Synthesis of 3-Mono- and 3,5-Difunctionalized Noriceanes (Tetracyclo-[5.3.1.$0^{2,6}$.$0^{4,9}$]undecanes) *via* Oxymetallation of 3,5-Dehydronoriceane (Pentacyclo[5.3.1.$0^{2,6}$.$0^{3,5}$.$0^{4,9}$]undecane).[1] Oxidation of Bicyclo-[2.1.0]pentane System by Mercury(II), Thallium(III), and Lead(IV) Acetates.

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Oxymercuration of 3,5-dehydronoriceane (**1**) followed by sodium borohydride reduction gives exclusively *endo*-3-noriceanol in 80% yield. The *trans*-1,3-addition organomercury intermediate is isolated as *endo*-3-acetoxy-*exo*-5-(chloromercurio)noriceane. Oxidation of **1** with thallium(III) acetate gives three diacetates, *exo,exo*- and *endo,exo*-3,5-diacetoxynoriceanes [(**9**) and (**10**)] and *endo,exo*-4,5-diacetoxytetracyclo[5.3.1.$0^{2,6}$.$0^{3,9}$]undecane (**11**) in a ratio of 6:61:27 in 68% combined yield. The analogous oxidation of **1** with lead(IV) acetate gives **9**, **10**, and **11** in a ratio of 50:25:25 in 80% combined yield. On the basis of the stereochemistry of the products as well as the products distribution, we propose that 1,3-bridged metal ion intervenes and plays an important role in the oxymetallation reaction of bicyclo[2.1.0]pentane system.

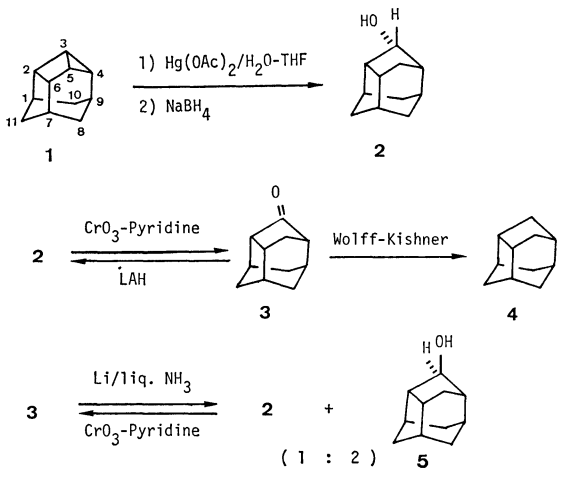
Electrophilic or radical-type cleavage of cyclopropane ring in a cage molecule has proved to become one of the powerful methods of functionalizing a cage compound.[2] Oxidative cleavages of cyclopropane rings by mercury(II), thallium(III), and lead(IV) salts give mono- and difunctionalized compounds *via* oxymetallations. We have recently reported the synthesis of 3,5-dehydronoriceane (**1**),[3] which incorporates bicyclo-[2.1.0]pentane moiety in its cage structure. Since oxidations of highly strained bicyclo[2.1.0]pentane with the metal salts have been reported to rupture the central bond exclusively,[4] we anticipate that **1** can give hitherto unknown 3-mono- and 3,5-difunctionalized noriceanes when allowed to react with the metal salts. In addition to this synthetic possibility, the bicyclo-[2.1.0]pentane system fixed in the cage structure is expected to provide some mechanistic insight which is concerned with the stereochemistry of the initial attack of the metal ion and remains to be explored.[5]

Results

*Oxidation of **1** with Mercury(II) Acetate.* When **1** was treated with mercuric acetate in aqueous THF and subsequently reduced with sodium borohydride, *endo*-3-noriceanol (**2**) was obtained as a sole product in 80% yield. The structure of **2** was determined as follows. Oxidation of **2** with CrO_3–pyridine complex gave a keto compound, 3-noriceanone (**3**), which was reduced to afford noriceane (**4**)[3] by Wolff-Kishner (W-K) method, confirming a parent skeleton of **2**. Whereas reduction of **3** with lithium aluminum hydride reproduced **2**, a treatment of **3** with lithium in liquid ammonia gave **2** and its stereoisomer, *exo*-3-noriceanol (**5**) in 85% combined yield (**2**:**5**=1:2 by ^{1}H-NMR (PMR) analysis). Although the separation of **5** from **2** was unsuccessful, the regeneration of **3** in the oxidation of the mixture indicated that **5** and **2** were stereoisomeric with each other in reference to the 3-position.[6] An inspection of molecular model (Dreiding) suggests us that *exo*-H on the 3-position should couple more with the adjacent protons in PMR spectroscopy than the *endo*-one does. Since the PMR spectra of **2** and **5** show a broad singlet with half-width of 8.0 Hz at 3.90 ppm and a singlet with half-width of 3.4 Hz at 4.30 ppm, respectively, we conclude that **2** is *endo*-3-noriceanol and that **5** is the *exo*-isomer.

In addition to the above elucidation, we inspected the PMR spectra of **2** and 3-noriceanol-5-*d* (**6**), which was prepared by the oxymercuration of **1** followed by the reduction with sodium borodeuteride, by using NMR shift reagent [Eu(dpm)$_3$]. As is shown in Fig. 1, the results of PMR shift experiment for **2** are compatible with the assigned structure of **2**. Figure 2 shows partial PMR spectra of **2** and **6** in the presence of Eu(dpm)$_3$. The signal shown as a doublet of doublet (J=5.5 and 12.0 Hz) at *ca.* 6.6 ppm (*viz.* H_{5X}) in Fig. 2a disappears in Fig. 2b and the signal shown as a doublet (J=12.0 Hz) at *ca.* 5.9 ppm (*viz.* H_{5N}) in Fig. 2a appears as a singlet in Fig. 2b. Since Fig. 1 indicates that the slope for H_{5X} is slightly steeper than that for H_{5N}, H_{5X}, and H_{5N} must be *exo*- and *endo*-protons, respectively. These results imply that deuterium is exclusively located on the *exo*-5-position and, therefore, **6** is determined to be *endo*-3-hydroxy-*exo*-5-deuteronoriceane.

