similar to that of **14**.

Discussion

As described above in the oxyplumbation, the ring-contracted products **4** and **6** are the primary products. They might form via the addition of lead tetraacetate to the strained cyclobutene moiety to form the bridged organolead compound (C) followed by the attack by an acetoxy anion to give an intermediate (D). This intermediate may be a precursor of the ring-contracted products which can be considered to arise from a pinacolic-type reaction as shown in Scheme V.

Scheme V

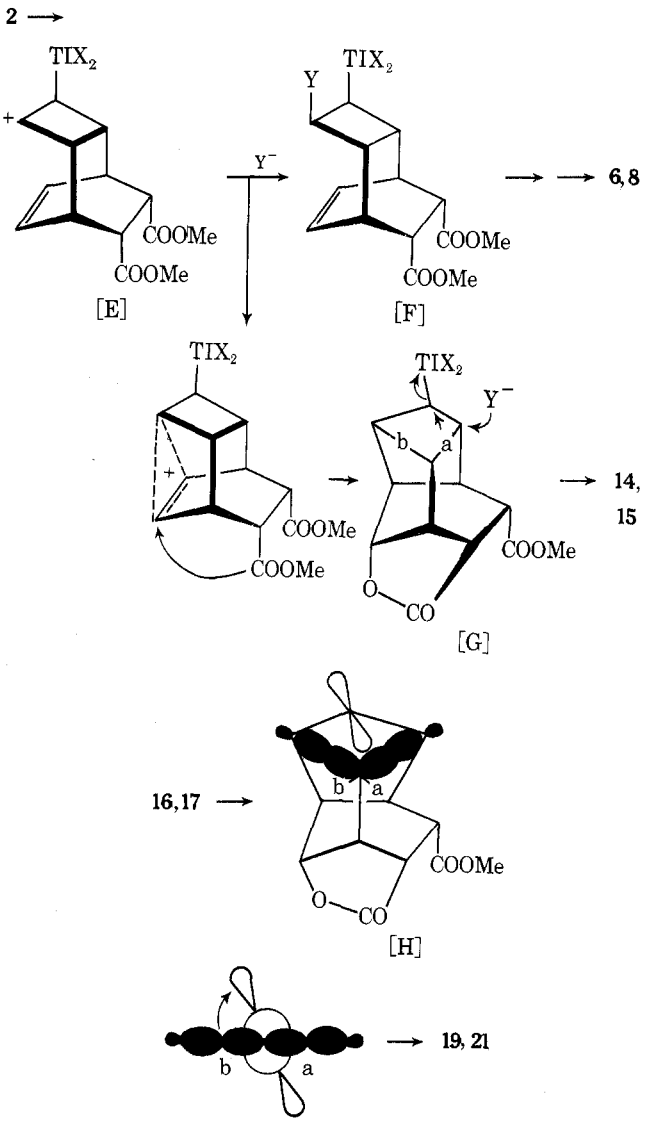


From the results, it is to be noted that Hg(II) affords an isolable organometallic adduct,[4] whereas none is obtained with lead. This may be due in part to the greater electron affinity of Pb(IV).

Oxidation of olefins with Hg(II), Tl(III), or Pb(IV) salts can lead to a variety of products depending on the nature of the metal cation, the anion, the solvent, and the conformation of the cyclic olefins. Previous studies of oxymetallation of olefins with acetate of the three metals have established the intermediate position of the thallium salt.[10]

In view of oxymercuration and oxyplumbation of **1** and **2**, the results of oxythallation are of particular interest; it is quite unexpected that the oxythallation of **2** gave the transannular products **14** and **15**. They might form via the unsymmetrical intermediate (E) followed by competitive attacks by an acetoxy anion and a double bond to give F and G. The experimental data show that at elevated reaction temperature the attack by an acetoxy anion is superior to that of a double bond. Intermediate F may lead to the ring contracted products, **6** and **8**, while intermediate G may give the rearrangement product **14** (or **15**) as shown in Scheme VI. It is pointed out that alkylthallium(III) compounds such as F and G are extremely unstable, and C–Tl bond heterolysis might proceed via a transition state approaching carbonium ion character. On the other hand, rearrangements of polycyclic hydrocarbon skeletons via carbonium ion are well documented. It is as-

Scheme VI



sumed that some of the stability of the new skeleton is felt at the transition state.[11] The transition state energy for a Wagner–Meerwein shift can also be influenced by the effectiveness of orbital overlap dependent on the initial alignment of relevant bonds; for a rearrangement that is concerted with ionization, the migrating group should ideally be antiplanar to the leaving group (sp^3-alignment factor), and for rearrangement to a carbocation site, the migrating group and the p orbital should ideally be in one plane (sp^2-alignment factor).

