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Selective Skeletal Rearrangement of Tricyclo[5.4.0.0^{1,5}]undecanes to Tricyclo[5.3.1.0^{1,5}]- and [5.4.0.0^{3,8}]undecanes

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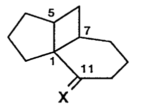
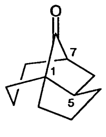
Synopsis. An acid-catalyzed rearrangement of tricyclo[5.4.0.0^{1,5}]undecan-11-one gave tricyclo[5.3.1.0^{1,5}]undecan-11-one in a nonnucleophilic media and tricyclo[5.4.0.0^{3,8}]undecane-7, 8-diol in the presence of a nucleophile, respectively. Tricyclo[5.4.0.0^{1,5}]undecan-11-ols also rearranged to tricyclo[5.4.0.0^{3,8}]undecan-7-ol. A reductive rearrangement with a hydride transfer of the alcohol gave only tricyclo[5.4.0.0^{3,8}]undecane.

A skeletal transformation of bicyclo[4.2.0]octane derivatives has been shown to be a convenient method for the construction of complex polycarbocyclic skeletons.[1] We have recently reported on skeletal rearrangements of 1,6-,[2] 5,6-,[3] and 6,7-trimethylenebicyclo[4.2.0]octanes[4] to the basic skeletons of diquinane- and triquinane-type natural products with high-selectivity as well as their application to both the syntheses of some natural products[3b,5] and biologically active compounds.[6] As an extension of this work, we describe here the selective skeletal rearrangement of the 1,8-trimethylene bridged analog, tricyclo[5.4.0.0]undecan-11-one (**1**), and its alcohol derivatives **2**, to tricyclo[5.3.1.0^{1,5}]undecan-11-one (**3**) having a basic skeleton of α-cedrene (**4**) and tricyclo[5.4.0.0^{3,8}]undecane derivatives, **5** and **6**. We also report on a reductive rearrangement with a hydride transfer of the alcohol **6**, since its parent hydrocarbon, tricyclo[5.4.0.0^{3,8}]undecane (**7**), is regarded as being a mechanistic dead-end in the homoadamantane rearrangement.[7,8]



1 X = O
2 X = H , OH



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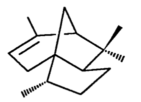

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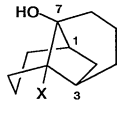
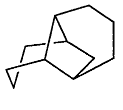


5 X = OH
6 X = H



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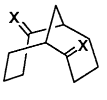
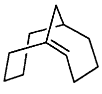
The acid-catalyzed reaction of the tricyclic ketone **1**[9] in a nonnucleophilic media, such as H_2SO_4 in benzene and $AlCl_3$ in CH_2Cl_2, gave the diquinane ketone **3** in 80 and 91% yields, respectively. The structure was determined by a comparison of the spectral data with those of a previously prepared sample.[4] On the other hand, in the presence of a nucleophile, a quite different behavior was observed. The reaction of **1** with H_2SO_4 in aqueous tetrahydrofuran (THF) gave the tricyclic diol **5** in 75% yield along with a small amount of **3** (10%). The structure of **5** was established by the following chemical transformations: Lead(IV) acetate oxidation of the symmetrical diol **5** to bicyclo[4.4.1]undecane-2, 7-dione (**8**) followed by reduction of the bis(dithioacetal) of **8** with Raney nickel furnished bicyclo[4.4.1]undecane (**9**) and bicyclo[4.4.1]undec-1-ene (**10**), whose ^{13}C NMR spectra were identical with those found in the literature.[10] Furthermore, a 5 : 1 diastereomeric mixture of alcohols **2**, which was derived by a reduction of **1** with $LiAlH_4$, rearranged in the presence of H_2SO_4 in aqueous THF to a known tricyclic alcohol **6**[11] in 85% yield as the sole product.



8 X = O
9 X = H , H



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Taking the previous rearrangement of trimethylenebicyclooctanones into account,[2a,3b] it is reasonable to explain the rearrangement pathway of ketone **1** as shown in Scheme 1. Namely, the C1–C5 bond of the cation intermediate **11** migrates to form the cation **12** (path a); the subsequent 1,2-alkyl shift in **12** gives **3** in the absence of nucleophiles. The trapping of **12** by a nucleophile affords **5**. Another migrating mode (path b) in **11**, which involves a 1,2-alkyl shift of the C1–C7 bond to produce the cation **13**, is less likely in both a thermodynamic[7] and a kinetic sense, though a second alkyl shift in **13** would give **3**. Similarly, in the case of the alcohols **2**, a migration of the C1–C5 bond is favored, regardless of the stereochemistry of the hydroxyl group.