In order to gain further insight about the stereochemistry of the oxymercuration of the bicyclo[2.1.0]-



Scheme 1.

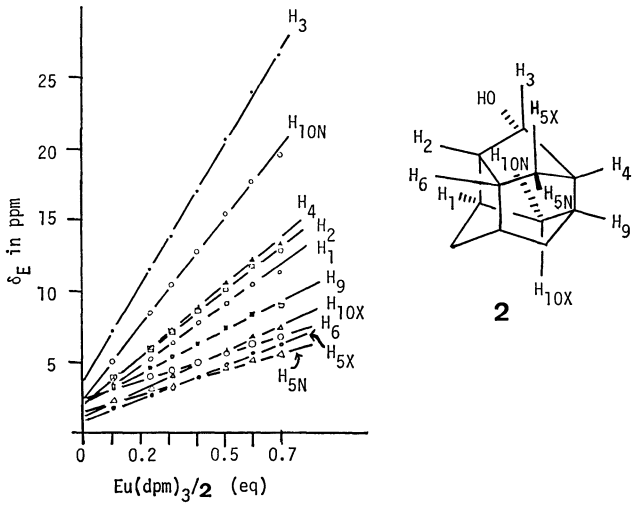


Fig. 1. Variation of chemical shift, δ_E, with molar ratio Eu(dpm)$_3$/**2**.

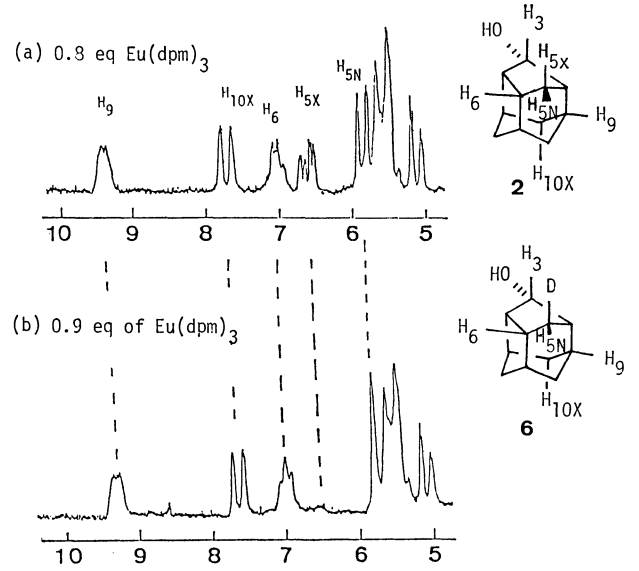
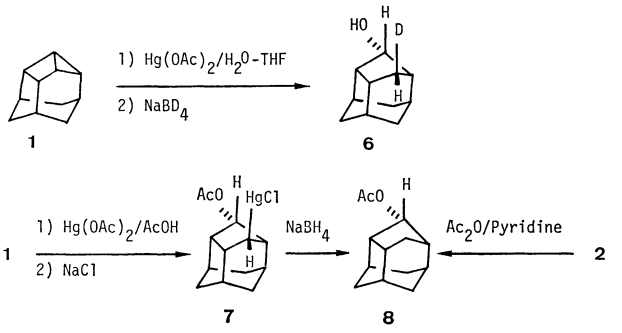


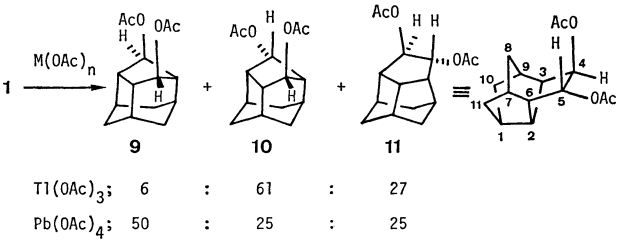
Fig. 2. Partial PMR spectra of **2** and **6** in the presence of Eu(dpm)$_3$; a for **2**, b for **6**.

pentane system, a organomercury intermediate was intentionally isolated and examined. A reaction of **1** with mercury(II) acetate in glacial acetic acid followed by an addition of sodium chloride gave an organomercury compound (**7**) in 95% yield. The compound, **7**, was reduced with sodium borohydride to give *endo*-3-acetoxynoriceane (**8**), which was also obtained by acetylation of the alcohol, **2**. A similar PMR shift experiments with **7** and **8** to the above led to the conclusion that **7** is *endo*-3-acetoxy-*exo*-5-(chloromercurio)noriceane (Scheme 2); this implies that the oxymercuration must proceed in a *trans*-fashion.

Oxidations of ***1*** *with Thallium(III) and Lead(IV) Acetates.* When **1** was oxidized with thallium(III) acetate in glacial acetic acid at room temperature for 4 h, three diacetates, *exo,exo*-3,5- and *endo,exo*-3,5-diacetoxynoriceanes (**9** and **10**) and *endo,exo*-4,5-diacetoxytetracyclo[5.3.1.0^{2,6}.0^{4,9}]undecane (**11**), were obtained along with a small amount of an unidentified product (**12**) (**9**:**10**:



Scheme 2.



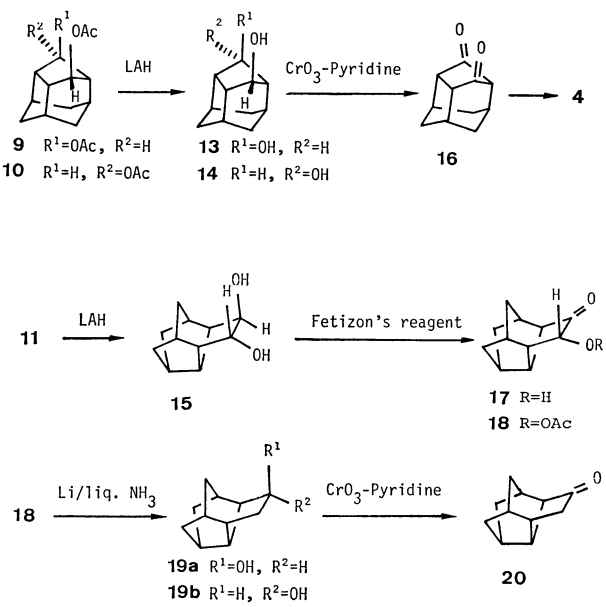
Tl(OAc)$_3$;	6	:	61	: 27
Pb(OAc)$_4$;	50	:	25	: 25

Scheme 3.