An examination of stereomodels shows that the sp^3-alignment factor would favor migration of a over b to give A. The sp^2-alignment factor or product stability factor would favor migration of b over a to give B.

According to the above arguments, the reaction of alkylthallium compound such as the intermediate G is assumed to be a concerted process. On the other hand, the solvolysis of **16** or **17** might proceed via an intermediacy of carbonium ion H as shown in Scheme VI.

Taylor reported that thallium nitrate, which is almost ionic, is more effective for ring contraction of cyclic olefins.[12] In this connection, our present results show that the transannular reaction product **15** was obtained in a moderate yield in the reaction of **2** with thallium nitrate in methanol, although the reaction rate was slow as evidenced by TLC inspection.

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. The HLC was done on a Shimazu-Du Pont LC 830 high-speed liquid chromatography using a column ODS (7.9 × 1.0 m).

General Procedure for the Oxidations of 1 and 2 with LTA. The diene was added to acetic acid (40 ml) in a three-necked flask (100 ml) equipped with a stirrer and a thermometer. To the solution was added equimolar lead tetraacetate (LTA) in one portion and the temperature of the bath was maintained at 70 or 100 °C. After stirring for 15 h, the bath was removed and the solution was allowed to cool to room temperature. The resulting solution was then added to water and extracted with chloroform. The extract was washed with aqueous sodium chloride, and then dried over sodium sulfate. After the solvent was evaporated by reduced pressure, the residue was subjected to silica gel chromatography (SGC) and recrystallized.

A. A solution of **1** (0.5 g) and LTA (lead tetraacetate) (2.25 g) in acetic acid was stirred at 70 °C. Workup gave **1** (0.45 g) and **4** (0.08 g).

4: mp 249–250 °C dec; ir (KBr) 1860, 1840, 1790, 1770 cm^{-1}; NMR ($CDCl_3$) δ 6.39 (d, J = 6.75 Hz), 5.93 (2 H, t, J = 4.5 Hz), 3.2–3.5 (4 H, m), 2.05 (6 H, s, 2 OAc), 1.47–0.84 (3 H, m).

Anal. Calcd for $C_{16}H_{16}O_7$: C, 60.00; H, 5.04. Found: C, 59.94; H, 5.10.

B. A solution of **1** (0.5 g) and LTA (2.25 g) in acetic acid was stirred for 15 h at 100 °C. Workup gave **1** (0.235 g), **4** (0.21 g), and **5** (0.02 g).

5: mp 284 °C dec; ir (KBr) 1860, 1800, 1690 cm^{-1}.

Anal. Calcd for $C_{12}H_{10}O_5$: C, 61.54; H, 4.30. Found: C, 61.24; H, 4.40.

C. A solution of **2** (0.5 g) and LTA (1.8 g) in acetic acid was stirred at 70 °C. Workup gave **2** (0.12 g) and **6** (0.49 g).

6: mp 167–169 °C; ir (KBr) 1770, 1745 cm^{-1}; NMR ($CDCl_3$) δ 6.32 (1 H, d, J = 6.75 Hz), 5.88 (2 H, t, J = 3.75 Hz), 3.52 (g H, s, COOMe 2), 2.90–3.30 (4 H, m), 2.01 (6 H s, OAc 2), 1.47–0.84 (3 H, m).

Anal. Calcd for $C_{18}H_{22}O_8$: 59.01; H, 6.05. Found: C, 58.95; H, 6.01.

