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Noriceane (Tetracyclo[5.3.1.$0^{2,6}$.$0^{4,9}$]undecane) and 3,5-Dehydronoriceane (Pentacyclo[5.3.1.$0^{2,6}$.$0^{3,5}$.$0^{4,9}$]undecane)[1]

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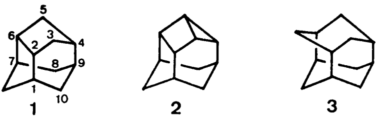
Heating a mixture of *endo, exo-* and *endo, endo*-2,4-dibromohomoadamantanes at 180 °C in hexamethylphosphoric triamide (HMPT) brings about a novel skeletal rearrangement with concomitant dehydrobromination to give tricyclo[5.3.1.$0^{4,9}$]undeca-2,5-diene (**5**) in 88% yield. Direct photoexcitation of **5** in diethyl ether induces an intramolecular [2+2] cycloaddition to produce 3,5-dehydronoriceane (**2**). The bicyclo[2.1.0]pentane moiety constrained in the cage structure of **2** shows almost the same ^{13}C–H coupling constants as those of bicyclo[2.1.0]-pentane itself. Finally hydrogenation of **2** over PtO_2 easily proceeds to afford noriceane, which is named after the structure of iceane.

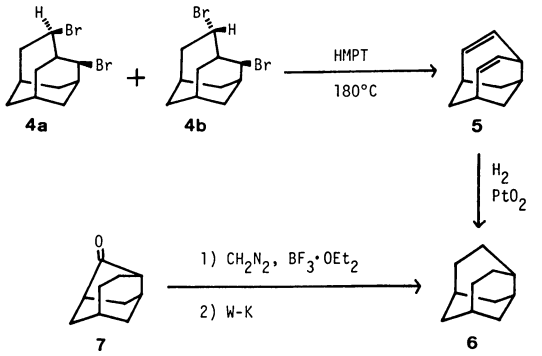
Among 2486 possible tetracyclic ring systems of empirical formula $C_{11}H_{16}$,[2] tetracyclo[5.3.1.$0^{2,6}$.$0^{4,9}$]-undecane (**1**) has a unique skeleton which is a nor-analogue of iceane (tetracyclo[5.3.1.$1^{2,6}$.$0^{4,9}$]dodecane) (**3**).[3] Iceane is named after the structure of crystalline water and, hence, we can term **1** as noriceane. In addition to its unique structure, **1** is a member of the tetracyclic $C_{11}H_{16}$ hydrocarbons which can be rearranged to the most stable isomer, 2,4-ethanonoradamantane by $AlBr_3$ catalyst.[2] In connection with our continuing interest in synthesis and reactions of strained cage molecules,[4] we could synthesize a highly strained compound, 3,5-dehydronoriceane (**2**), which has the partial bicyclo[2.1.0]pentane structure fixed in the rigid cage structure. Thus, taking account of its expected high chemical reactivity,[5] **2** can be a useful precursor of noriceane derivatives. We now describe here synthesis of noriceane (**1**) as well as 3,5-dehydronoriceane (**2**) in detail.[6]



Scheme 1.