11:**12**=6:61:27:6, estimated from the area ratio in GLC analysis) in 68% combined yield. A similar oxidation of **1** with lead(IV) acetate at room temperature for 24 h gave the same three products, **9**, **10**, and **11** (**9**:**10**:**11**=50:25:25 by GLC analysis) in 80% combined yield.

The structures of **9** and **10** were determined as follows. The diacetates, **9** and **10**, were separated by preparative GLC and reduced to the corresponding diols (**13** and **14**) with lithium aluminum hydride, respectively. Oxidations of **13** and **14** with CrO_3–pyridine complex gave one kind of diketone, 3,5-noriceanedione (**16**), which afforded noriceane (**4**) on base-catalyzed reduction of the semicarbazone of **16**. Accordingly, it is evident that **9** and **10** are stereoisomeric 3,5-diacetoxynoriceanes. Out of three possible isomers, *endo,endo*-3,5- and *exo,exo*-3,5-isomers have a plane of symmetry, whereas *endo,exo*-one does not. Since ^{13}C-NMR (CMR) and PMR spectra of **10** showed a lack of the symmetry, **10** was determined to be *endo, exo*-3,5-diacetoxynoriceane. On the other hand, CMR spectrum of **9** indicated the presence of symmetry and its PMR spectrum showed a singlet with a half-width of 2.7 Hz at 5.17 ppm, indicating the *exo*-configuration of the substituents at 3- and 5-positions (*vide supra*). Thus, **9** was determined to be *exo,exo*-3,5-diacetoxynoriceane.

The structure of **11** was determined by the following chemical transformations. Reduction of **11** followed by oxidation with Fetizon's reagent[7] gave *exo*-5-hydroxytetracyclo[5.3.1.0^{2,6}.0^{3,9}]undecan-4-one (**17**).[8] Acetylation of **17** with acetic anhydride in pyridine gave *exo*-5-acetoxytetracyclo[5.3.1.0^{2,6}.0^{3,9}]undecan-4-one (**18**). Reductive cleavage of **18** with lithium in liquid ammonia gave a mixture of stereoisomeric tetracyclo[5.3.1.0^{2,6}.0^{3,9}]undecan-4-ols (**19a** and **19b**).[6] Subsequent oxidation of the mixture gave tetracyclo[5.3.1.0^{2,6}.0^{3,9}]undecan-4-one (**20**).[6] As the PMR and



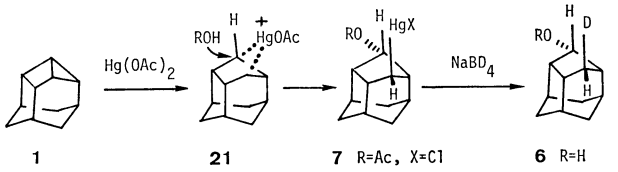
Scheme 4.

CMR spectra of **11** showed a lack of a plane of symmetry, **11** was determined to be *endo,exo*-4,5-diacetoxytetracyclo[5.3.1.$0^{2,6}$.$0^{3,9}$]undecane.

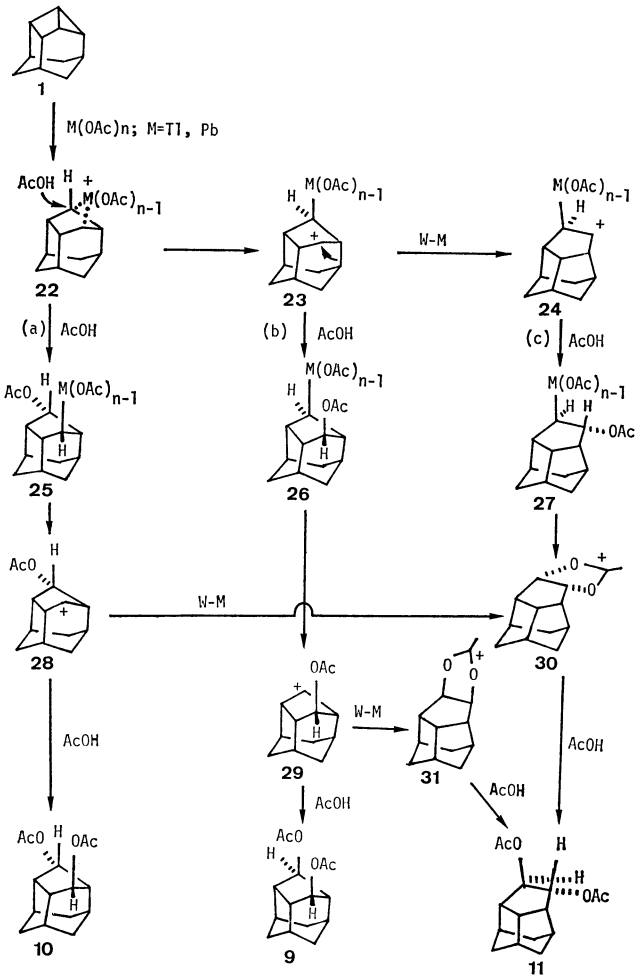
Discussion

The structures of **6** as well as **7** allow us to delineate the following scheme as a possible reaction pathway (Scheme 5). An initial electrophilic attack on the bicyclo[2.1.0]pentane system by mercury(II) ion must take place from the front side of the central bond with retention of configuration to produce the 1,3-bridged acetoxymercurium ion (**21**).[9] This is subsequently captured by nucleophilic solvent with complete inversion of configuration. By taking account of the fact that solvolyses of 3-noricyl tosylates give nothing but *exo*-3-noricyl acetate and a considerable amount of the rearranged products,[6] we can safely conclude that the 1,3-bridged ion (**21**) intervenes significantly in the oxymercuration reaction of bicyclo-[2.1.0]pentane system. Although Levina *et al.* reported that the oxymercuration of bicyclo[2.1.0]pentane itself gave 3-hydroxycyclopentylmercury(II) acetate,[4b] the stereochemistry of the product was not studied. We believe that the present result is the first example which clarifies a stereochemical course and provides a strong evidence for an intervention of an 1,3-bridged mercurium ion in oxymercuration reaction of bicyclo-[2.1.0]pentane system. In addition, it is noteworthy that reduction of the organomercury compound with sodium borohydride proceeds with retention of configuration.