D. A solution of **2** (0.5 g) and LTA (1.8 g) in acetic acid was stirred at 100 °C. Workup gave **6** (0.46 g).

E. A solution of **2** (0.5 g), LTA (1.8 g), and BF_3·2AcOH (0.38 g) in acetic acid was stirred at 70 °C. Workup gave **2** (0.06 g) and **7** (0.372 g).

7: mp 149–151 °C; ir (KBr) 1735, 1675 cm^{-1}; NMR ($CDCl_3$) δ 9.67 (broad s, 1 H, D_2O exchangeable), 6.00 (2 H, t, J = 4.0 Hz), 3.63 (6 H, s, COOMe 2), 3.0–3.2 (4 H, m), 1.73 (2 H, m), 1.38 (1 H, t, J = 2.0 Hz).

Anal. Calcd for $C_{14}H_{16}O_6$: C, 59.99; H, 5.75. Found: C, 59.72; H, 5.71.

F. A solution of **2** (0.5 g), LTA (1.8 g), and BF_3·2AcOH (0.38 g) in acetic acid was stirred at 100 °C. Workup gave **7** (0.114 g).

Reaction of Diacetoxy Acetal of 2,4,6-Cycloheptatriene and Maleic Anhydride. A solution of the acetal (0.3 g) and maleic anhydride (0.14 g) in benzene (20 ml) was refluxed for 30 h. The precipitated solids was filtered to give **4** (0.18 g).

Reaction of 4 with Methanol–Sulfuric Acid. A solution of **4** (0.15 g) in methanol (10 ml) and sulfuric acid (1 ml) was refluxed for 4 h. The mixture was cooled and then diluted with water.

The solution was extracted with chloroform and the extract was evaporated by reduced pressure. The residue was subjected to SGC using chloroform to give **8** (0.115 g): mp 87–88 °C; ir (KBr) 2850, 2750, 1750, 1700 cm^{-1}; NMR ($CDCl_3$) δ 9.35 (1 H, d, J = 3.0 Hz), 6.00 (2 H, t, J = 4.0 Hz), 3.63 (6 H, s, COOMe 2), 3.1–3.5 (4 H, m), 1.77 (3 H, m).

2,4-Dinitrophenylhydrazone of **4** (**11**), mp 228–229 °C.

Anal. Calcd for $C_{20}H_{20}O_8N_4$: C, 54.05; H, 4.54; N, 12.61. Found: C, 54.04; H, 4.48; N, 12.67.

Reaction of 4 with Methanol–Boron Trifluoride Etherate. A solution of **4** (0.15 g) and BF_3·Et_2O (0.02 g) in methanol (20 ml) was refluxed for 8 h. Workup gave **8** (0.136 g).

Reaction of 6 with Methanol–Sulfuric Acid. A solution of **6** (0.3 g) in methanol (20 ml) and sulfuric acid (2 ml) was refluxed for 4 h. Workup gave **8** (0.25 g).

Reaction of 6 with Acetic Acid–Boron Trifluoride Acetic Acid Complex. A solution of **6** (0.2 g) and boron trifluoride acetic acid complex (0.02 g) in acetic acid (20 ml) was heated at 80 °C for 4 h. The mixture was diluted with water and extracted with chloroform. The solvent was evaporated by reduced pressure and the residue was subjected to SGC using chloroform to give **7** (0.15 g): mp 149–151 °C; ir (KBr) 1735, 1675 cm^{-1}; NMR ($CDCl_3$) δ 9.67 (1 H, exchangeable by D_2O), 6.00 (2 H, t, J = 4.0 Hz), 3.63 (6 H, s, COOMe 2), 3.43–3.00 (4 H, m), 1.73 (2 H, m), 1.38 (1 H, m).

Reaction of 4 with Acetic Acid–Boron Trifluoride Acetic Acid Complex. A solution of **4** (0.15 g) and boron trifluoride acetic acid complex (0.1 g) in acetic acid (20 ml) was heated at 80 °C in a sealed tube for 8 h. After removal of the solvent, the residue was recrystallized from benzene to give **9** (0.087 g): mp 169–170.5 °C; ir (KBr) 1840, 1785, 1705 cm^{-1}; NMR ($CDCl_3$) δ 9.50 (1 H, d, J = 3.25 Hz), 5.96 (2 H, t, J = 3.75 Hz), 3.60 (2 H, m), 3.30 (2 H, t, J = 1.5 Hz), 1.6–2.0 (3 H, m).