Next, in connection with the homoadamantane rearrangement of tricycloundecanes, a reductive rearrangement along with a hydride transfer of the alcohol **6** was carried out. The treatment of **6** with H_2SO_4 in pentane gave unrearranged hydrocarbon **7**[11] as the sole product. The structure was confirmed by a comparison of an authentic sample prepared independently from **6** according to a method in the literature.[11] The present result confirmed that tri-

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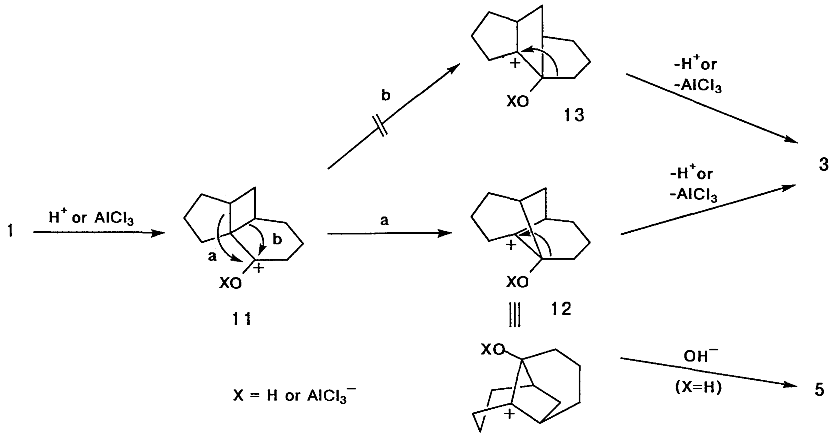

Scheme 1.

cyclo[5.4.0.0^{3,8}]undecane (**7**) is, indeed, a mechanistic dead-end in the homoadamantane rearrangement.

Experimental

All melting points are uncorrected. The instruments used for the measuring the spectra and the chromatography technique were the same as those used in previous work.[8a] Tricyclo[5.4.0.0^{1,5}]undecan-11-one (**1**) was prepared by an intramolecular photocycloaddition of 2-(4-pentenyl)-2-cyclohexen-1-one according to a method of Cargill *et al.*[9]

Tricyclo[5.4.0.0^{1,5}]undecan-11-ols (2). The reduction of **1** (483 mg, 2.95 mmol) with $LiAlH_4$ (56 mg, 1.48 mmol) in dry ether (15 ml) was performed as previously described[3b] to give a diasteromeric mixture of alcohols **2** (404 mg, 83%) after column chromatography on silica gel (20% ether–petroleum ether), which could not be separated. The stereochemistry of the hydroxyl group was not determined. **2**: IR (neat) 3350 (br), 1040 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.0—2.4 (m, ca. 16H), 2.63 (m, 0.83H), 3.57 (dd, *J*=9, 5 Hz, 0.83H), 3.79 (t, *J*=4 Hz, 0.17H); MS *m/z* (%) 166 (M$^+$, 15), 123 (48), 111 (44), 97 (100), 84 (67), 79 (64), 67 (47), 55 (40), 41 (48). Found: C, 79.05; H, 11.20%. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92%.

Tricyclo[5.3.1.0^{1,5}]undecan-11-one (3).[4] To a solution of **1** (95 mg, 0.58 mmol) in dry benzene (5 ml) was added one drop of H_2SO_4. The mixture was stirred at 40 °C for 14 h. A cold $NaHCO_3$ solution was added to the cooled mixture and the mixture was extracted with ether. The ether extract was washed with brine and dried over $MgSO_4$. Evaporation of the solvent followed by flash chromatography (10% ether–petroleum ether) of the crude product gave **3** (76 mg, 80%), which was identical with a previously prepared sample.[4] The reaction of **1** (95 mg, 0.58 mmol) with aluminum(III) chloride ($AlCl_3$) in dichloromethane (CH_2Cl_2) (5 ml) for 18 h was performed as previously described[3b] to give **3** (86 mg, 91%): IR (neat) 1740, 1080 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.8—1.2 (m, 2H), 1.3—2.4 (m, 14H); MS *m/z* (%) 164 (100), 136 (56), 121 (73), 108 (47), 107 (41), 95 (52), 94 (89), 93 (63), 81 (42), 80 (66), 79 (83), 67 (88), 41 (45). Found: C, 80.08; H, 10.09%. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83%.

Tricyclo[5.4.0.0^{3,8}]undecane-7,8-diol (5). The reaction of **1** (1.00 g, 6.10 mmol) with H_2SO_4 (10 ml) and water (10 ml) in THF (50 ml) at 55 °C for 65 h was carried out as previously described[2a] to give **3** (0.10 g, 10%) (elution with 5% ether–petroleum ether) and **5** (0.83 g, 75%) (elution with ether) after column chromatography on silica gel. **5**: Mp 138—139 °C (recrystallized from ether–petroleum ether); IR (KBr) 3300 (br), 1145, 1100, 1070, 1050 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.1—2.3 (m); ^{13}C NMR ($CDCl_3$) δ=18.0 (t, 2C), 25.6 (t, 3C), 33.7 (t, 2C), 39.5 (d, 2C), 77.5 (s, 2C); MS *m/z* (%) 182 (M$^+$, 79), 164 (65), 136 (76), 97 (62), 95 (45), 84 (100), 67 (45), 55 (59), 41 (51). Found: C, 72.24; H, 9.97%. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96%.

