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Silver(I) Ion-catalyzed Rearrangement of 3,5-Dehydronoriceane (Pentacyclo[5.3.1.$0^{2,6}$.$0^{3,5}$.$0^{4,9}$]undecane). Empirical Force-field Calculations and Behavior of 3-Noricyl (Tetracyclo[5.3.1.$0^{2,6}$.$0^{4,9}$]undec-3-yl) Cation[1]

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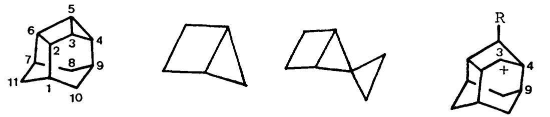
Treatment of 3,5-dehydronoriceane (**1**) with a catalytic amount of silver tetrafluoroborate results in a novel skeletal rearrangement to afford tetracyclo[5.3.1.$0^{2,6}$.$0^{3,9}$]undec-4-ene (2,4-ethenonoradamantane) (**5**) in 85% yield. Empirical force-filed calculations suggest that there is no substantial difference in strain energies between **1** and bicyclo[2.1.0]pentane which is inert toward silver(I) ion. Acetolysis of *endo*-3-noricyl (*endo*-tetracyclo[5.3.1.$0^{2,6}$.$0^{4,9}$]undec-3-yl) tosylate (**7**) gives *exo*-3-acetoxynoriceane (*exo*-3-acetoxytetracyclo[5.3.1.$0^{2,6}$.$0^{4,9}$]undecane) (**11**), *exo*-4-acetoxytetracyclo[5.3.1.$0^{2,6}$.$0^{3,9}$]undecane (**12**), and **5** in a ratio of 36:42:22. Similar acetolysis of the *exo*-isomer of **7** gives the same products but in a different ratio (**11**:**12**:**5**=9:47:44). A stepwise carbocation mechanism is proposed for the above mentioned silver(I) ion-catalyzed rearrangement.

Transition metal-catalyzed rearrangement of strained organic molecules has become one of the most exciting and intriguing fields of chemistry in a past decade and a number of unexpected and interesting isomerizations have been reported.[2] Among them, silver(I) ion-catalyzed rearrangements of strained σ-bonds have demonstrated remarkable and unique carbon-carbon σ-bond reorganization reactions.[2–4] Meanwhile, in spite of their high strain energies, bicyclo[2.1.0]pentane (**2**) and the even more strained spiro compound (**3**) have been found to be inert toward silver(I) ion.[5–7] We have recently reported the synthesis of 3,5-dehydronoriceane (**1**),[8] which possesses the partial bicyclo[2.1.0]pentane structure constrained within a rigid cage molecule. Although **1** has shown similar reactivities in hydrogenation[8] and other reactions[9] to bicyclo[2.1.0]pentane (**2**) itself,[10] we have found that **1**, unlike **2**, does react with silver(I) ion to follow a skeletal rearrangement.[11] Since nonconcerted mechanism involving carbocation intermediate has been strongly suggested to account for the hitherto known silver(I) ion-catalyzed rearrangements,[2–4] behavior of the supposed carbocation intermediate such as **4** may deserve to be investigated. In this paper, we would like to describe a new silver(I) ion-catalyzed rearrangement of bicyclo[2.1.0]pentane system together with empirical force-field calculations of strain energies of **1** and **2**, and acetolyses of *exo*- and *endo*-3-noricyl tosylates (**7** and **8**).

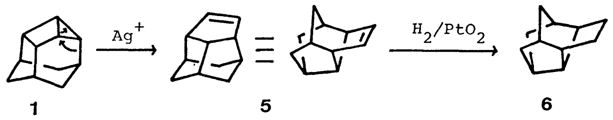


1 2 3 4 R=Ag or H

Scheme 1.