In the cases of oxidations with thallium(III) and lead(IV) acetates, the reaction pathways are more speculative than the above because an isolation of the corresponding organometallic intermediates has been impossible and, accordingly, their decomposition modes are unknown. Judging from the fact that the reactions lack the stereoselectivity and that some amount of the rearranged product, **11**, is obtained, it is highly



Scheme 5.



Scheme 6.

probable that a free carbocation character is involved in the reactions. The following rather simple scheme (Scheme 6) may reasonably explain the results. The initial attack on the bicyclo[2.1.0]pentane system by the metal ion would take place from the front-side to produce the 1,3-bridged metal ion (**22**) analogous to **21** in the case of the oxymercuration. Nucleophilic capture of **22** with the solvent gives an *endo*-acetoxyorganometallic intermediate (**25**), which, on decomposition, could produce a "free" carbocation intermediate (**28**). The *endo,exo*-diacetates (**10**) is the expected product in nucleophilic capture of **28** with the solvent, because, as described before, 3-noricyl cation formed in the solvolysis is attacked by nucleophile exclusively from the *exo*-side[6] (path a in Scheme 6).

When the 1,3-bridged metal ion (**22**) is so unstable as to convert into a "free" carbocation (**23**), an *exo*-acetoxyorganometallic intermediate (**26**) may be formed by the same reason as described above. Subsequent

decomposition and nucleophilic capture could afford the *exo,exo*-diacetate (**9**) (path b in Scheme 6). The "free" carbocation (**23**) is also possibly subjected to Wagner-Meerwein rearrangement into tetracyclo[5.3.1.$0^{2,6}$.$0^{3,9}$]undecane system (**24**), which could give the *trans*-diacetate (**11**) *via* 1,2-acetoxyl-participation (path c). The diacetate (**11**) could be also formed from **28** as well as **29** through the pathways shown in the Scheme.

Thus, it can be safely said that the amount of the *endo,exo*-diacetate (**10**) depends on the stability of the 1,3-bridged metal ion (**22**). The fact that the yield of **10** is higher with thallium(III) acetate than with lead(IV) acetate implies that **22** (M=Tl) is more stable than **22** (M=Pb). In addition, it is evident that **22** (M=Hg, namely **21**) is much more stable than the both (**22**, M=Tl and Pb). This order of stability of the 1,3-bridged metal ions (Hg>Tl>Pb) is consistent with the order of the stability of C–M bonds (Hg>Tl>Pb).[10]

In conclusion, it has been found that oxymetallations of 3,5-dehydronoriceane (**1**) with mercury(II), thallium(III), and lead(IV) acetates give 3-mono- and 3,5-difunctionalized noriceanes in good yields along with a small amount of *trans*-4,5-difunctionalized tetracyclo[5.3.1.$0^{2,6}$.$0^{3,9}$]undecane. The present results also provide the first evidence for an intervention of an 1,3-bridged metal ion in oxymetallation reaction of bicyclo[2.1.0]pentane system.

Experimental

All the temperatures were uncorrected. The melting points were measured in sealed capillaries. The IR spectra were obtained on a Shimadzu IR-27 spectrometer. The mass spectra were taken by using a Hitachi RMS-4 mass spectrometer. The PMR and CMR spectra were obtained on Varian EM-390 and CFT-20 spectrometers, TMS being chosen as the internal standard. The microanalyses were performed by Kyoto University Elemental Analysis Center.

endo-*Tetracyclo*[*5.3.1.*$0^{2,6}$.$0^{4,9}$]*undecan-3-ol* (***2***). To a solution of $Hg(OAc)_2$ (478 mg; 1.5 mmol) in THF (3 ml) and water (3 ml) was added pentacyclo[5.3.1.$0^{2,6}$.$0^{3,5}$.$0^{4,9}$]-undecane (**1**) (219 mg; 1.5 mmol) and the mixture was stirred for 1 h at room temperature. Then, 3 M aqueous NaOH (3 ml) and subsequently 3 ml of a solution of 0.5 M $NaBH_4$ in 3 M aqueous NaOH were added and the mixture was stirred for additional 1 h. After the precipitated mercury was removed by filtration, organic materials were extracted with CH_2Cl_2, washed with brine, and dried (Na_2SO_4). After filtration, the solvent was evaporated and the residue was chromatographed on silica gel. Elution by hexane and ether (1:1) gave **2** (198 mg, 80%): mp 270 °C. MS *m/e* (rel intensity): 164 (M^+, 70), 146 (45), 135 (51), 92 (50), 91 (46), 80 (99), 79 (95), 68 (100). IR (KBr): 3200, 2930, 1465, 1300, 1290, 1160, 1090, 1055 cm^{-1}. PMR δ ($CDCl_3$): 3.90 (1H, br. s, $W_{1/2}$=8.0 Hz), 2.67—0.80 (15H, br, complex m). CMR δ ($CDCl_3$): 76.9 (CH), 44.8 (CH), 42.1 (CH), 41.4 (CH_2), 38.5 (CH), 38.4 (CH), 36.7 (CH), 31.9 (CH_2), 31.4 (CH_2), 30.7 (CH), 24.4 (CH_2). Found: C, 80.51; H, 9.89%. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83%.