Anal. Calcd for $C_{12}H_{10}O_4$: C, 66.05; H, 4.62. Found: C, 66.17; H, 4.72.

Reaction of 8 with Sodium Borohydride. To a solution of **8** (0.3 g) in methanol (20 ml), sodium borohydride (0.04 g) was added. After stirring for 2 h, the solution was diluted with water and extracted with chloroform. After evaporation of the solvent, the residue was subjected to SGC using chloroform to give **12**: mp 81–82 °C; ir (KBr) 1740 cm^{-1}; NMR ($CDCl_3$) δ 5.87 (2 H, t, J = 4.0 Hz), 3.57 (6 H, s, COOMe 2), 3.4–2.8 (7 H, m, 1 H exchangeable by D_2O), 0.9 (3 H, m).

Anal. Calcd for $C_{14}H_{18}O_5$: C, 63.14; H, 6.81. Found: C, 63.26; H, 6.61.

Reaction of 12 with *p*-Nitrobenzoyl Chloride. A solution of **12** (0.4 g) and *p*-nitrobenzoyl chloride (0.36 g) in pyridine (10 ml) was stirred for 6 h at room temperature. The reaction mixture was added with water and then extracted with chloroform. Evaporation of the solvent gave **13** (0.65 g), mp 161–162 °C.

Anal. Calcd for $C_{21}H_{21}O_8N$: C, 60.72; H, 5.10; N; 3.37. Found: C, 60.96; H, 5.02; N, 3.64.

Reaction of 5 with Methanol–Sulfuric Acid. A solution of **5** (0.2 g) in methanol (10 ml) and sulfuric acid (1 ml) was refluxed for 2 h. Workup gave **10** (0.21 g): mp 59–60 °C; ir (KBr) 1750, 1730 cm^{-1}; NMR ($CDCl_3$) δ 5.95 (2 H, t, J = 4.0 Hz), 3.55 (9 H, s, COOMe 3), 3.50–2.95 (4 H, m), 1.80–1.50 (2 H, m), 1.50–1.30 (1 H, m).

Anal. Calcd for $C_{15}H_{18}O_6$: C, 61.21; H, 6.17. Found: C, 61.30; H, 6.10.

Reaction of 7 with Methanol–Sulfuric Acid. A solution of **7** (0.15 g) in methanol (10 ml) and sulfuric acid (1 ml) was refluxed for 2 h. Workup gave **10** (0.15 g).

Reaction of 2 with TTA. A. A mixture of **2** (1.5 g) and thallium triacetate (TTA, 2.3 g) in acetic acid (30 ml) was stirred for 96 h at room temperature. The mixture was diluted with water and extracted with chloroform. The extract was washed with saturated sodium chloride and then water, and dried over sodium sulfate. After the solvent was evaporated by reduced pressure, the residue was subjected to SGC using benzene–chloroform to give **6** (1.28 g) and **14** (0.09 g).

14: mp 181–183 °C; ir (KBr) 1790, 1730 cm^{-1}; NMR ($CDCl_3$) δ 5.0 (1 H, s), 4.20 (1 H, d, J = 7.0 Hz), 3.57 (3 H, s, COOMe), 3.3–2.5 (5 H, m), 3.07 (3 H, s, OAc), 1.7–1.1 (3 H, m).

Anal. Calcd for $C_{15}H_{16}O_6$: C, 61.64; H, 5.52. Found: C, 61.79; H, 5.62.

B. A mixture of **2** (2.0 g) and TTA (3.0 g) in acetic acid (30 ml) was refluxed for 8 h. Workup gave **8** (1.55 g) and **7** (0.697 g).

Reaction of 2 with TTN. A. A solution of **2** (1.7 g) and thallium trinitrate (2.65 g) in methanol (30 ml) was stirred for 5 days at room temperature. After separation of thallium(I) nitrate, the solution was diluted with water and extracted with chloroform. The solvent was evaporated by reduced pressure, and the residue was subjected to SGC

using benzene–chloroform to give **8** (0.15 g), **2** (1.24 g), and **15** (0.187 g).

