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Hydride Transfer Reduction–Rearrangements of Tricyclodecylcarbinols and Tricycloundecanols. Formation of Tricyclo[6.2.1.$0^{2,6}$]undec-2(6)-ene under Phosphoric Acid Catalysis

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Hydride transfer reduction–rearrangements of 5,6-*exo*-trimethylene-2-norbornylcarbinol (1), 2- and 3-hydroxy-6,7-*exo*-trimethylenebicyclo[3.2.1]octane (**2** and **3**), and 2-hydroxy-5,6-*endo*-trimethylenebicyclo[2.2.2]octane (**4x** and **4n**) in 95% sulfuric acid and excess *n*-pentane at room temperature gave 4-homoisotwistane (tricyclo[5.3.1.$0^{3,8}$]undecane, **5**) with high selectivity (92–97%). In contrast to this, treatment of **1**, **2**, **3**, and **4** with refluxing 85% phosphoric acid–*n*-heptane resulted in the predominant formation of a novel olefin, tricyclo[6.2.1.$0^{2,6}$]undec-2(6)-ene (**6**). The structure of **6** was established by an independent synthesis of the hydrogenation product (**6h**) of **6**. The olefin **6** selectively (94%) isomerized to **5** in sulfuric acid–*n*-pentane. The result suggests that tricyclo[6.2.1.$0^{2,6}$]undec-2-yl cation (**6c**) would be a key intermediate in the rearrangement sequence leading to **5**.

In the course of the identification of intermediates in adamantane rearrangement of 2,3-*exo*-tetramethylenenorbornane and 2,3-trimethylenebicyclo[2.2.2]octane, it was necessary for us to prepare an authentic specimen of 6,7-*exo*-trimethylenebicyclo[3.2.1]octane.[1] A synthesis was planned involving hydride transfer reduction–rearrangement[2–4] of 5,6-*exo*-trimethylene-2-norbornylcarbinol (1). This route seemed quite promising, since the isomerization of the cation (**1a**) from the carbinol 1 could give rise to the hoped-for 6,7-*exo*-trimethylenebicyclo[3.2.1]octane system, in view of the well-documented ring expansion of 2-norbornylcarbinyl to bicyclo[3.2.1]octyl cation.[5]

Sulfuric Acid Catalyzed Rearrangements of Carbinols. 5,6-*exo*-Trimethylene-2-norbornylcarbinol (1) was prepared from 2-*exo*-chloro-5,6-*exo*-trimethylenenorbornane[6] via Grignard reaction followed by addition to formaldehyde.[7] The carbinol thus obtained consisted of two epimers in 53:47 ratio, as shown on conventional VPC. The mixture **1** was then stirred with 95% sulfuric acid and *n*-pentane at room temperature. Samples were withdrawn at intervals from the pentane layer of the reaction mixture and examined on Golay column GC–MS, which determined the composition and established the identities of the products. Results are shown in Table I. Contrary to our expectation, no 6,7-*exo*-trimethylenebicyclo[3.2.1]octane was obtained, but 4-homoisotwistane (tricyclo[5.3.1.$0^{3,8}$]undecane, **5**)[1,3,4] was found to be the main product (95%) (Scheme I).

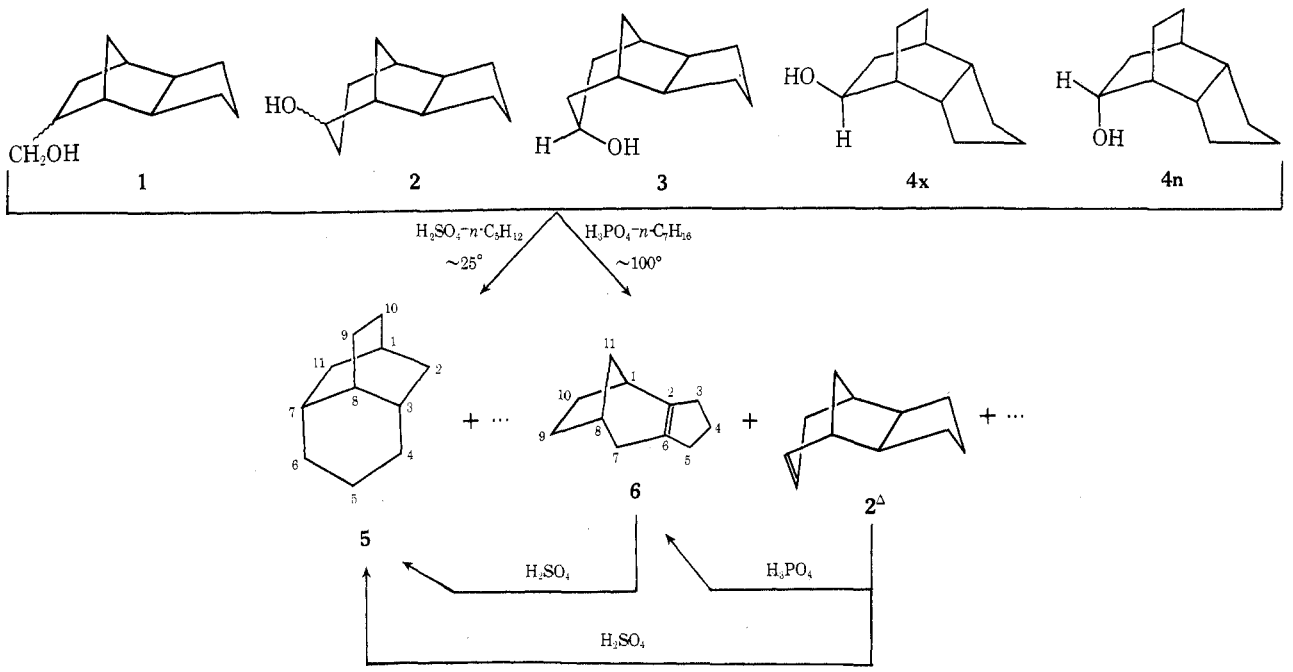
Since the first step in the rearrangement of **1** should be ring expansion to a bicyclo[3.2.1]octyl cation (**2a**),[4,5,8] reaction of 2-hydroxy-6,7-*exo*-trimethylenebicyclo[3.2.1]octane (**2**) was also examined. The alcohol **2** was prepared from 5,6-*exo*-trimethylene-2-norbornene (**7**)[6] by the application of the method of Bergman[9] (dichlorocarbene ring expansion,[1] hydrolysis of allylic chlorine atom, and dechlorination–hydrogenation). The alcohol **2** thus synthesized was a mixture (89:11) of two epimers separable on conventional VPC. Reaction of **2** with sulfuric acid and *n*-pentane also gave **5** predominantly (90%) (Table I).