Tetracyclo[*5.3.1.*$0^{2,6}$.$0^{4,9}$]*undecan-3-one* (***3***). To a solution of pyridine (5 ml) in CH_2Cl_2 (25 ml) was added gradually CrO_3 (730 mg; 7.3 mmol) and then a solution of **2** (195 mg; 1.2 mmol) in CH_2Cl_2 (20 ml). The reaction mixture was stirred for 1 h at room temperature and washed with 5% aqueous NaOH, 5% aqueous HCl, and brine, and dried (Na_2SO_4). After filtration, the solvent was evaporated and the residue was chromatographed on silica gel. Elution by hexane and ether (3:1) afforded **3** (183 mg, 95%): mp 259—261 °C. MS *m/e* (rel intensity): 162 (M^+, 98), 134 (92), 92 (99), 79 (100). IR (Nujol): 2925, 1750, 1460, 1370 cm^{-1}. PMR δ ($CDCl_3$): 2.95—1.10 (14H, br. complex m). CMR δ ($CDCl_3$): 221.7 (C=O), 51.5 (CH), 45.7 (CH), 43.5 (CH), 41.8 (CH_2), 41.4 (CH), 38.6 (CH), 34.0 (CH), 32.3 (CH_2), 30.2 (CH_2), 21.6 (CH_2). Found: C, 81.31; H, 8.69%. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70%.

Wolff-Kishner Reduction of ***3*** *to Tetracyclo*[*5.3.1.*$0^{2,6}$.$0^{4,9}$]-*undecane* (***4***). A solution of **3** (120 mg; 0.74 mmol), KOH (600 mg; 10.7 mmol), 100% $NH_2NH_2 \cdot H_2O$ (470 mg; 9.4 mmol) in diethylene glycol (3 ml) was stirred at 110 °C for 30 min and then at 180 °C for 3 h. Sublimate on the condenser was dissolved in hexane and washed with brine, and dried (Na_2SO_4). After filtration, the solvent was evaporated to give almost pure **4** (96 mg, 88%), which was identical with the authentic specimen[3] in all respects (GLC retention time, mass, PMR, and CMR spectra).

Reduction of ***3***. (*a*): To a suspension of $LiAlH_4$ (146 mg; 3.8 mmol) in dry ether (5 ml) was added dropwise a solution of **3** (125 mg; 0.77 mmol) in dry ether (5 ml). The reaction mixture was stirred at room temperature for 30 min and then quenched with sat aqueous Na_2SO_4. The organic layer was separated, washed with brine, and dried (Na_2SO_4). After filtration, the solvent was evaporated to give **2** (118 mg, 97%) as a sole product (PMR analysis). (*b*): A solution of **3** (230 mg; 1.4 mmol) in dry ether (10 ml) was added to dry liq ammonia (50 ml) at −78 °C. To this mixture were added NH_4Cl (6.15 g; 115 mmol) and then Li (559 mg; 80 mmol) in small pieces over 30 min. The reaction mixture was refluxed until the blue color disappeared. The ammonia was evaporated and water (50 ml) was added. The aqueous solution was acidified with 5% aqueous HCl and extracted with ether. The ethereal solution was washed with sat aqueous $NaHCO_3$ and brine, and dried (Na_2SO_4). After filtration, the solvent was evaporated and the residue was chromatographed on silica gel. Elution by hexane and ether (1:1) gave a mixture of **2** and *exo*-tetracyclo[5.3.1.$0^{2,6}$.$0^{4,9}$]undecan-3-ol (**5**) (197 mg, 85%). Although **5** could not be separated from **2** by either column chromatography or GLC, a comparison of the PMR spectrum of the mixture with that of pure **5**[6] indicated that a ratio of **2** to **5** was 1:2. Furthermore, the mixture (39 mg; 0.24 mmol) was oxidized with CrO_3 (204 mg; 2.0 mmol) and pyridine (0.8 ml) in CH_2Cl_2 (5 ml) reproduced **3** (32 mg, 83%).

endo-*3-Hydroxy*-exo-*5-deuterotetracyclo*[*5.3.1.*$0^{2,6}$.$0^{4,9}$]*undecane* (***6***). A similar oxymercuration reaction of **1** (292 mg; 2.0 mmol) to the above followed by reduction with $NaBD_4$ gave **6** (200 mg, 61%). The extent of monodeuteration was shown to be 90% by mass spectroscopic analysis. ***6***: Mp >270 °C. MS *m/e* (rel intensity): 165 (M^+, 76), 147 (32), 136 (40), 93 (44), 92 (50), 80 (100), 79 (82), 69 (82). IR (KBr): 3320, 2940, 1485, 1385, 1295, 1160, 1095, 1055 cm^{-1}. PMR δ ($CDCl_3$): 3.88 (1H, br. s, $W_{1/2}$=7.8 Hz), 2.70—1.20 (12H, br. complex m), 1.03 (2H, d, J=12.0 Hz). CMR δ ($CDCl_3$): 76.9 (CH), 44.7 (CH), 42.0 (CH), 41.4 (CH_2), 38.4 (2CH), 36.7 (CH), 31.9 (CH_2), 31.4 (CH_2), 30.6 (CH), 25.0, 24.0, 23.0 (CHD). Found: C, 79.93; H(D), 10.53%. Calcd for $C_{11}H_{15}DC$: C, 79.95; H(D), 10.37%.

endo-*3-Acetoxy*-exo-*5-(chloromercurio)tetracyclo*[*5.3.1.*$0^{2,6}$.$0^{4,9}$]-*undecane* (***7***). A solution of $Hg(OAc)_2$ (118 mg; 0.37

mmol) and **1** (50 mg; 0.34 mmol) in glacial AcOH (1 ml) was stirred at room temperature for 1 h. To the mixture was added a solution of NaCl (242 mg; 4.1 mmol) in ice-water (10 ml). After 20 min, white precipitates were collected by filtration and washed with water, and dried over P_2O_5 at reduced pressure to give **7** (144 mg, 95%): mp 183—186 °C. IR (KBr): 2925, 1735, 1370, 1455, 1065 cm^{-1}. PMR δ ($CDCl_3$): 4.58 (1H, dd, J=5.5 and 2.5 Hz), 2.08 (3H, s), 3.00—0.85 (13H, br. complex m). Found: C, 35.65; H, 4.15%. Calcd for $C_{13}H_{17}ClHgO_2$: C, 35.38; H, 3.88%.