15: mp 131–132 °C; ir (KBr) 1785, 1720 cm^{-1}; NMR ($CDCl_3$) δ 4.07 (1 H, d, J = 6.0 Hz), 3.70 (4 H, s, COOMe and 1 H), 3.37 (3 H, s, OMe), 3.2–2.6 (5 H, m), 1.2–1.83 (3 H, m).

Anal. Calcd for $C_{14}H_{16}O_5$: C, 67.73; H, 6.50. Found: C, 67.76; H, 6.47.

B. A solution of **2** (2.0 g) and TTN (3.1 g) in methanol (30 ml) was refluxed for 24 h. Workup gave **2** (0.925 g), **8** (0.505 g), and **15** (0.22 g).

Reaction of 16 with Silver Acetate. A. A mixture of **16** (0.4 g) and silver acetate (0.2 g) in acetic acid (20 ml) was refluxed for 2 h. The reaction mixture was filtered for precipitated silver salts, and the solvent was evaporated by reduced pressure. The residue was subjected to SGC using chloroform–benzene to give a mixture of **18** and **19** (0.31 g), which could not be separated by SGC. The mixture consisted of a 1:1 ratio as evidenced by HLC analysis, which was recrystallized from benzene–*n*-hexane to give **18** and **19.**

18: mp 120–120.5 °C; ir (KBr) 1760, 1740 cm^{-1}; NMR ($CDCl_3$) δ 4.80 (1 H, dd, J = 2.0 and 8.0 Hz), 4.65 (1 H, t, J = 2.0 Hz), 3.70 (3 H, s, COOMe), 3.20 (1 H, m), 2.3–2.9 (7 H, m), 2.00 (3 H, s, OAc).

Anal. Calcd for $C_{15}H_{16}O_6$: C, 61.64; H, 5.52. Found: C, 61.57; H, 5.70.

19: mp 138–139 °C ir (KBr) 1770, 1740, 1720 cm^{-1}; NMR ($CDCl_3$) δ 5.00 (1 H, s), 4.42 (1 H, d, J = 7.0 Hz), 3.37 (3 H, s, COOMe), 3.4–2.7 (4 H, m), 2.3–1.8 (2 H, m), 2.06 (3 H, s, OAc), 1.68 (2 H, m).

Anal. Calcd for $C_{15}H_{16}O_6$: C, 61.64; H, 5.52. Found: C, 61.54; H, 5.70.

B. A mixture of **16** (1.92 g) and silver acetate (0.96 g) in acetone (20 ml) and water (20 ml) was refluxed for 30 h. Workup gave **16** (0.34 g) and a mixture of **20** and **21** 0.7 g). The mixture consisted of a 1:1 ratio as evidenced by HLC analysis, which could not be separated.

Acetolysis of 17. A solution of **17** (0.44 g) and sodium acetate (0.09 g) in acetic acid (20 ml) was heated at 170 °C in a sealed tube for 36 h. Workup gave a mixture of **18** and **19** (0.25 g).

Reaction of 20 and 21 with Chromic Anhydride. To a mixture of chromic anhydride (0.5 g) and pyridine (5 g) a mixture of **20** and **21** (0.7 g) was added. After stirring for 24 h, the mixture was diluted with water and extracted with chloroform. The organic solvent was dried over sodium sulfate and then evaporated by reduced pressure. The residue was subjected to SGC using chloroform to give **25** (0.18 g). Compound **20** was recovered from the reaction mixture, which was treated with chromic anhydride in acetic acid; to a solution of **20** (0.1 g) in acetic acid (20 ml) chromic anhydride (0.03 g) was added. The mixture was stirred for 4 h. After dilution with water, the reaction mixture was extracted with chloroform. Evaporation of the solvent gave **22** (0.03 g).