Table I. Sulfuric Acid Catalyzed Hydride Transfer Reduction–Rearrangement[a]

Run	Reactant	Reaction time, min	Product,[b] %[c] 15	Unknown D[d]	5	Others[e]
1	1	1	2.1	3.1	93.7	1.1
		10	2.0	2.9	94.9	0.2
		30	1.7	2.4	95.0	0.9[f]
2	2	1	1.8	2.8	89.7	5.7
		10	2.2	2.8	89.2	5.8
		30	1.8	2.7	89.0	6.5[g]
3	3	1	1.1	2.9	94.0	2.0
		15	0.8	1.3	96.8	1.1
4	4x	1	1.9	2.7	89.7	5.7[h]
		10	2.1	2.6	89.8	5.5[i]
		30	1.9	2.7	89.8	5.6[i]
5	4n	1	0.8	2.5	94.4	2.3
		10	2.0	2.4	92.1	3.5[k]
11	2Δ	30	1.1	2.2	85.0	11.7[l]
12	6	1	1.6	2.3	92.3	3.8
		5	1.4	2.1	91.7	4.5
		10	1.1	2.2	91.8	5.8[m]

[a] 100 mg of reactant, 1 g of 95% sulfuric acid, and 5 ml of *n*-pentane stirred vigorously at room temperature (~25 °C). Combined yields of pentane-soluble products were 25–35%, the balance being tarry materials. [b] Identified on Golay GC–MS by comparison with authentic specimens.[13] [c] Calculated from Golay VPC peak areas. [d] A tricycloundecane (M^+ *m/e* 150) of unknown structure detected in adamantane rearrangement of various precursors.[1,12,13] [e] Consisting of several, unidentified compounds with M^+ *m/e* 146, 148, or 150. [f] Including 0.8% 2-methyladamantane (2-Me-Ad). [g] 0.4% 2-Me-Ad. [h] 0.3% 1,2-*exo*-tetramethylenenorbornane (B_2)[13] and 1.0% 1,2-*endo*-tetramethylenenorbornane (B_3).[13] [i] 0.6% B_2, 0.4% B_3, 0.5% 2-Me-Ad, and 0.3% 6,7-*exo*-trimethylenebicyclo[3.2.1]octane (**2h**).[1] [j] 0.5% B_2, 0.5% B_3, 0.2% 2-Me-Ad, and 0.1% **2h**. [k] 1.0% 1,2-*exo*-trimethylene-*cis*-bicyclo[3.3.0]octane (B_1).[13] [l] 0.7% 2-Me-Ad and two tricycloundecadienes (M^+ *m/e* 146) in 6.2 and 1.4%, respectively. [m] 0.4% 2-Me-Ad.

Scheme I



3-*endo*-Hydroxy-6,7-*exo*-trimethylenebicyclo[3.2.1]octane (**3**),[10] obtained by lithium aluminum hydride reduction of the corresponding ketone,[1] behaved similarly as its 2-hydroxy isomer (**2**) on treatment with sulfuric acid–*n*-pentane, giving **5** with 97% selectivity (Table I).