Results and Discussion

When **1** was treated with 3.6 mol% of silver tetrafluoroborate in chloroform at room temperature for 18 h, a novel skeletal rearrangement similar to those of cubyl systems[2,3] took place to give tetracyclo[5.3.1.$0^{2,6}$.$0^{3,9}$]undec-4-ene (2,4-ethenonoradamantane) (**5**) in 85% yield. Catalytic hydrogenation of **5** gave known tetracyclo[5.3.1.$0^{2,6}$.$0^{3,9}$]undecane (**6**),[12] confirming the structure of **5**.



1 5 6

Scheme 2.

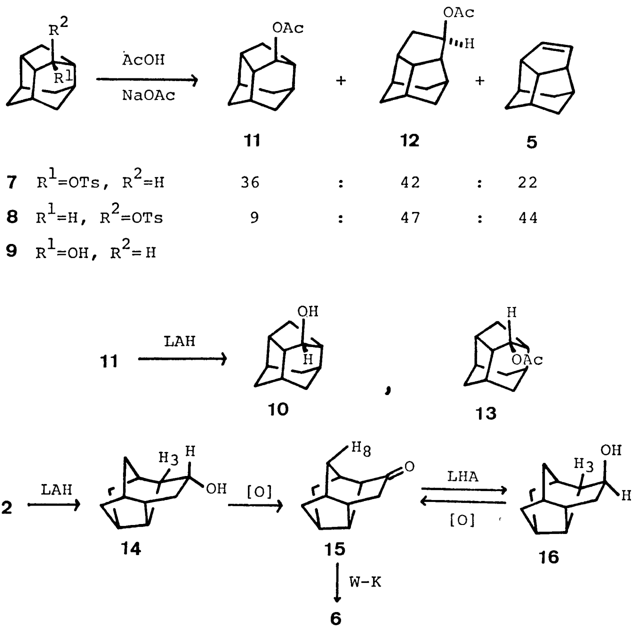
Primarily we anticipated that the strain around the central bond of **1** would be higher than that of the corresponding bond of **2** in order to explain the observed different reactivity toward silver(I) ion between **1** and **2**. Despite the acknowledged inadequacy of the presently available force-field models for cyclopropane derivatives,[13] we hoped that errors due to the force-field would cancel each other when closely related molecules were compared in molecular mechanics calculations (Table 1). The force-field[13] reproduces the geometry of **2** well, though it overestimates the strain in **2** by *ca.* 30 kcal/mol. Attention should be directed to the small difference in energy terms between **1** and **2**.[14] For **1** and **2** there appears to be no substantial difference in strain around the central bonds as well as in the whole molecule. In addition, the bow-and-stern C···C as well as flagpole H···H nonbonded interactions in the boat cyclohexane ring of **1** amount to only *ca.* 2 kcal/mol. Thus, any rationalization of the observed reactivity of **1** toward silver(I) ion compared with **2** must be based on something besides strain.

Although two mechanisms, concerted $[_{\sigma}2_{a}+_{\sigma}2_{a}]$[15] and step-wise carbocation rearrangements, have been considered for silver(I) ion-catalyzed rearrangements, many experiments strongly favor the latter.[2–4] If so, 3-noricyl cation such as **4** (R=Ag) should be a supposed intermediate in the present reaction. There are two possibilities for 1,2-alkyl shift. Migration of the C_1–C_2 bond to C_3 gives again the noriceane skeleton, while shift of the C_4–C_9 bond leads to the more stable tetracyclo[5.3.1.$0^{2,6}$.$0^{3,9}$]undecane system.[12] However, our calculation has shown that there is

TABLE 1. MOLECULAR MECHANICS CALCULATIONS ON **1** AND **2** USING THE ENGLER FORCE-FIELD

	1	**2**	
	Calcd	Calcd	Exp.[a]
Length of the central bond (Å)	1.514	1.530	1.525(8) X[b] 1.536(1) M.W.[c]
Dihedral angle around the central bond (deg)	115.6	124.7	112.5(3) X[b] 112.74(18) M.W.[c]
Sum of strain around bridgehead carbons (kcal/mol)	88.87(C-3) 59.93(C-4)	84.45(C-5) 56.43(C-5)	
ΔH_f° (g, 25 °C) (kcal/mol)	74.50	73.01	37.6[d]
Strain energy (kcal/mol)	107.17	92.72	57.3[e]
Heat of the central bond hydrogenolysis (kcal/mol)	−81.92[f]	−91.45	−55.14(36)[g]