endo-*3-Acetoxytetracyclo*[*5.3.1.0*^{2,6}*.0*^{4,9}]*undecane* (***8***). *(a)*: A solution of **2** (51 mg; 0.31 mmol) in pyridine (0.5 ml) and acetic anhydride (0.25 ml) was kept at room temperature overnight. The mixture was poured onto 5% aqueous HCl and extracted with CH_2Cl_2. The organic layer was washed with aqueous Na_2CO_3 and brine, and dried (Na_2SO_4). After filtration, the solvent was evaporated and the residue was chromatographed on silica gel. Elution by hexane and CH_2Cl_2 (4:1) afforded **8** (59 mg, 91%): bp 90 °C (bath temp)/1995 Pa. MS *m/e* (rel intensity): 206 (M^+, 7), 146 (100). IR (neat): 2930, 1745, 1365, 1245, 1070, 1055 cm^{-1}. PMR δ (CCl_4): 4.55 (1H, br. s), 2.00 (3H, s), 2.70—0.85 (14H, br. complex m). CMR δ ($CDCl_3$): 170.9 (C=O), 78.2 (CH), 42.7 (CH), 41.7 (CH), 41.3 (CH_2), 38.4 (CH), 36.8 (CH), 36.3(CH), 31.6 (CH_2), 31.5 (CH_2), 30.6 (CH), 23.9 (CH_2), 21.5 (CH_3). Found: C, 75.74; H, 8.86%. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80%.

(b): To a solution of **7** (42 mg; 0.10 mmol) in THF (2 ml) was added a solution of $NaBH_4$ (23 mg; 0.61 mmol) in 3 mol dm^{-3} aqueous NaOH (1 ml) and the mixture was stirred at room temperature. After 1 h, CH_2Cl_2 was added to the mixture and the mercury was removed by filtration. The organic solution was washed with brine and dried (Na_2SO_4). After filtration, the solvent was evaporated and the residue was chromatographed on silica gel. Elution by hexane and CH_2Cl_2 (4:1) gave **8** (10 mg, 50%) which was identical with that prepared above.

Oxidation of ***1*** *with Thallium(III) Acetate.* A solution of **1** (147 mg; 1.0 mmol) and $Tl(OAc)_3$ (572 mg, 1.5 mmol) in glacial AcOH (10 ml) was stirred at room temperature for 4 h under argon. Then, CH_2Cl_2 and water was added to the mixture. After filtration, the organic layer was washed with brine and aqueous $NaHCO_3$, and dried (Na_2SO_4). After filtration, the solvent was evaporated and the residue was chromatographed on silica gel. Elution by hexane and CH_2Cl_2 (7:3) gave a mixture of the three diacetates (**9**, **10**, and **11**) along with a small amount of an unidentified product (**12**) (181 mg, 68%). A ratio of **9**, **10**, **11**, and **12** was estimated to be 6:61:27:6 (GLC analysis, AP 180 °C). Each of **9**, **10**, and **11** was isolated by preparative GLC. *exo,exo*-3,5-Diacetoxytetracyclo[5.3.1.$0^{2,6}$.$0^{4,9}$]undecane (**9**): mp 77—79 °C. MS *m/e* (rel intensity): 264 (M^+, 5), 221 (26), 162 (100). IR (neat): 2925, 1730, 1370, 1270, 1240, 1050 cm^{-1}. PMR δ (CCl_4): 5.17 (2H, s), 1.95 (6H, s), 2.80—1.40 (10H, br. complex m), 1.07 (2H, d, J=13.5 Hz). CMR δ ($CDCl_3$): 170.5 (C=O), 76.8 (CH), 47.9 (CH), 41.2 (CH), 40.4 (CH_2), 39.8 (CH), 33.5 (CH), 31.0 (CH_2), 21.3 (CH_3). Found: C, 68.06; H, 7.50%. Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63%. *endo,exo*-3,5-Diacetoxytetracyclo[5.3.1.$0^{2,6}$.$0^{4,9}$]undecane (**10**): mp 71—73 °C. MS *m/e* (rel intensity): 264 (M^+, 10), 221 (37), 162 (100). IR (neat): 2930, 1740, 1730, 1365, 1245, 1080, 1050, 1025 cm^{-1}. PMR δ (CCl_4): 5.20 (1H, dd, J=5.7 and 2.0 Hz), 5.02 (1H, d, J=1.2 Hz). 2.02 (6H, s), 2.80—1.40 (10H, br. complex m), 1.08 (2H, d, J=13.5 Hz). CMR δ ($CDCl_3$): 170.7 (C=O), 74.1 (CH), 72.9 (CH), 47.8 (CH), 42.5 (CH), 42.0 (CH_2), 40.5 (CH), 38.8 (CH), 36.6 (CH), 32.1 (CH+CH_2), 30.9 (CH_2), 21.4 (CH_3). Found: C, 68.16; H, 7.45%. Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63%. *endo,exo*-4,5-Diacetoxytetracyclo[5.3.1.$0^{2,6}$.$0^{3,9}$]undecane (**11**): bp 90—100 °C (bath temp)/133 Pa. MS *m/e* (rel intensity): 204 (M^+—AcOH, 17), 162 (100). IR (neat): 2935, 1750, 1735, 1370, 1240, 1045, 1025 cm^{-1}. PMR δ (CCl_4): 5.20 (1H, dd, J=3.0 and 6.0 Hz), 5.07 (1H, d, J=3.0 Hz), 2.03 (3H, s), 2.00 (3H, s), 2.93—1.20 (12H, br. complex m). CMR δ ($CDCl_3$): 170.4 (C=O), 83.5 (CH), 80.8 (CH), 54.5 (CH), 53.9 (CH), 47.6 (CH), 43.0 (CH_2), 42.8 (CH_2), 39.3 (CH), 39.1 (CH), 37.1 (CH), 31.0 (CH_2), 21.1 (CH_3), 20.9 (CH_3). Found: C, 68.11; H, 7.73%. Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63%.