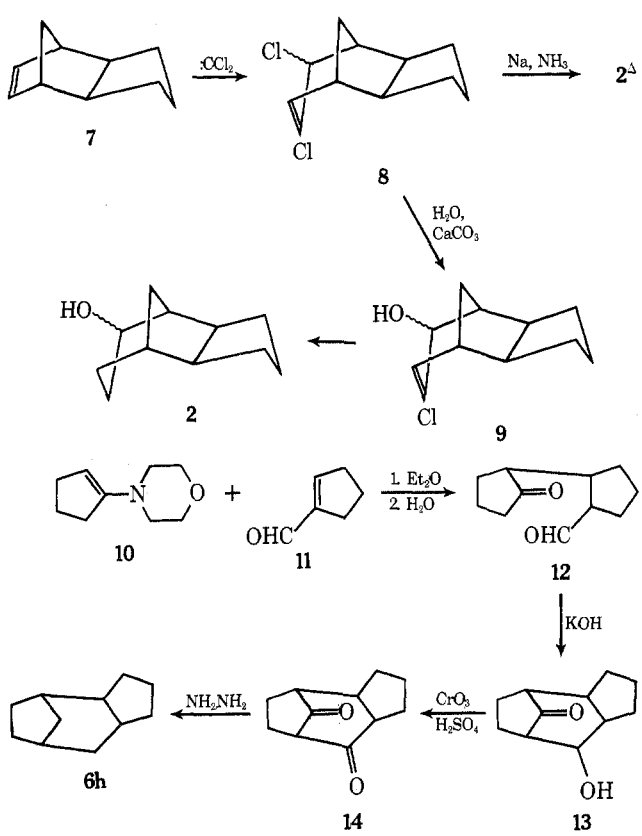
2-*exo*-Hydroxy-5,6-*endo*-trimethylenebicyclo[2.2.2]octane (**4x**), prepared by hydroboration of 5,6-*endo*-trimethylenebicyclo[2.2.2]oct-2-ene,[11] and 2-*endo*-hydroxy-5,6-*endo*-trimethylenebicyclo[2.2.2]octane (**4n**), obtained from the corresponding ketone[11] by lithium aluminum hydride reduction,[11] also gave **5** with 92–95% selectivity (Table I, Scheme I).

Phosphoric Acid Catalyzed Rearrangements of Carbinols. It has been shown in acid-catalyzed rearrangements of tricycloundecanes that product distributions varied appreciably with the kind of the catalyst used.[1,12,13] Therefore, 85% phosphoric acid in place of sulfuric acid was employed as catalyst for the hydride transfer reduction–rearrangement of the alcohols **1–4.** Since the phosphoric acid was found in preliminary experiments to catalyze the reaction quite slowly at room temperature, the reactions were run at reflux (~100 °C). It was necessary at this higher reaction temperature to change the hydride source from *n*-pentane to *n*-heptane.

Major products of the reaction under phosphoric acid catalysis were entirely different from those under sulfuric acid catalysis (Table II, Scheme I). Two tricycloundecenes, tricyclo[6.2.1.$0^{2,6}$]undec-2(6)-ene (**6**) and 6,7-*exo*-trimethylenebicyclo[3.2.1]oct-2-ene (**2Δ**), consisted 70–90% of the product mixtures. The olefin **2Δ** was identified by comparison of its ir, ^{1}H NMR, and mass spectra with those of an authentic specimen prepared from 3,4-dichloro-5,6-*exo*-trimethylenebicyclo[3.2.1]oct-2-ene (**8**) by dechlorination[12,14] (Scheme II).

Hydrogenation of the olefin **6** over palladium on charcoal catalyst gave two major products in 50 and 20% yields, respectively. The more abundant component was identical with an authentic 2,3-trimethylenebicyclo[3.2.1]octane (**6h**) of yet undetermined configuration, which was prepared from a cyclopentanone enamine (**10**) and 1-formylcyclopentene (**11**) by two-step condensations and the subsequent Wolff–Kishner reduction (Scheme II). The less