Results and Discussion

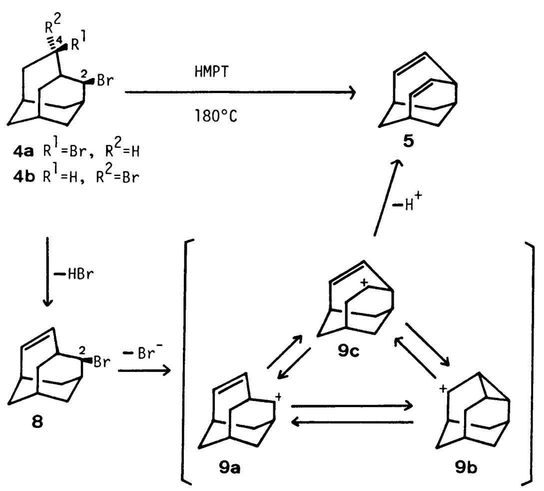
When a mixture of *endo,exo-*,and *endo,endo*-2,4-dibromohomoadamantane (**4a** and **4b**)[4b] was heated at 180 °C in HMPT for 3 h, a novel skeletal rearrangement with concomitant dehydrobromination[7] took place to give a geometrically interesting diolefin, tricyclo[5.3.1.$0^{4,9}$]-undeca-2,5-diene (**5**) in 88% yield. The structure of **5** was confirmed by the following experimental results. Hydrogenation of **5** gave a saturated hydrocarbon, tricyclo[5.3.1.$0^{4,9}$]undecane (**6**). This hydrocarbon, **6**, was authentically prepared by reaction of protoadamantan-2-one (**7**)[8] with diazomethane under catalysis of $BF_3 \cdot OEt_2$ followed by Wolff-Kishner reduction of the resulting ring-enlarged ketone.[9]



Scheme 2.

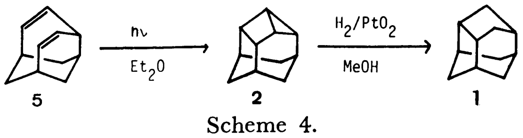
On the other hand, *endo*-2-bromohomoadamant-4-ene (**8**), which was prepared by the elimination of one equivalent of hydrogen bromide under base-promoted reaction conditions,[4b] gave also **5** in 96% yield when heated at 180 °C in HMPT. Therefore, this novel skeletal rearrangement is supposed to proceed through a pathway such as shown in Scheme 3. Initially, the bromine atom on C_4 and its β-hydrogen were eliminated to give **8**. Subsequently, the loss of the remaining bromine atom on C_2 would lead to the homoallyl-cyclopropylcarbinyl rearrangement of carbocation intermediates (**9a**, **9b**, and **9c**) and only **9c** could release its β-hydrogen[10] to produce **5**. Although the mechanism of dehydrohalogenation with HMPT has not been established,[7] the degenerated homoallyl-cyclopropylcarbinyl rearrangement of **9a**, **9b**, and **9c** under stable ion conditions has been proposed.[11]

It can be expected from the geometry of **5** that the two



Scheme 3.

π-orbitals are juxtaposed to interact efficiently with each other. Indeed, the UV spectrum of **5** shows a π-π^* absorption at 231 nm (ε=1360 in EtOH) and indicates a homoconjugation between two olefinic moieties. Thus, direct irradiation of **5** in diethyl ether through quartz-filter by means of medium-pressure mercury lamp induced an efficient intramolecular [2+2] cycloaddition to afford 3,5-dehydronoriceane (**2**) in 87% yield. (Scheme 4) The IR spectrum of **2** showed an absorption band at 3100 cm^{-1} due to cyclopropane ring. In addition, the presence of C_{2v} symmetry was clearly indicated by the ^{13}C NMR spectrum which showed only 7 absorption signals.



Scheme 4.

The compound (**2**) has partially a bicyclo[2.1.0]-pentane moiety within the rigid cage structure and is expected to possess significant chemical reactivity.[12] The observed ^{13}C–H coupling constants of **2** are almost the same as those of bicyclo[2.1.0]pentane[13] itself (Fig. 1) and strongly suggest the high strained nature of **2**. Thus, **2** was easily hydrogenated over PtO$_2$ in MeOH to afford noriceane (**1**). The C_{2v} symmetry of **1** was also clearly established by ^{13}C NMR spectroscopy. This hydrogenation is in good agreement with the well-known fact that cleavage of the central bond of bicyclo[2.1.0]pentane ring system easily occurs in a number of reactions.[12]