a) Standard deviations in parentheses. b) X-Ray analysis of *exo*-5-tosylate: W. Saenger, C. H. Schwalbe, K. Fellenberger, and U. Schollkopf, *Chem. Ber.*, **106**, 2883 (1973). c) Microwave analysis of hydrocarbon: R. D. Suenram and M. D. Harmony, *J. Chem. Phys.*, **56**, 3837 (1972). d) Taken from: S. W. Benson, F. R. Cruickshank, D. M. Golden, R. G. Haugen, H. E. O'Neal, A. S. Rodgers, R. Show, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969). e) P. von R. Schleyer, J. E. Williams, and K. Blanchard, *J. Am. Chem. Soc.*, **93**, 2377 (1970). f) $\Delta H_f^\circ - \Delta H_f^\circ$(noriceane)(Ref. 12). g) R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *J. Am. Chem. Soc.*, **90**, 4315 (1968).



Scheme 3.

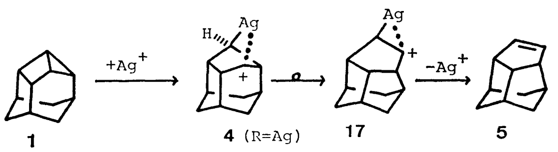
a large dihedral angle (45°) between sp^2-vacant orbital at C_3 of **4** (R=H) and the migrating C_4–C_9 bond, suggesting that such a rearrangement would be unfavorable. We, therefore, have studied the behavior of 3-noricyl cation (**4**, R=H) generated under solvolytic conditions in order to know whether the rearrangement is feasible or not.

Two isomeric *endo*- and *exo*-3-noricyl tosylates (**7** and **8**), prepared from the corresponding alcohols (**9** and **10**) by the usual way, were solvolyzed in acetic acid containing sodium acetate as a buffer. Acetolysis of the *endo*-tosylate (**7**) gave *exo*-3-acetoxynoriceane (**11**), *exo*-4-acetoxytetracyclo[5.3.1.0^{2,6}.0^{3,9}]undecane (**12**), and **5** in 95% yield in a ratio of 36:42:22. A similar acetolysis of the *exo*-isomer (**8**) gave the same products but in a different ratio (**11**:**12**:**5**=9:47:44). Lithium aluminum hydride reduction of **11** gave *exo*-3-noriceanol (**9**), which was shown to be identical with the one obtained in the reduction of 3-noriceanone with lithium in liquid ammonia.[16] Reduction of **12** with lithium aluminum hydride gave the alcohol, *exo*-tetracyclo[5.3.1.0^{2,6}.0^{3,9}]undecan-4-ol (**14**), which was oxidized with CrO_3–pyridine complex to afford tetracyclo[5.3.1.0^{2,6}.0^{3,9}]undecan-4-one (**15**).[12,17] Wolff-Kishner (W-K) reduction of **15** gave **6** confirming the parent skeleton. Lithium aluminum hydride reduction of **15** gave exclusively the isomeric *endo*-tetracyclo[5.3.1.0^{2,6}.0^{3,9}]undecan-4-ol (**16**), which reproduced **15** upon treatment with CrO_3–pyridine complex. The ^{1}H-NMR (PMR) spectra of **14** and **16** showed a doublet of doublet (J=6.9 and 2.7 Hz) at 4.33 ppm and the quintet (J=10.5, 6.3, and 4.8 Hz) at 4.58 ppm due to C_4-protons, respectively. Model investigations (Dreiding model) tell us that the *endo*-proton should not couple with the adjacent bridg-head proton (H_3) because of the large dihedral angle (*ca.* 90°). Accordingly, **14** and **15** were assigned to be *exo*- and *endo*-tetracyclo[5.3.1.0^{2,6}.0^{3,9}]undecan-4-ols, respectively. This elucidation does not contradict the exclusive formation of **16** due to the steric hindrance of H_8 in the reduction of **15** with lithium aluminum hydride.