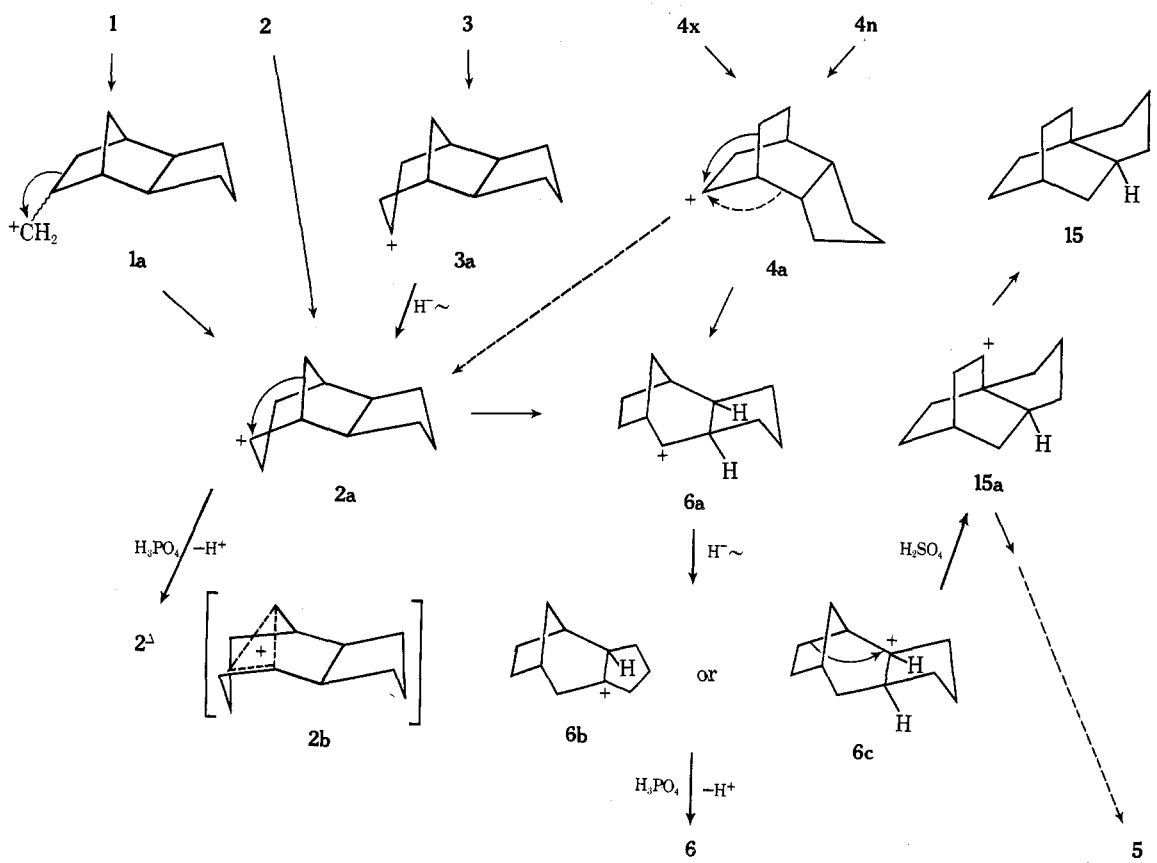
Scheme II



abundant hydrogenation product was eluted on VPC immediately after **6h** and showed an almost identical mass spectrum as that of **6h.** This suggests that **6h** and the less abundant product are configurational isomers, and an exo structure, that would presumably be more stable, might be assigned to **6h** on the basis of the abundance as well as the shorter retention time on VPC.[13]

Rearrangements of Intermediate Olefins. In the phosphoric acid catalyzed reaction of **1–4,** the ratio of the olefins **2Δ** to **6** was fairly small for the carbinol **1** (12:72), as

Scheme III



compared to those for the alcohols **2–4** (20–30:70–50). A long reaction time (7 h) required for the disappearance of **1** may have caused a secondary conversion of once formed **2Δ** into **6**. This was found to be actually the case, treatment of **2Δ** with phosphoric acid for 7 h giving a 6:80 ratio of **2Δ:6** (Table II, Scheme I).

Olefins **2Δ** and **6** formed under phosphoric acid catalysis were not found among products of sulfuric acid catalyzed reactions. An explanation for this difference in the product would be that the olefins, if ever formed at all, further isomerize to **5** and other minor products in the presence of sulfuric acid. Indeed, treatment of these olefins with sulfuric acid–*n*-pentane gave **5** selectively (85–94%) (Table I, Scheme I), as expected.

Discussion

Since all the alcohols **1–4** gave an almost identical proportion of the three main products in sulfuric acid catalyzed hydride transfer reduction–rearrangements, it would be reasonable to presume the formation of a common cationic species from these reactants. This species would most probably be 6,7-*exo*-trimethylenebicyclo[3.2.1]oct-2-yl cation (**2a**), or a symmetrical bicyclooctyl cation[5a,15] (**2b**), a nonclassical equivalent of **2a** (Scheme III). Ionization of **2** directly leads to **2a**, and any other reactant may be isomerized to **2a** in a single step by 1,2-alkyl or -hydride shift. Charge delocalization in **2a** to form a stabilized **2b** might be a driving force for these isomerizations.

The next key intermediate in the rearrangement sequence seems to be a tricyclo[6.2.1.$0^{2,6}$]undecyl cation (**6b** or **6c**, or both), which may be derived from **2a** via **6a** by 1,2-alkyl shift followed by intramolecular hydride shift. Alternatively, intramolecular hydride shift in the nonclassical cation **2b** might lead to the formation of **6b** and **6c**, thus eliminating the supposition for the existence of **6a**. Intermediacy of **6b** or **6c** would be highly probable in view of the predominant formation of the olefin **6** in phosphoric acid catalyzed reactions as well as of the isomerization of **6** to **5** in sulfuric acid with almost the same selectivity as those for the alcohols **1–4**. Since phosphoric acid has been known as an effective dehydrating agent for alcohols,[16] while their isomerizations are best accomplished in sulfuric acid, the same intermediate **6b** or **6c** may give rise to diverse products according to the change in catalyst. Similarly, deprotonation in the cation **2a** (or **2b**) under the influence of phosphoric acid would lead to 6,7-*exo*-trimethylenebicyclo[3.2.1]oct-2-ene (**2Δ**).