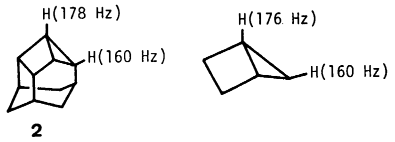


Fig. 1. ^{13}C–H coupling constants of **2** and bicyclo-[2.1.0]pentane.[13]

The fixed bicyclo[2.1.0]pentane ring in the cage structure of **2** is interesting in that any attacking species must approach the bicyclo[2.1.0]pentane unit from the *exo* side alone and, in addition, isomerization to cyclopentene derivatives is impeded on the stereochemical grounds.[10] Therefore, 3,5-dehydronoriceane (**2**) is expected to provide some information on reaction mechanism of bicyclo[2.1.0]pentane system which has been scarcely investigated.[5]

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 UV spectrum was recorded on a Hitachi ESP-spectrometer. The MS spectra were taken by using a Hitachi RMS-4 mass spectrometer. The exact mass spectrum was obtained on a Hitachi RMU-8GN mass spectrometer. The ^{1}H NMR spectra were obtained on a Varian EM-360 or EM-390 spectrometer and the ^{13}C NMR spectra were obtained on a Varian CFT-20 spectrometer, TMS being chosen as the inernal standard. ^{13}C–H coupling constants were measured by Gated decoupling method. Microanalyses were performed by Kyoto University Elemental Analysis Center.

Tricyclo[5.3.1.0^{4,9}]undeca-2,5-diene (5). A solution of a mixture of **4a** and **4b** (7.958 g; 25.8 mmol)[4b] in HMPT (100 ml) was heated at 180 °C for 3 h under nitrogen. To the cooled reaction mixture was then added hexane, and the organic layer was washed with water several times and dried (Na$_2$SO$_4$). The solvent was evaporated and the residue was chromatographed on alumina. Elution by hexane gave **5** (3.314 g, 88%): mp 155—158 °C. MS *m/e* (rel intensity): 146 (M$^+$, 84), 80 (100). IR (CCl$_4$): 3080, 2920, 1630, 1455, 1375, 910, 700 cm^{-1}. UV λ_{max} (EtOH): 231 nm (ε=1360). ^{1}H NMR δ (CCl$_4$): 6.00 (2H, d.d, J=9.0 and 5.4 Hz), 5.70 (2H, d.d, J=9.0 and 7.2 Hz), 2.93 (1H, d.t, J=8.7 and 5.1 Hz), 2.70—1.00 (9H, br complex m). ^{13}C NMR δ (CDCl$_3$): 137.0 (d), 132.8 (d), 39.4 (t), 38.2 (d), 32.2 (d), 26.9 (d), 24.0 (t). Found: C, 90.23; H, 9.66%. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.66%.

The same treatment of pure **4a** (622 mg; 2.02 mmol) in HMPT as above gave **5** (186 mg, 63%). Additionally the similar reaction of *endo*-2-bromotricyclo[4.3.1.1^{3,8}]undec-4-ene (**8**)[4b] (54 mg; 0.24 mmol) in HMPT (1 ml) to the above gave also **5** (33 mg, 96%).

Pentacyclo[5.3.1.0^{2,6}.0^{3,5}.0^{4,9}]undecane (2). A solution of **5** (201 mg; 1.39 mmol) in Et$_2$O (20 ml) was directly irradiated by 300-W medium pressure mercury lamp in a quartz vessel under nitrogen for 5 h. The solvent was evaporated and the residue was chromatographed on alumina. Elution by hexane gave **2** (175 mg, 87%): mp 183—186 °C. MS *m/e* (rel intensity): 146 (M$^+$, 52), 105 (67), 92 (89), 91 (60), 80 (100), 79 (93). IR (CCl$_4$): 3100, 2950, 1460, 1440, 1275, 1060, 895 cm^{-1}. ^{1}H NMR δ (CCl$_4$): 2.87—1.10 (14H, br complex m). ^{13}C NMR δ (CDCl$_3$): 43.3 (t), 38.3 (d), 33.1 (t), 30.3 (d), 22.5 (d), 20.0 (d), 7.3 (d). Found: C, 90.06; H, 9.81%. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65%.