Oxidation of ***1*** *with Lead(IV) Acetate.* A solution of **1** (219 mg; 1.5 mmol) and $Pb(OAc)_4$ (665 mg; 1.5 mmol) in glacial AcOH (22 ml) was stirred at room temperature for 24 h. The mixture was poured onto water and extracted with CH_2Cl_2. The organic layer was washed with aqueous $NaHCO_3$ and brine, and dried (Na_2SO_4). After filtration, the solvent was evaporated to give a crude mixture of **9**, **10**, and **11** (430 mg, **9**:**10**:**11**=50:25:25), which was purified by preparative TLC (silica gel, hexane:ether=1:1) to afford a mixture of **10** and **11** (153 mg, 39%) and **9** (161 mg, 41%).

exo,exo-*3,5-Dihydroxytetracyclo*[*5.3.1.0*^{2,6}*.0*^{4,9}]*undecane* (***13***). To a suspension of $LiAlH_4$ (268 mg; 7.1 mmol) in dry ether (10 ml) was added dropwise a solution of **9** (155 mg; 0.59 mmol) in dry ether (10 ml). The mixture was refluxed overnight and quenched with AcOEt and sat aqueous Na_2SO_4, and the organic layer was separated and dried (Na_2SO_4). After filtration, the solvent was evaporated to give **13** (103 mg, 97%): mp 186—190 °C. MS *m/e* (rel intensity): 180 (M^+, 8), 162 (59), 134 (100). IR (KBr): 3225, 2920, 1235, 1095, 1070, 1045 cm^{-1}. PMR δ ($CDCl_3$): 5.10 (2H, s, 20H), 4.48 (2H, s), 2.75—2.20 (6H, br. complex m), 1.95—1.40 (4H, br. complex m), 0.98 (2H, d, J=13.5 Hz). CMR δ ($CDCl_3$): 75.4 (CH), 50.6 (CH), 42.8 (CH), 41.4 (CH), 38.8 (CH), 33.0 (CH), 30.9 (CH_2). Found: C, 73.01; H, 9.10%. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95%.

endo,exo-*3,5-Dihydroxytetracyclo*[*5.3.1.0*^{2,6}*.0*^{4,9}]*undecane* (***14***). A similar reduction of **10** (87 mg; 0.33 mmol) with $LiAlH_4$ (150 mg; 3.9 mmol) to the above gave **14** (58 mg, 98%): mp >270 °C. MS *m/e* (rel intensity): 180 (M^+, 7), 162 (40), 134 (98), 91 (100). IR (KBr): 3300, 2925, 1085, 1065, 1040, 1020 cm^{-1}. PMR δ (DMSO-d_6): 4.57 (2H, s, 20H), 4.40 (1H, dd, J=3.2 Hz), 3.97 (1H, s), 2.67 (1H, d, J=12.0 Hz), 2.45—1.07 (9H, br. complex m), 0.90 (2H, d, J=12.0 Hz). CMR δ (DMSO-d_6): 69.2 (CH), 67.9 (CH), 49.9 (CH), 44.1 (CH), 43.6 (CH), 41.9 (CH_2), 37.9 (CH), 36.1 (CH), 31.7 (CH_2), 31.5 (CH), 30.7 (CH_2). Found: C, 73.44; H, 9.24%. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95%.

endo,exo-*4,5-Dihydroxytetracyclo*[*5.3.1.0*^{2,6}*.0*^{3,9}]*undecane* (***15***). A similar reduction of **11** (56 mg; 0.21 mmol) with $LiAlH_4$ (143 mg: 3.8 mmol) to the above gave **15** (37 mg, 96%): mp 197—199 °C. MS *m/e* (rel intensity): 180 (M^+, 40), 162 (41), 96 (100), 83 (94), 82 (91). IR (KBr): 3330, 2925, 1090, 1035, 1015, 1005 cm^{-1}. PMR δ (DMSO-d_6): 4.60 (2H, s, 20H), 4.10 (1H, br. s), 3.87 (1H, s), 2.85—1.10 (12H, br. complex m). CMR δ (DMSO-d_6): 84.2 (CH), 80.1 (CH), 57.5 (CH), 56.4 (CH), 46.8 (CH), 42.8 (CH_2), 42.5 (CH_2), 39.0 (CH), 38.3 (CH), 36.3 (CH), 30.8 (CH_2). Found: C, 73.00; H, 9.08%. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95%.

Tetracyclo[*5.3.1.0*^{2,6}*.0*^{4,9}]*undecane-3,5-dione* (***16***). Oxida-

tion of **13** (134 mg; 0.74 mmol) with CrO_3 (1350 mg; 13.5 mmol)-pyridine complex in a similar manner to the above gave **16** (80 mg, 61%): mp 184—187 °C. MS *m/e* (rel intensity): 176 (M^+, 93), 166 (66), 79 (50), 66 (100). IR (KBr): 2935, 1770, 1735, 1215, 1145, 1080 cm^{-1}. PMR δ (CCl_4): 3.30—2.50 (6H, br. complex m), 2.20—1.50 (6H, br. complex m). CMR δ ($CDCl_3$): 210.3 (C=O), 63.5 (CH), 59.9 (CH), 46.9 (CH), 44.7 (CH), 42.6 (CH_2), 33.0 (CH_2). Found: C, 74.71; H, 7.12%. Calcd for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86%. A similar oxidation of **14** (52 mg; 0.29 mmol) with CrO_3 (515 mg; 5.2 mmol)-pyridine complex also afforded **16** (43 mg, 85%).