A higher selectivity of **4n** for the formation of **6** (69%) than those of **2**, **3**, and **4x** (52, 46, and 46%, Table II) suggests that ionization of endo hydroxyl group (formation of **4a**) and migration of the exo ethano bridge (rearrange-

Table II. Phosphoric Acid Catalyzed Rearrangement[a]

Run	Reactant	Reaction time, min (h)	Product,[b] %[c] 2Δ	6	Others[d]
21[e]	1	(7)	11.5	71.8	16.7[f]
22	2	17	33.2	51.5	15.3
23	3	45	28.0	46.1	25.9[g]
24[h]	4x	25	30.6	45.5	23.9
25	4n	10	22.9	68.8	8.3[i]
31	2Δ	(7)	6.3	80.2	13.5

[a] 100 mg of reactant, 3 g of 85% phosphoric acid, and 5 ml of *n*-heptane stirred at reflux (~100°). [b] Identified on Golay GC–MS by comparison with authentic specimens. [c] Calculated from Golay VPC peak areas. [d] Consisting of several, unidentified compounds with M^+ *m/e* 146, 148, or 150. [e] Combined yield of the isolated heptane-soluble products was 66%. [f] Containing 4.6% **5**. [g] Including 18.2% **5**. [h] Combined yield, 80%. [i] Including 4.5% **5**.

ment of **4a** to **6a**) might be concerted, probably with the participation of the ethano methylene in the ionization. This same process should be unfavorable for **4x**, in which participation of the methine to form **2a**[15,17] (as indicated by a broken arrow in **4a**) would rather be expected.

Isomerization of 2^{Δ} to **5** under sulfuric acid catalysis (run 11, Table I) occurred with a somewhat low selectivity (85%), compared to those (90–97%) in other alcohols **1–4** and olefin **6**. This result, however, does not seem to invalidate the supposition of the intermediacy of the cation **2a** (**2b**) in the rearrangement sequence, because the olefin 2^{Δ} itself would not be involved in the main pathways of the sulfuric acid catalyzed reaction. On the other hand, most of the neutral olefin 2^{Δ} may ionize in sulfuric acid to **2a** (**2b**) which enter the rearrangement reaction leading to **5**, while the remaining, small proportion could react along different pathways, that might cause the formation of a fairly large amount (7.6%) of diolefinic products (Table I, footnote *l*).

Out of a number of conceivable pathways from the cation **6b** or **6c** to **5**, the one involving 1,2-trimethylenebicyclo[2.2.2]octyl cation (**15a**) seems to be the most probable (Scheme III). Only two main intermediates, **15** and unknown D, were detected in the present rearrangement reactions (Table I). However, **15** could be considered to be the only true intermediate to **5**, since unknown D was shown[1] to be formed from and in equilibrium with **5** under sulfuric acid catalysis. In addition, **15** was demonstrated to be one of a variety of true intermediates in the trifluoromethanesulfonic acid catalyzed tricycloundecane rearrangement,[1,12,13] that would exclude the possibility of **15** being in a mechanistic dead end, as was the case for 2,4-*exo*-ethanobicyclo[3.3.1]nonane.[4] Detection of **15** as the only intermediate, in turn, may suggest that the route from **6c** to **5** should be relatively simple, possibly being a single pathway containing no competitive reaction. Thus **15a** might isomerize with appropriate hydride transfers and 1,2-alkyl shifts to 2,7-*endo*-trimethylenebicyclo[3.2.1]octyl cations and then to a cation of **5**, as imagined in our previous work.[13]

Experimental Section

All melting and boiling points are uncorrected. Instruments for the measurement of spectra and for Golay GC–MS were the same as used in the previous works,[1,12,13] except that ^{13}C NMR spectra were recorded in a Fourier transform mode at 15.03 MHz on a JEOL JNM FX-60 spectrometer. Deuteriochloroform was used as the solvent for NMR spectroscopy, and chemical shifts were reported in δ for protons and in parts per million downfield from the internal tetramethylsilane standard for ^{13}C nuclei.

5,6-*exo*-Trimethylene-2-norbornylcarbinol (**1**),[7] 3,4-dichloro-6,7-*exo*-trimethylenebicyclo[3.2.1]oct-2-ene (**8**),[1] 6,7-*exo*-trimethylenebicyclo[3.2.1]octan-3-one,[1] and 2-*exo*- and -*endo*-hydroxy-5,6-*endo*-trimethylenebicyclo[2.2.2]octane (**4x** and **4n**)[11] were prepared before.

3-Chloro-4-hydroxy-6,7-*exo*-trimethylenebicyclo[3.2.1]oct-2-ene (9). A mixture of 63 g (0.29 mol) of 3,4-dichloro-6,7-*exo*-trimethylenebicyclo[3.2.1]oct-2-ene (**8**), 87 g (0.87 mol) of calcium carbonate, and 130 ml of water was heated under reflux overnight. The organic layer was separated, and the aqueous layer was extracted with two 300-ml portions of ether. The combined organic layer and ether extracts were washed with water and dried over anhydrous sodium sulfate. Evaporation of the ether and fractional distillation of the residue gave 21 g (34% yield) of **9**, which solidified on standing at room temperature: bp 91–96 °C (0.15 mm); mp 49–52 °C; ir (neat) 3350 (br), 3040, 2940, 2870, 1630, 1040 (sh), 1020 cm^{-1}; ^1H NMR δ 0.9–2.8 (complex m, 12 H), 3.08 (s, 1 H, vanished on treatment with D_2O, OH), 3.85 (d, J = 5 Hz, 1 H, CHOH), 6.24 (d, J = 7 Hz, 1 H, -CH=); mass spectrum *m/e* (rel intensity) 200 (8, M^+), 198 (12, M^+), 163 (100), 145 (50), 129 (35), 95 (83), 91 (39), 85 (54), 79 (46), 77 (37), 67 (67), 41 (37).