Tetracyclo[5.3.1.0^{2,6}.0^{4,9}]undecane (1). A solution of **2** (100 mg; 0.68 mmol) in MeOH (10 ml) was vigorously stirred in the presence of PtO$_2$ under hydrogen. After one equivalent of hydrogen was absorbed, the catalyst was removed by filtration. After removal of the solvent under reduced pressure the residue was chromatographed on alumina. Elution by pentane gave **1** (61 mg, 60%): mp 212—215 °C. MS *m/e* (rel intensity): 148 (M$^+$, 100), 119 (33), 92 (41), 91 (31), 80 (31), 79 (65). IR (CCl$_4$): 2910, 1465, 1065 cm^{-1}. ^{1}H NMR δ (CCl$_4$): 2.67—0.60 (16H, br complex m). ^{13}C NMR δ (CDCl$_3$): 41.9 (d), 40.9 (t), 38.1 (d), 33.7 (d), 30.9 (t), 30.5 (d), 29.5 (t). Found: C, 88.86; H, 11.04%. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88%.

Tricyclo[5.3.1.0^{4,9}]undecane (6). A mixture of **5** (124 mg; 0.85 mmol) and a small amount of PtO$_2$ in MeOH (10 ml) was vigorously stirred under hydrogen. After two equivalents of hydrogen had been absorbed, the catalyst was removed by filtration and the solvent was evaporated. The residue was chromatographed on alumina. Elution by pentane gave **6** (85 mg, 66%): mp 242—246 °C. MS *m/e* (rel intensity): 150 (M$^+$, 100), 121 (43), 80 (43), 79 (50). IR (CCl$_4$): 2920, 1455 cm^{-1}. ^{1}H NMR δ (CCl$_4$): 3.10—0.90 (18H, br complex m). ^{13}C NMR δ (CDCl$_3$): 41.4 (t), 31.3 (t), 30.1 (t), 28.1 (t), 26.6 (d), 26.5 (d), 25.3 (d). Found: *m/e* 150.1382. Calcd for $C_{11}H_{18}$: M, 150.1408.

*Preparation of **6** from Tricyclo[4.3.1.0^{3,8}]decan-2-one (7).*[8] A solution of CH$_2$N$_2$ in Et$_2$O prepared from *N*-nitroso-*N*-methylurea (1.6 g) was added dropwise to a solution of **7**

(149 mg; 1.00 mmol) and a small amount of $BF_3 \cdot OEt_2$ in Et_2O (5 ml) under cooling with an ice–salt bath and then a small amount of acetic acid was added to the reaction mixture. The precipitates were removed by filtration and the filtrate was washed with aq $NaHCO_3$ and brine, and dried (Na_2SO_4). The solvent was evaporated and the residue was chromatographed on silica gel. Elution by hexane–Et_2O (9 : 1) gave the ring-enlarged ketone[9] (104 mg, 63%): MS *m/e* (rel intensity): 164 (M^+, 100). IR (nujol): 2930, 1710, 1460, 1375, 720 cm^{-1}. ^1H NMR δ ($CDCl_3$): 3.00—1.00 (16H, br complex m).

A mixture of the above ketone (41 mg; 0.25 mmol), KOH (200 mg; 3.56 mmol), 100% hydrazine hydrate (150 mg; 3.00 mmol) in diethylene glycol (0.6 ml) was stirred at 110 °C for 0.5 h and subsequently at 180 °C for 3 h. The sublimate on the condenser was collected and dissolved in pentane. The solution was washed with brine and dried (Na_2SO_4). Evaporation of the solvent gave crude **6** (30 mg, 80%). This compound was identical with **6** obtained by hydrogenation of **5** in every respect.

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