20: mp 140–141 °C; ir (KBr) 3420, 1730 cm^{-1}; NMR ($CDCl_3$) δ 4.83 (1 H, dd, J = 8.0 and 2.0 Hz), 4.07 (1 H, m, changed to triple by D_2O, J = 3.0 Hz), 3.73 (3 H, s, COOMe), 3.20 (1 H, m), 2.9–2.5 (7 H, m, 1 H exchangeable by D_2O), 2.2 (1 H, m).

Anal. Calcd for $C_{13}H_{14}O_5$: C, 62.39; H, 5.04. Found: C, 62.49; H, 5.78.

22: mp 203–205 °C; ir (KBr) 1805, 1770, 1740 cm^{-1}; NMR (Me_2SO-d_6) δ 4.98 (1 H, dd, J = 9.0 and 2.0 Hz), 3.63 (3 H, s, COOMe), 3.5–2.5 (8 H, m). Anal. Calcd for $C_{13}H_{12}O_5$: C, 62.90; H, 4.87. Found: C, 62.80; H, 4.82.

25: mp 187–189 °C; ir (KBr) 1770, 1720 cm^{-1}; NMR ($CDCl_3$) δ 4.70 (1 H, d, J = 6.5 Hz), 3.73 (3 H, s, COOMe), 3.6–2.8 (4 H, m), 2.5–2.0 (4 H, m).

Anal. Calcd for $C_{13}H_{12}O_5$: C, 62.90; H, 4.87. Found: C, 62.98; H, 5.02.

Reaction of 20 and 21 with Acetic Anhydride. A solution of a mixture of **20** and **21** (1:1 ratio) (0.1 g) in acetic anhydride (1 ml) and pyridine (5 ml) was stirred for 24 h at room temperature. The solution was diluted with water and then extracted with chloroform. The extract was washed with 2 N hydrochloric acid and then with water. The organic solvent was dried over sodium sulfate and evaporated by reduced pressure to give **18** and **19** (total 0.15 g).

Reaction of 23 with Chromic Anhydride. To a solution of **23** (0.5 g) in acetic acid (20 ml), chromic anhydride (0.15 g) was added. Workup as described above gave **22** (0.374 g).

Registry No.—**1,** 51447-09-7; **2,** 35211-83-7; **4,** 58832-37-4; **5,** 58865-34-2; **6,** 58832-38-5; **7,** 58832-39-6; **8,** 58832-40-9; **9,** 58832-41-0; **10,** 58832-42-1; **11,** 58832-43-2; **12,** 58832-44-3; **13,** 58832-45-4; **14,** 58832-46-5; **15,** 58832-47-6; **16,** 58832-48-7; **18,** 58865-35-3; **19,** 58832-49-8; **20,** 58865-36-4; **21,** 58832-50-1; **22,** 58832-51-2; **25,** 58832-52-3; LTA, 546-67-8; *p*-nitrobenzoyl chloride, 122-04-3; TTA, 2570-63-0; TTN, 13746-98-0; silver acetate, 563-63-3; diacetoxy acetal of 2,4,6-cycloheptatriene, 58832-53-4; maleic anhydride, 108-31-6.

References and Notes

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Annulated Cyclopentadienone Ketals. A Route to 1,2-Bridged Norbornenes

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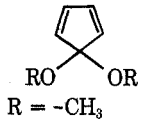
The preparation and properties of a new set of cyclopentadienone ketals are described. These annulated cyclopentadienone ketals are interesting theoretically and are useful in the synthesis of new types of polycyclic systems.

The ketals of cyclopentadienone (**1a–c**) are exceedingly reactive substances; Diels–Alder dimerization occurs very rapidly.[1] The dimethyl ketal **1a,** the least reactive of the set, dimerizes about 270 times faster than cyclopentadiene; the ethylene ketal **1c** dimerizes more than another 1000 times faster. A significant bathochromic shift in the ultraviolet absorption maximum of these dienes has been noted [cyclopentadiene, λ_{max}(pentane) 239 nm; **1a,** 270 nm; **1b,** 272 nm; **1c,** 280 nm] and is most probably related to these large changes in reactivity. The interactions of the cyclopentadiene π system with the nonbonding electrons of the ketal oxygens



1a, R = $-CH_3$
b, RR = $-CH_2CH_2CH_2-$
c, RR = $-CH_2CH_2-$