Anal. Calcd for $C_{11}H_{15}OCl$: C, 68.4; H, 7.2; Cl, 16.8. Found C, 68.8; H, 7.5; Cl, 17.3.

2-Hydroxy-6,7-*exo*-trimethylenebicyclo[3.2.1]octane (2). In an autoclave were placed 11.4 g (0.054 mol) of 3-chloro-4-hydroxy-6,7-*exo*-trimethylenebicyclo[3.2.1]oct-2-ene (**9**), 75 ml of tetrahydrofuran, 50 ml of 13% sodium hydroxide solution, and 6.5 g of 10% palladium on charcoal catalyst. The reaction mixture was vigorously stirred for 5 h at ambient temperature under 10 kg/cm^2 pressure of hydrogen. The catalyst was filtered off, and the filtrate was extracted with three 100-ml portions of ether. The combined ether extracts were washed with water and dried over anhydrous sodium sulfate. The ether solution was concentrated and fractionally distilled to give 6.1 g (67% yield) of **2**, which solidified on standing at room temperature: bp 22° (0.4 mm); mp 58–60 °C; ir (neat) 3330 (br), 2940, 2860, 1470, 1450, 1020, 960 cm^{-1}; ^1H NMR δ 0.8–2.4 (complex m, 16 H), 2.71 (s, 1 H, OH), 3.86 (br s, 1 H, CHOH).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.5; H, 10.9. Found: C, 79.3; H, 10.6.

The alcohol **2** thus obtained was found to consist of two isomers in 89:11 ratio, which were separable on conventional VPC. These isomers were considered to be epimers because of the similarity in their mass spectra: the major component, *m/e* (rel intensity) 166 (33, M^+), 148 (44), 120 (56), 107 (100), 81 (33), 80 (55), 79 (86), 67 (72), 44 (56), 41 (61), 39 (34); the minor component, *m/e* (rel intensity) 166 (33), 148 (42), 122 (37), 120 (56), 107 (100), 81 (44), 80 (74), 79 (96), 67 (84), 41 (72), 39 (45).

6,7-*exo*-Trimethylenebicyclo[3.2.1]oct-2-ene (2^{Δ}). Freshly cut sodium (35.4 g, 1.54 g-atom) was added in small portions to 285 ml (168 g) of liquid ammonia with efficient stirring in a period of 30 min, and the mixture was stirred for a further 20 min. A solution of 17.4 g (0.08 mol) of 3,4-dichloro-6,7-*exo*-trimethylenebicyclo[3.2.1]oct-2-ene (**8**) in 50 ml of ether was added dropwise to the above mixture in a period of 30 min, and the reaction was stirred for a further 1 h. Ether (200 ml) was added dropwise to the reaction mixture while ammonia was allowed to evaporate freely. Unreacted sodium and sodium amide were decomposed by the addition of 100 ml of methanol–ether (50:50), and then by 500 ml of water. The mixture was extracted with four 200-ml portions of ether. The combined ether extracts were washed with four 200-ml portions of water and dried over anhydrous calcium chloride. Evaporation of the solvent and fractional distillation of the residue gave 5.1 g (43% yield) of 2^{Δ} (91% purity, as measured on Golay GC–MS): bp 62–63 °C (5 mm); ir (neat) 3020, 2940, 2920 (sh), 2850, 2820, 1640, 1470, 1450, 1430, 780, 700, 680 cm^{-1}; ^1H NMR δ 0.8–2.7 (complex m, 14 H), 5.3 (m, 1 H), 5.9 (m, 1 H); ^{13}C NMR (multiplicity) 28.30 (t), 30.01 (t), 33.34 (t), 34.72 (t), 36.26 (t), 40.24 (d), 40.81 (d), 50.15 (d), 54.82 (d), 123.61 (d), 135.63 ppm (d); mass spectrum *m/e* (rel intensity) 148 (20, M^+), 91 (15), 80 (35), 79 (100), 78 (74), 77 (15), 67 (16), 41 (20), 39 (18), 18 (17).

Anal. Calcd for $C_{11}H_{16}$: C, 89.1; H, 10.9. Found: C, 88.7; H, 10.6.