Tricyclo[5.4.0.0^{3,8}]undecan-7-ol (6).[11] The reaction of **2** (5: 1 mixture, 100 mg, 0.60 mmol) with H_2SO_4 (0.5 ml) and water (0.5 ml) in THF (5 ml) at 55 °C for 17 h was carried out as previously described[2b] to give **6** (86 mg, 86%) after flash chromatography (30% ether–petroleum ether): Mp 90—91.5 °C (recrystallized from ether–petroleum ether) (lit,[11] mp 90—91 °C). ^{13}C NMR ($CDCl_3$) δ=16.4 (t), 19.3 (t), 24.7 (t), 26.7 (t), 28.8 (t), 32.2 (t), 37.2 (d), 40.0 (t), 40.9 (d), 49.6 (d), 77.6 (s).

Tricyclo[5.4.0.0^{3,8}]undecane (7).[11] The reaction of **6** (598 mg, 3.58 mmol) with H_2SO_4 (3 ml) in pentane (30 ml) for 1 h was performed as previously described[8a] to give **7** (182 mg, 34%) after purification by preparative GLC. ^{13}C NMR ($CDCl_3$) δ=18.4 (t, 2C), 30.9 (t), 31.7 (t, 2C), 33.6 (t, 2C), 39.4 (d, 2C), 47.5 (d, 2C).

Chemical Transformation of 5. Bicyclo[4.4.1]undecane-2,7-dione (8). The reaction of **5** (233 mg, 1.28 mmol) with lead(IV) acetate (682 mg, 1.53 mmol) in benzene (40 ml) for 1 h was performed as previously described[2a] to give **8** (179 mg, 93%) and the recovered **5** (39 mg) after flash chromatography (ether). **8**: Mp 116—117 °C (recrystallized from ether–petroleum ether); IR (KBr) 1690, 1315, 1175, 990, 920 cm^{-1}; ^{1}H NMR (CCl_4) δ=1.2—2.0 (m, 6H), 2.2—2.9 (m, 10H); MS *m/z* (%) 180 (M$^+$, 45), 97 (56), 94 (96), 69 (65), 55 (100), 41 (57). Found: C, 73.11; H, 8.89%. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95%.

Bicyclo[4.4.1]undecane (9) and Bicyclo[4.4.1]undec-1-ene (10).[10] The reaction of **8** (340 mg, 1.89 mmol) with 1,2-ethanedithiol (1.56 ml, 14.8 mmol) and boron trifluoride etherate (1.12 ml, 7.01 mmol) for 67 h was carried out as previously described[2a] to give the bis(ethylene dithioacetal): IR (neat) 1420 cm^{-1}. The treatment of crude acetal with Raney nickel (W-4) (ca. 15 g) for 4 h was performed as previously described[2a] to give **9** (85 mg, 30% from **8**) and **10** (91 mg, 33% from **8**) after column chromatography on silica gel (petroleum ether), whose ^{13}C NMR spectra were identical with those found in the literature.[10]

Synthesis of an Authentic Sample of 7. An authentic sample was prepared by a method similar to that found in the literature.[11] A solution of **6** (179 mg, 1.08 mmol) in thionyl chloride (4.5 ml) was stirred at 0 °C for 1.5 h. Ice-water was added and the mixture was extracted with ether. The ether extract was washed with a cold $NaHCO_3$ solution and brine and then dried ($MgSO_4$). Evaporation of the solvent followed by flash chromatography (petroleum ether) of the crude product gave chloride (182 mg, 92%), which showed peaks in the MS m/z (%) 186 ($M^{+}+2$, 1), 184 (M^{+}, 4), 148 (100), 94 (40), 79 (36). To a solution of the chloride (97 mg, 1.05 mmol) and azobis(isobutyronitrile) (50 mg) in cyclohexane (5 ml) was added a solution of tributyltin hydride (330 mg, 0.79 mmol) in cyclohexane (5 ml) at room temperature under a nitrogen atmosphere. The solution was heated at 81 °C for 3 h and then concentrated. The residue was chromatographed on silica gel (petroleum ether) followed by purification by preparative GLC to give a hydrocarbon (51 mg, 65% yield), whose ^{13}C NMR spectrum was identical with that of **7** obtained by a reductive rearrangement of **6**.

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