No formation of *endo*-3-acetoxynoriceane (**13**)[16] in either acetolysis of *endo*- or *exo*-3-tosylate (**7** or **8**) may be due to large steric hindrance of the "bowsprit" hydrogen (*viz.* *endo*-H_{10}) in the boat conformation. The same steric hindrance is shown in the hydride reduction of 3-noriceanone giving exclusively *endo*-3-noriceanol (**9**).[16] The steric effect can be also responsible for the exclusive formation of **12**, as is seen in the hydride reduction of **15** (*vide supra*). More interesting is the difference in the ratio of the rearranged products (*viz.* **12** and **5**) to the unrearranged one (*viz.* **11**) between the two tosylates (**7** and **8**). The ratio is 1.8 for the *endo*-tosylate (**7**), while that is 9.1 for the *exo*-one (**8**). The stereoelectronic control can give rise to the large difference; the leaving group (*viz.* tosyloxyl group) in **8** is arranged in an almost perfect antiperiplanar position with reference to the migrating C_4–C_9 bond, where the rearrangement can take place most easily. Furthermore, it should be also noted that almost twice as much the rearranged products as the unrearranged one are formed even in the acetolysis of the *endo*-tosylate (**7**), in which the orientation of the leaving group is not favorable for the rearrangement. Thus, 3-noricyl cation (**4**, R=H) is decisively a mutable entity into tetracyclo[5.3.$1.0^{2,6}.0^{3,9}$]undecane system; this implies that a stepwise carbocation mechanism is quite possible in the present silver(I) ion-catalyzed rearrangement of **1**.

An attempt was also made to trap the supposed carbocation intermediate (**4**, R=Ag) by a nucleophilic solvent. Treatment of **1** with silver(I) ion in methanol caused no rearrangement and **1** was recovered almost quantitatively.[18] Furthermore, in order to make it clear whether proton can induce the same rearrangement, **1** was treated with a catalytic amount of *p*-toluensulfonic acid in refluxing benzene. However, no substantial change was observed; this indicates that proton is far from effective for the rearrangement.

The following scheme can be delineated for a stepwise carbocation mechanism. The strain energy difference between **1** and **5** is estimated to be *ca.* 40 kcal/mol[19] sufficient for the rearrangement.[2,3] In addition, the recently proposed stabilizing interaction between silver and a carbocation center[4] appears to be more efficient in the rearranged carbocation (**17**) than in the unrearranged one (**4**, R=Ag). Judging from the fact that halonium ion and certain metal ions approach the central bond of the bicyclo[2.1.0]pentane system of **1** from the front side,[9] it is highly probable that silver(I) ion also behaves in a similar manner and, consequently, the silver takes the suitable orientation for the interaction with the carbocation center, as is shown in the scheme.



Scheme 4.

In conclusion, the present results have clearly demonstrated that both of ring strain and suitable geometry are equally important in silver(I) ion-catalyzed rearrangements of strained polycylic molecules.[3,4]

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 conventional mass spectra were taken by using a Hitachi RMS-4 mass spectrometer and the exact mass spectrum was obtained on a Hitachi RMU-8GN mass spectrometer. The PMR and ^{13}C-NMR (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. All the reactions were carried out under nitrogen unless otherwise noted.