3-*endo*-Hydroxy-6,7-*exo*-trimethylenebicyclo[3.2.1]octane (3). A solution of 2.4 g (0.0146 mol) of 6,7-*exo*-trimethylenebicyclo[3.2.1]octan-3-one in 10 ml of ether was dropped into a suspension of 0.56 g (0.0147 mol) of lithium aluminum hydride in 60 ml of ether under reflux, and the reaction was heated at reflux for a further 1.5 h. After unreacted metal hydride had been destroyed by the addition of ethyl acetate, the mixture was treated with methanol and then with water. Precipitates were filtered off, and the filtrate was washed with water and dried over anhydrous sodium sulfate. Evaporation of the solvent left 1.6 g (66% yield) of crude **3**, which was purified on preparative VPC to give a pure sample: mp 82–83°; ir (neat) 3300 (br), 2940, 2860, 1470, 1370, 1270, 1050, 970, 800 cm^{-1}; ^1H NMR δ 0.8–2.6 (complex m, 16 H), 2.28 (s, 1 H, vanished on treatment with D_2O, OH), 3.8 (m, 1 H, CHOH); mass spectrum *m/e* (rel intensity) 148 (61), 119 (33), 107 (100), 106 (61), 94 (26), 81 (30), 80 (53), 79 (58), 78 (23), 67 (47).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.5; H, 10.9. Found: C, 79.6; H, 11.2.

2-(2-Formylcyclopentyl)cyclopentanone (12). A solution of 9.0 g (0.094 mol) of 1-formylcyclopentene (**11**)[18] in 25 ml of dry ether was dropped in a period of 40 min to a stirred solution of 21.3 g (0.14 mol) of cyclopentanone morpholine enamine (**10**)[19] in 125 ml of dry ether kept at −7 °C. The reaction mixture was stirred at the same temperature for a further 2 h, and then set aside at ambient temperature overnight. The reaction mixture was mixed with 5 ml of water and stirred for 2 h. The mixture was washed with two 50-ml portions of 1% hydrochloric acid and then with water, and dried over anhydrous sodium sulfate. Ether was evaporated off from the mixture, and the residue was fractionally distilled to give 3.1 g (18% yield) of 2-(2-formylcyclopentyl)cyclopentanone (**12**): bp 107–111° (0.6 mm); ir (neat) 2950, 2860, 2700, 1730, 1710 cm^{-1}.

7-Hydroxytricyclo[6.2.1.$0^{2,6}$]undecan-11-one (13). To 50 ml of 30% potassium hydroxide solution kept at 0° was dropped with

efficient stirring a solution of 3.0 g (0.017 mol) of 2-(2-formylcyclopentyl)cyclopentanone (12) in 5 ml of ether in a period of 30 min, and the mixture was stirred overnight at ambient temperature. The organic layer was separated, and the aqueous layer was extracted with three 20-ml portions of ether. The combined organic layer and ether extracts were washed with water and dried over anhydrous sodium sulfate. Ether was evaporated, and the residue was analyzed on conventional VPC to consist of 74% **13** and 26% unreacted **12**. Pure **13** was isolated by fractionation on preparative VPC: ir (neat) 3430, 2940, 2860, 1740 cm^{-1}; mass spectrum *m/e* (rel intensity) 180 (20, M^+), 162 (14), 97 (30), 84 (100), 83 (30), 67 (35), 55 (40), 41 (30), 39 (25).

Tricyclo[6.2.1.$0^{2,6}$]undeca-7,11-dione (14). To a solution of 1.6 g (0.0089 mol) of 7-hydroxytricyclo[6.2.1.$0^{2,6}$]undecan-11-one (**13**) in 10 ml of acetone was dropped at ambient temperature a mixture of 1.0 g (0.01 mol) of chromium trioxide, 0.9 ml of 95% sulfuric acid, and 7 ml of water in a period of 1 h, and the mixture was stirred for another 30 min. The reaction mixture was extracted with three 10-ml portions of ether, and the combined ether extracts were washed with water and dried over anhydrous sodium sulfate. Evaporation of ether gave 0.8 g (51% yield) of crude **14**: ir (neat) 2950, 2880, 1750, 1740, 1720, 1680 cm^{-1}.

Tricyclo[6.2.1.$0^{2,6}$]undecane (6h). A mixture of 0.44 g (0.0025 mol) of crude tricyclo[6.2.1.$0^{2,6}$]undeca-7,11-dione (**14**), 3 ml of 80% hydrazine hydrate, 2.2 g of potassium hydroxide, and 25 ml of diethylene glycol was heated under reflux for 3 h. Water and excess hydrazine hydrate were distilled off, and the residue was refluxed for a further 4 h. After addition of 100 ml of cold water, the mixture was extracted with five 20-ml portions of ether. The combined ether extracts were washed with a saturated sodium chloride solution and dried over anhydrous calcium chloride. Evaporation of the ether gave 0.17 g (45% yield) of crude **6h**. Fractionation on preparative VPC gave a pure sample: ir (neat) 2950, 2870, 1470, 1450, 1350, 1320, 1310, 1250, 890, 870 cm^{-1}; ^1H NMR δ 0.8–2.4 (complex m); ^{13}C NMR (multiplicity) 24.08 (t), 27.45 (t), 27.86 (t), 31.39 (t), 32.37 (t), 33.30 (t), 33.79 (d), 34.84 (d), 37.24 (t), 37.93 (d), 47.55 ppm (d); mass spectrum *m/e* (rel intensity) 150 (66, M^+), 94 (33), 93 (51), 81 (52), 80 (98), 79 (78), 67 (100), 66 (60), 41 (73), 39 (51).