*Reduction of **16** to **4**.* Semicarbazide hydrochloride (300 mg; 2.7 mmol) and KOAc (300 mg; 3.1 mmol) were dissolved in a mixture of water (1 ml) and methanol (3 ml), and undissolved materials were removed by filtration. The diketone (**16**) (52.8 mg; 0.30 mmol) was dissolved in the above solution (1 ml) and kept at room temperature for one week. The precipitates (61 mg) were collected by filtration and dissolved in diethylene glycol (2 ml) containing KOH (153 mg; 2.7 mmol). The mixture was heated at 110 °C for 1 h and subsequently at 180 °C for 20 h. Sublimate on the condenser was dissolved in pentane and washed with brine, and dried (Na_2SO_4). After filtration, the solvent was evaporated and the residue was chrmatographed on silica gel. Elution by pentane gave **4** (4 mg, 9%) as a sole product, which was identical with authentic specimen.[3]

exo-*5-Hydroxytetracyclo[5.3.1.$0^{2,6}$.$0^{3,9}$]undecan-4-one (**17**).* A suspension of **15** (37 mg; 0.21 mmol) and Fetizon's reagent (1.2 g)[7] in dry benzene (50 ml) was stirred under reflux for 1 d. After filtration, the solvent was evaporated to give **17** (31 mg, 85%): mp 141—143 °C. MS *m/e* (rel intensity): 178 (M^+, 100), 150 (32), 79 (42). IR (KBr): 3375, 2930, 2880,1735, 1175, 1035 cm^{-1}. PMR δ ($CDCl_3$): 4.03 (1H, s), 3.30—1.15 (13H, br. complex m). CMR δ ($CDCl_3$): 221.5 (C=O), 75.5 (CH), 60.3 (CH), 53.6 (CH), 47.2 (CH), 44.2 (CH_2), 43.0 (CH_2), 42.2 (CH), 39.7 (CH), 39.3 (CH), 31.0 (CH_2). Found: C, 74.28; H, 8.08%. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92%.

exo-*5-Acetoxytetracyclo[5.3.1.$0^{2,6}$.$0^{3,9}$]undecan-4-one (**18**).* A solution of **17** (31 mg; 0.17 mmol) and acetic anhydride (0.2 ml) in pyridine (0.4 ml) was kept at room temperature overnight and poured onto 5% aqueous HCl. The mixture was extracted with CH_2Cl_2 and washed with aqueous Na_2CO_3 and brine, and dried (Na_2SO_4). After filtration, the solvent was evaporated to give **18** (33 mg, 73%): bp 90—100 °C (bath temp)/133 Pa. MS *m/e* (rel intensity): 220 (M^+, 13), 178 (100), 160 (20), 91 (14). IR (neat): 2930, 2880, 1745, 1370, 1225, 1175, 1035 cm^{-1}. PMR δ (CCl_4): 4.48 (1H, s), 2.07 (3H, s), 3.20—1.15 (12H, br. complexm). CMR δ ($CDCl_3$): 216.5 (C=O), 169.9 (C=O), 76.5 (CH), 60.9 (CH), 52.2 (CH), 47.3 (CH), 44.1 (CH_2), 42.8 (CH_2), 42.1 (CH), 39.7 (CH), 39.5 (CH), 30.8 (CH_2), 20.8 (CH_3). Found: C, 71.04; H, 7.28%. Calcd for $C_{13}H_{16}O_2$: C, 70.89; H, 7.32%.

*Chemical Transformation of **18** to Tetracyclo[5.3.1.$0^{2,6}$.$0^{3,9}$]-undecan-4-one (**20**).* To liquid ammonia (10 ml) was added at −78 °C a solution of **18** (33 mg; 0.15 mmol) in dry ethyl ether (3 ml) and subsequently small pieces of lithium (112 mg; 16 mmol). The mixture was refluxed for 5 h and ammonia was evaporated. After an addition of water, the mixture was extracted with ether, washed with brine, and dried (Na_2SO_4). After filtration, the solvent was evaporated to give a mixture of tetracyclo[5.3.1.$0^{2,6}$.$0^{3,9}$]-undecan-4-ols (**19a** and **19b**, *ca.* 1:1 by PMR analysis, 20 mg, 81%),[6] which, on oxidation with CrO_3-pyridine complex, afforded **20** as a sole product (13 mg, 63%). The ketone (**20**) was identical with that prepared by the different route.[6]

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References

1) In cases where there is no ambiguity, we have used trivial nomenclatures for simplicity. The IUPAC names are described in Experimental Section.

2) For example, a) A. C. Udding, J. Strating, and H. Wynberg, *Tetrahedron Lett.*, **1968**, 1345; b) D. Farcasiu and P. v. R. Schleyer, *ibid.*, **1973**, 1835; c) R. Yamaguchi, T. Katsushima, and M. Kawanisi, *Bull. Chem. Soc. Jpn.*, **48**, 2328 (1975); d) R. Yamaguchi and M. Kawanisi, *Chem. Lett.*, **1975**, 649; e) D. F. Covey and A. Nickon, *J. Org. Chem.*, **42**, 794 (1977).

3) T. Katsushima, R. Yamaguchi, and M. Kawanisi, *J. Chem. Soc., Chem. Commun.*, **1975**, 692.

4) a) R. Criegee and A. Rimmelin, *Chem. Ber.*, **90**, 414 (1957); b) R. Y. Levina, V. N. Kostin, and T. K. Ustynyuk, *Zhur. Obshch. Khim.*, **30**, 359 (1960), *Chem. Abstr.* **54**, 24457c (1960); c) R. J. Quellette, A. South, Jr., and D. L. Shaw, *J. Am. Chem. Soc.*, **87**, 2602 (1965).

5) We have used **1** as a model compound for a mechanistic investigation of halogenation of bicyclo[2.1.0]pentane system; see the succeeding paper.

6) See the preceding paper.

7) M. Fetizon and M. Golfier, *C. R. Acad. Sci.*, **267**, 900 (1968); M. Fieser and L. Fieser, "Reagents for Organic Synthesis," **2**, 363 (1969).

8) The configuration of the substituent at 5-position was determined to be *exo* by comparison of its PMR spectrum with those of **19a** and **19b** (see the preceding paper).

9) An intervention of 1,2-bridged acetoxymercurium ion is strongly suggested in oxymercuration reaction of olefin. See H. O. House, "Modern Synthetic Reactions," 2nd ed., Benjamin, Menlo Park (1972), p. 387.

10) a) R. J. Quellette, "Oxidation in Organic Chemistry, Part B," ed by W. S. Trahanovsky, Academic Press, New York (1973), p. 135; b) A. Lethbridge, R. O. C. Norman, and C. B. Thomas, *J. Chem. Soc., Perkin Trans. 1*, **1974**, 1929.