Silver(I) Ion-catalyzed Rearrangement of Pentacyclo[5.3.1.$0^{2,6}$.$0^{3,5}$.$0^{4,9}$]undecane (1) to Tetracyclo[5.3.1.$0^{2,6}$.$0^{3,9}$]undec-4-ene (5). A solution of **1** (1.00 g; 6.88 mmol) in $CHCl_3$ (7 ml) was stirred in the presence of $AgBF_4$ (48 mg; 0.25 mmol) at room temperature for 18 h in the dark. After evaporation of the solvent, the residue was dissolved in hexane and insoluble materials were removed by filtration. The solvent was evaporated and the residue was chromatographed on silica gel. Elution by hexane gave **5** (0.86 g, 85%): mp 150—153 °C. MS *m/e* (rel intensity): 146 (M^+, 43), 92 (53), 80 (100), 79 (56), 68 (70). IR (CCl_4): 2930, 1470, 1450, 1340, 1305, 1080, 1025, 710 cm^{-1}. PMR δ (CCl_4): 5.68 (2H, t, J=1.5 Hz), 3.10 (1H, q, J=6.3 Hz), 2.60 (2H, br. s), 2.23 (1H, br. s), 2.00—1.20 (8H, complex m). CMR δ ($CDCl_3$): 128.0 (CH), 59.2 (CH), 55.8 (CH), 44.9 (CH_2), 35.9 (CH), 35.1 (CH), 31.2 (CH_2). Found: *m/e* 146.1095. Calcd for $C_{11}H_{14}$: M, 146.1095.

Reduction of 5 to Tetracyclo[5.3.1.$0^{2,6}$.$0^{3,9}$]undecane (6). A solution of **5** (148 mg; 1.01 mmol) and a small amount of PtO_2 in ethyl acetate (7 ml) was vigorously stirred under hydrogen. After one equivalent of hydrogen was absorbed, the catalyst was removed by filtration and the solvent was evaporated. The residue was chromatographed on silica gel. Elution by hexane gave **6** (118 mg, 79%), which was identical with the authentic specimen.[12]

endo-*Tetracyclo[5.3.1.$0^{2,6}$.$0^{4,9}$]undec-3-yl* p-*Toluenesulfonate (7).* To a solution of *endo*-tetracyclo[5.3.1.$0^{2,6}$.$0^{4,9}$]-undecan-3-ol (**10**)[16] (429 mg; 2.62 mmol) in pyridine (10 ml) was added *p*-toluenesulfonyl chloride (1003 mg; 5.26 mmol) at 0 °C. The mixture was allowed to stand overnight at room temperature and then poured onto ice–water. The organic materials were extracted with ether and washed with cold 5% HCl aq and brine, and dried (Na_2SO_4). After filtration, the solvent was evaporated to give a solid (816 mg). Recrystallization from hexane afforded **7** (745 mg, 89%): mp 89—92 °C. IR (KBr): 2930, 1350, 1180, 1165, 1095, 1020, 1015, 975, 960, 895, 850, 840, 820, 670 cm^{-1}. PMR δ (CCl_4): 8.73 (2H, d, J=8.4 Hz), 7.27 (2H, d, J=8.4 Hz), 4.32 (1H, s), 2.43 (3H, s), 2.53—0.77 (14H, br. complex m). CMR δ ($CDCl_3$): 144.5 (C), 134.5 (C), 129.8 (CH), 127.7 (CH), 85.0 (CH), 42.9 (CH), 41.3 (CH), 41.0 (CH_2), 38.3 (CH), 36.7 (CH), 31.2 (CH_2), 30.3 (CH), 23.2 (CH), 21.6 (CH_3). Found: C, 67.61; H, 7.11%. Calcd for $C_{18}H_{22}O_3S$: C, 67.89; H, 6.96%.

exo-*Tetracyclo[5.3.1.$0^{2,6}$.$0^{4,9}$]undec-3-yl* p-*Toluenesulfonate (8).* The reaction of *exo*-tetracyclo[5.3.1.$0^{2,6}$.$0^{4,9}$]undecan-3-ol (**9**) (62 mg; 0.38 mmol) with *p*-toluenesulfonyl chloride (145 mg; 0.76 mmol) in a similar manner to the above gave **8** (88 mg, 74%) after recrystallization from hexane. **8**: mp 62—64 °C. IR (KBr): 2930, 1600, 1355, 1180, 950, 925, 860, 845, 820, 670 cm^{-1}. PMR δ(CCl_4): 7.71 (2H, d, J=8.4 Hz), 7.28 (2H, d, J=8.4 Hz), 4.90 (1H, s), 2.47 (3H, s), 2.60—0.80 (13H, br. complex m). CMR δ($CDCl_3$): 144.6 (C), 135.1 (C), 130.0 (CH), 127.6 (CH), 85.7 (CH), 48.5 (CH), 41.3 (CH+CH_2), 38.8 (CH), 38.7 (CH), 37.6 (CH), 31.7 (CH), 30.9 (CH_2), 29.7 (CH_2), 21.6 (CH_3). Found: C, 67.63; H, 6.59%. Calcd for $C_{18}H_{22}O_3S$: C, 67.89; H, 6.96%.