Anal. Calcd for $C_{11}H_{18}$: C, 87.9; H, 12.1. Found: C, 87.6; H, 11.8.

Tricyclo[6.2.1.$0^{2,6}$]undec-2(6)-ene (6). A sample of tricyclo[6.2.1.$0^{2,6}$]undec-2(6)-ene (**6**) was isolated from combined mixtures of phosphoric acid catalyzed rearrangement product on preparative VPC (retention time 15.0 min; column 0.375 in. × 10 ft, packed with 30% Carbowax 20M on Chromosorb W AW, at 144°; He pressure 1.5 kg/cm^2; injection port temperature 200 °C; detector temperature 240 °C). This sample of **6** consisted of 88.6% **6** and three tricycloundecenes of unknown structure in the amount of 9.1, 1.5, and 1.2%, respectively: ir (neat) 3050 (sh), 2940, 2860, 1660 (w), 1450, 1290, 1050, 940 cm^{-1}; ^1H NMR δ 0.8–3.0 (complex m); ^{13}C NMR (multiplicity, rel intensity) 22.54 (t, 1), 30.74 (t, 1), 33.75 (d, 1), 34.60 (t, 2), 35.37 (t, 1), 36.30 (d, 1), 36.71 (t, 1), 37.12 (t, 1), 130.11 (s, 1), 142.29 ppm (s, 1).

Anal. Calcd for $C_{11}H_{16}$: C, 89.1; H, 10.9. Found: C, 88.9; H, 11.0.

The mass spectrum of **6** was taken in the Golay GC–MS instrument: *m/e* (rel intensity) 148 (35, M^+), 120 (23), 119 (100), 105 (14), 92 (18), 91 (72), 80 (15), 79 (33), 77 (16), 66 (14), 53 (8), 51 (8), 41 (20), 39 (19).

Hydrogenation of Tricyclo[6.2.1.$0^{2,6}$]undec-2(6)-ene (6). A sample of **6** (0.43 g, 0.0029 mol) isolated in the preceding paragraph was mixed with 0.11 g of a 5% palladium on charcoal catalyst and 15 ml of ethyl acetate, and hydrogenated at 120° under 50 kg/cm^2 of hydrogen for 18 h. The catalyst was filtered off, and the filtrate was concentrated to give 0.42 g (96% yield) of the residue. This residue was analyzed on Golay GC–MS to contain four major components in the amount of 1.9, 11.0, 51.6, and 21.3%, as listed in the order of increasing retention time. The three, early eluted components were identified as unreacted **6**, 1,2-trimethylenebicyclo[2.2.2]octane (**15**), and tricyclo[6.2.1.$0^{2,6}$]undecane (**6h**), respectively, by comparison of their retention times and mass spectra with those of authentic specimens.

The last eluted component was of unknown structure, and had a mass spectrum *m/e* 150 (84, M^+), 122 (69), 121 (100), 93 (60), 80 (82), 79 (88), 67 (99), 66 (54), 41 (77), 39 (49). This mass spectrum was almost identical with that of **6h**, except that two peaks with *m/e* 122 and 121 were of low intensity in the spectrum of **6h**.

Hydride Transfer Reduction–Rearrangement under Sulfuric and Phosphoric Acid Catalysis. A reactant (0.1 g) dissolved in 5 ml of *n*-pentane was mixed with 1 g of 95% sulfuric acid, and the mixture was stirred vigorously at room temperature. Samples were withdrawn from the pentane layer of the reaction mixture while stirring was interrupted, and examined on Golay GC–MS. After the reaction was completed, the pentane layer was separated, washed with water, and dried over anhydrous sodium sulfate. Pentane was evaporated off from the solution, and the residue was weighed to calculate yields. The ratio of reactants to pentane and sulfuric acid was the same for preparative as for analytical runs.

In phosphoric acid catalyzed rearrangement reactions, 5 ml of *n*-heptane and 3 g of 85% phosphoric acid were used for 0.1 g of a reactant. Reactions were run at reflux. Analysis and treatment of the reaction mixture were the same as for sulfuric acid catalyzed reactions.

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Registry No.—**1**, 57526-50-8; **2** *exo*-OH, 57496-69-2; **2** *endo*-OH, 57526-51-9; **2^{Δ}**, 57526-52-0; **3**, 57526-98-4; **4n**, 56846-34-5; **4x**, 56804-83-2; **6**, 57496-70-5; **6h**, 51027-86-2; **8**, 53432-47-6; **9**, 57496-71-6; **10**, 936-52-7; **11**, 6140-65-4; **12**, 57496-72-7; **13**, 57496-73-8; **14**, 57496-74-9; 6,7-*exo*-trimethylenebicyclo[3.2.1]octan-3-one, 53432-46-5; sulfuric acid, 7664-93-9; phosphoric acid, 7664-38-2.

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