Acetolysis of 7. A solution of **7** (842 mg; 2.64 mmol) and sodium acetate (328 mg; 4.00 mmol) in glacial acetic acid (26 ml) was refluxed for 4 h. The reaction mixture was poured onto water and extracted with CH_2Cl_2. The organic layer was washed with brine, aqueous $NaHCO_3$ and brine, and dried (Na_2SO_4). After filtration, the solvent was evaporated to give a colorless oil (519 mg) which was chromatographed on silica gel. Elution by hexane gave **5** (82 mg, 21%) and the subsequent elution by hexane and CH_2Cl_2 (4:1) afforded a mixture of **11** and **12** (401 mg, 74%) in a ratio of 23:27 [GLC (PEG 20 M, 180 °C)]. The calculated ratio of **11**:**12**:**5** was 36:42:22. Each of the acetates was isolated by preparative GLC. *exo*-3-Acetoxytetracyclo[5.3.1.$0^{2,6}$.$0^{4,9}$]undecane (**11**): bp 85—90 °C (bath temp)/2000 Pa. MS *m/e* (rel intensity): 206 (M^+, 4), 164 (11), 146 (100). IR (neat): 2930, 1735, 1370, 1245, 1055, 1025 cm^{-1}. PMR $\delta(CCl_4)$: 5.07 (1H, s, $W_{1/2}=3.0$ Hz), 1.95 (3H, s), 2.60—0.90 (14H, br. complex m). CMR $\delta(CDCl_3)$: 170.7 (C), 76.8 (CH), 47.9 (CH), 41.5 (CH_2) 41.3 (CH), 38.4 (CH), 37.9 (CH), 37.7 (CH), 31.5 (CH), 31.0 (CH_2), 30.1 (CH_2), 23.2 (CH_2), 21.4 (CH_3). Found: C, 75.50; H, 8.72%. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80%. *exo*-4-Acetoxytetracyclo[5.3.1.$0^{2,6}$.$0^{3,9}$]undecane (**12**): bp 90—97 °C (bath temp)/3066 Pa. IR (neat): 2930, 1740, 1360, 1250, 1020 cm^{-1}. PMR $\delta(CCl_4)$: 5.05 (1H, dd, $J=7.5$ and 3.0 Hz), 1.93 (3H, s), 2.87—1.37 (14H, br. complex m). CMR $\delta(CDCl_3)$: 170.8 (C), 78.2 (CH), 56.9 (CH), 51.2 (CH), 49.0 (CH), 44.0 (CH_2), 39.9 (CH), 83.4 (CH), 36.9 (CH_2), 30.6 (CH_2), 21.4 (CH_3). Found: C, 75.55; H, 9.06%. Calcd for $C_{13}H_{18}O_2$: H, 75.69; H, 8.80%.

Acetolysis of ***8***. A solution of **8** (71 mg; 0.22 mmol) and sodium acetate (28 mg: 0.34 mmol) in glacial acetic acid (2.5 ml) was refluxed for 4 h. Similar work-up and subsequent column chromatography to the above gave **5** (8 mg, 24%) and a mixture of **11** and **12** (14 mg, 30%) in a ratio of 3:17 [GLC (PEG 20 M, 180 °C)]. The calculated ratio of **11**:**12**:**5** was 9:47:44.

exo-*Tetracyclo[5.3.1.$0^{2,6}$0.^{4,9}]undecan-3-ol* ***(10)***. To a suspension of $LiAlH_4$ (59 mg; 1.55 mmol) in dry ether (5 ml) was added dropwise a solution of **11** (110 mg; 0.53 mmol) in dry ether (2 ml). The mixture was stirred under reflux for 1 h and quenched with saturated aqueous Na_2SO_4. The organic layer 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 a mixture of hexane and CH_2Cl_2 (4:1) gave **10** (78 mg, 89%): mp 243—244 °C. MS *m/e* (rel intensity): 164 (M^+, 80), 146 (49), 135 (57), 92 (45), 91 (46), 79 (89), 68 (100). IR (KBr): 3260, 2925, 1075 cm^{-1}. PMR $\delta(CDCl_3)$: 4.30 (1H, s, $W_{1/2}=3.0$ Hz), 2.70—0.80 (15H, br. complex m). CMR $\delta(CDCl_3)$: 72.6 (CH), 50.5 (CH), 41.7 (CH_2), 41.0 (CH), 40.0 (CH), 38.2 (CH), 37.6 (CH), 31.5 (CH), 31.3 (CH_2), 30.0 (CH_2), 22.5 (CH_2). Found: C, 80.30; H, 10.09%. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83%.

exo-*Tetracyclo[5.3.1.$0^{2,6}$.$0^{3,9}$]undecan-4-ol* ***(14)***. The reduction of **12** (34 mg; 0.17 mmol) with $LiAlH_4$ (41 mg; 1.08 mmol) in a similar manner to the above gave **14** (24 mg, 99%): mp 128—132 °C. MS *m/e* (rel intensity): 164 (M^+, 65), 146 (57), 80 (95), 79 (100), 68 (91). IR (KBr): 3300, 2925, 1025 cm^{-1}. PMR $\delta(CDCl_3)$: 4.33 (1H, dd, $J=6.9$ and 2.7 Hz), 2.78 (1H, q, $J=6.0$ Hz), 2.63—1.30 (14H, br. complex m). CMR $\delta(CDCl_3)$: 75.2 (CH), 60.4 (CH), 51.5 (CH), 48.4 (CH), 43.1 (CH_2), 42.9 (CH_2), 40.0 (CH), 39.7 (CH_2), 38.5 (CH), 30.6 (CH_2). Found: C, 80.31; H, 10.05%. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83%.

Tetracyclo[5.3.1.$0^{2,6}$.$0^{3,9}$]undecan-4-one ***(15)***. To a solution of pyridine (0.7 ml) in CH_2Cl_2 (3.5 ml) was added portionwise CrO_3 (169 mg; 1.69 mmol) under stirring. After 10 min, a solution of **14** (27 mg; 0.16 mmol) in CH_2Cl_2 (2 ml) was added to the above mixture and stirred for 1.5 h. The reaction mixture was 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 a mixture of hexane and CH_2Cl_2 (9:1) gave **15** (24 mg, 90%): mp 180—182 °C. MS *m/e* (rel intensity): 162 (M^+, 100), 120 (33), 92 (30), 79 (62). IR (KBr): 2925, 1750, 1180 cm^{-1}. PMR $\delta(CDCl_3)$: 3.00—1.10 (14H, br. complex m). CMR $\delta(CDCl_3)$: 221.0 (C), 60.4 (CH), 49.2 (CH), 46.5 (CH), 44.0 (CH_2), 43.1 (CH_2), 42.2 (CH_2), 41.5 (CH), 39.8 (CH), 30.1 (CH_2). Found: C, 81.39; H, 8.83%. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70%.

Wolff-Kishner Reduction of ***15***. A solution of **15** (12 mg; 0.07 mmol), KOH (68 mg), and 100% $NH_2NH_2 \cdot H_2O$ (0.07 ml) in diethylene glycol (0.5 ml) was stirred at 110 °C for 30 min and subsequently at 180 °C for 3 h. The materials on the condenser was dissolved in pentane and washed with brine, and dried (Na_2SO_4). After filtration, the solvent was evaporated to give **6** (5 mg, 44%), which was shown to be identical with the authentic specimen.[12)]

endo-*Tetracyclo[5.3.1.$0^{2,6}$.$0^{3,9}$]undecan-4-ol* ***(16)***. The reduction of **15** (23 mg; 0.14 mmol) with $LiAlH_4$ (26 mg; 0.68 mmol) in a similar manner to the above gave **16** (22 mg, 94%): mp 178—180 °C. MS *m/e* (rel intensity): 164 (M^+, 5), 146 (57), 80 (90), 79 (67), 68 (100). IR (KBr): 3300, 2925, 1100, 1050, 1015 cm^{-1}. PMR $\delta(CDCl_3)$: 4.58 (1H, quintet, $J=10.5$, 6.3, and 4.8 Hz), 2.75—1.20 (br. complex m). CMR $\delta(CDCl_3)$: 76.0 (CH), 55.9 (CH), 50.1 (CH), 49.0 (CH), 43.6 (CH_2), 41.1 (CH), 38.8 (CH), 37.3 (CH), 36.6 (CH_2), 30.8 (CH_2). Found: C, 80.61; H, 10.08%. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83%. The oxidation of **16** (13 mg; 0.08 mmol) with CrO_3 (77 mg; 0.77 mmol)-pyridine (0.38 ml)-CH_2Cl_2 (2 ml) in a similar manner to the above reproduced **15** (12 mg, 93%).

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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 recent review; K. C. Bishop III, *Chem. Rev.*, **76**, 461 (1976). See also A. Greenberg and J. F. Liebman, "Strained Organic Molecules," Academic Press, New York (1978), p. 245.

3) L. A. Paquette, *Acc. Chem. Res.*, **4**, 280 (1971).

4) P. E. Eaton, L. Cassar, R. A. Hadson, and D. R. Hwang, *J. Org. Chem.*, **41**, 1445 (1976) and references cited therein.

5) L. A. Paquette and R. C. West, unpublished observation, quoted in Ref. 3.

6) Compound **2** undergoes rapid isomerization to cyclopentene upon treatment with a rhodium complex: P. G. Gassman, T. J. Atkins, and J. T. Lumb, *J. Am. Chem. Soc.*, **94**, 7757 (1972).

7) 1-Phenylbicyclo[2.1.0]pentane was reported to be isomerized to cyclopentene derivatives when reacted with Zn(II), Rh(I), and Ag(I) salts: M. A. Mckinney and S. K. Chou, *Tetrahedron Lett.*, **1974**, 1145.

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

9) See two succeeding papers.

10) R. M. Moriarty, "Topics in Stereochemistry," ed by E. L. Eliel and N. L. Allinger, Wiley, New York (1974), Vol. VIII, p. 347.

11) For preliminary report: T. Katsushima, R. Yamaguchi, M. Kawanisi, and E. Ōsawa, *J. Chem. Soc., Chem. Commun.*,

1976, 39.

12) S. A. Godleski, P. von R. Schleyer, and E. Ōsawa, *J. Chem. Soc., Chem. Commun.*, **1976**, 38; S. A. Godleski, P. von R. Schleyer, E. Ōsawa, Y. Inamoto, and Y. Fujikura, *J. Org. Chem.*, **41**, 2596 (1976).

13) E. M. Engler, J. D. Andose, and P. von R. Schleyer, *J. Am. Chem. Soc.*, **95**, 8005 (1973).

14) The Allinger 1971 force-field [N. L. Allinger, M. T. Tribble, M. A. Miller, and D. H. Wertz, *J. Am. Chem. Soc.*, **93**, 1673 (1971)] gave essentially the same conclusions.

15) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., Germany, 1970.

16) See the succeeding paper.

17) Although **16** has been mentioned in literature,12) it has never been isolated in a pure form.

18) It was found that a trace amount of moisture significantly retarded the rearrangement in chloroform.

19) Since the present force-filed calculations overestimate the strain energy in **2** by 35 kcal/mol (Table 1), the corrected strain energy in **1** can be *ca.* 72 kcal/mol. The strain energy in **5** is estimated to be *ca.* 30 kcal/mol by adding the calculated strain energy in **6** (25.4 kcal/mol)12) to 4.6 kcal/mol for the introduction of the double bond [*cf.* 22.8 kcal/mol (norbornene) −18.2 kcal/mol (norbornane)].