Adamantane Rearrangement of [3.3.2]Propellanes

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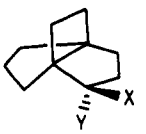
Abstract: For elucidation of the isomerization pathway of the [3.3.2]propellane ring system into "adamantaneland" by effective skeletal transformations, hydride-transfer reduction of [3.3.2]propellanols [(*exo*-**4**) and (*endo*-**4**)] and [3.3.2]propellene (**5**) was carried out. It was found that tricyclo[5.3.0.0^{4,8}]decane (**6**) was obtained as a sole initial product in 25, 32, and 38% yields, respectively. Similar reaction of 1,7-trimethylenenorbornanol (**9**) furnished **6** in a 27% yield, and $AlCl_3$-catalyzed rearrangement of 1,7-trimethylenenorbornane (**12**) gave **6** as well as adamantane (**2**) and *exo*-tetrahydrodicyclopentadiene (**3**). Moreover, **6** readily isomerized to **2** with H_2SO_4 or $AlCl_3$. These results indicate that the adamantane rearrangement of the [3.3.2]propellane ring system follows the route [3.3.2]propellane → **12** → **6** → **2**.

There has been considerable interest in the carbonium ion rearrangement of polycarbocyclic hydrocarbons into the most stable isomers, "stabilomers",[1] and, especially, numerous efforts have been made on the elucidation of the isomerization pathways from various isomers of $C_{10}H_{16}$ hydrocarbons into adamantane.[2] However, as for an entry from tricyclic propellanes, being one of the $C_{10}H_{16}$ isomers, into "adamantaneland", there has not been noted so far.[3] As part of our studies on the transformation of propellane skeletons into other important carbocyclic ring systems, we have been interested in the skeletal rearrangement of [*m.n*.2]propellane derivatives,[4] which are readily accessible by means of photocycloaddition of the bicyclic enones to olefins.[5] In this connection, we wish to report herein the first example of the adamantane rearrangement of [3.3.2]propellanes.

In the Lewis-acid-catalyzed rearrangement of [3.3.2]propellane (**1**)[6] with aluminum chloride in dichloromethane at 15 °C for 10 h, or in refluxing hexane for 2 h, the formation of a small quantity of adamantane (**2**) along with trace of *exo*-tetrahydrodicyclopentadiene (**3**) was observed with quick disappearance of **1**, but, under these severe conditions, a large quantity of unidentified higher boiling hydrocarbons was formed probably due to unfavorable cleavage of the highly strained cyclobutane ring present in this molecule. Therefore, taking into consideration that the initial generation of carbocation intermediates at the cyclopentane ring might be absolutely necessary to effect much more selective skeletal transformation, the hydride-transfer reductions of



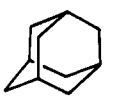
1, X=Y=H

exo-**4**, X=OH, Y=H

endo-**4**, X=H, Y=OH

exo-**10**, X=OTs, Y=H

endo-**10**, X=H, Y=OTs



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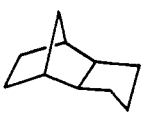

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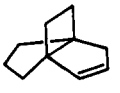
[3.3.2]propellanols [(*exo*-**4**)[5] and (*endo*-**4**)[5]] and [3.3.2]propellene (**5**)[4c] were carried out (Table I, runs 1–3).

Significantly, when the exo propellanol (*exo*-**4**) was stirred vigorously in *n*-pentane with 98% sulfuric acid at 15 °C for 2 min, tricyclo[5.3.0.0^{4,8}]decane (**6**)[2h,7] was obtained as a sole tricyclo-



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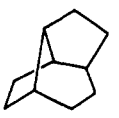
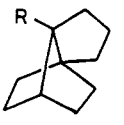


6

8



9, R=OH

11, R=OCHO

12, R=H

(1) For reviews see: (a) McKervey, M. A. *Chem. Soc. Rev.* **1974**, *3*, 479. (b) Fort, R. C., Jr. "Adamantane, Chemistry of Diamond Molecules"; Marcel Dekker: New York, 1976.

(2) (a) Whitlock, H. W.; Siefken, M. W. *J. Am. Chem. Soc.* **1968**, *90*, 4929. (b) Paquette, L. A.; Meehan, G. V.; Marshall, S. J. *Ibid.* **1968**, *90*, 6779. (c) Baldwin, J. E.; Fogelsong, W. D. *Ibid.* **1968**, *90*, 4303. (d) Vogt, B. R. *Tetrahedron Lett.* **1968**, 1575. (e) Engler, E. M.; Farcasiu, M.; Sevin, A.; Cense, J. M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 5769. (f) Majerski, Z.; Djigas, S.; Vinković, V. *J. Org. Chem.* **1979**, *44*, 4064. (g) Paquette, L. A.; Doecke, C. W.; Klein, G. *J. Am. Chem. Soc.* **1979**, *101*, 7599. (h) Schleyer, P. v. R.; Grubmuller, P.; Maier, W. F.; Vostrowsky, O.; Skattebøl, L.; Holm, K. H. *Tetrahedron Lett.* **1980**, 921.

(3) Interestingly, the formation of [3.3.3]propellane, a higher homologue of [3.3.2]propallane, was observed in the $AlCl_3$-catalyzed rearrangement of *exo*-2,3-tetramethylenenorbornane, albeit in a low concentration.[3a] However, this propellane was shown to be a mechanistic deadend[3b] and was inert even under the strongly acidic conditions.[3c] (a) Takaishi, N.; Inamoto, Y.; Tsuchihashi, K.; Yamashita, K.; Aigami, K. *J. Org. Chem.* **1975**, *40*, 2929. (b) Osawa, E.; Aigami, K.; Takaishi, N.; Inamoto, Y.; Fujikura, Y.; Majerski, Z.; Schleyer, P. v. R.; Engler, E. M.; Farcasiu, M. *J. Am. Chem. Soc.* **1977**, *99*, 5361. (c) Inamoto, Y.; Aigami, K.; Fujikura, Y.; Takaishi, N.; Tsuchihashi, K. *J. Org. Chem.* **1979**, *44*, 854.

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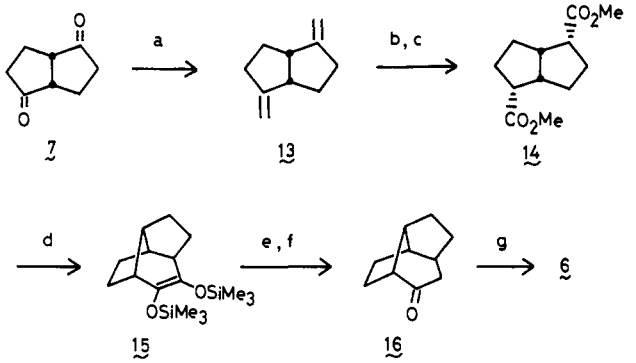
Table I. Acid-Catalyzed Rearrangement of [3.3.2]Propellanes and 1,7-Trimethylenenorbornanes

run	reactant	catalyst[a]	react time, min	combined yield of isolated prod, %	tricyclodecanes, % yield				
					5	12	2	6	3
1	*exo*-4	S	2	25[b]				100	
2	*endo*-4	S	2	32[b]				100	
			30				38.1	61.9	
3	5	S	5		84.4			15.6	
			10		53.9			46.1	
			20		5.8		16.4	77.8	
			30	38[b]	0		29.4	70.6	
4	6	A	1				34.2	65.8	
			3				59.6	40.4	
			10	90			100	0	
5	9	S	2	27[b]				100	
			10				21.2	78.8	
6	12	A	2			23.6	17.3	30.0	29.1
			3			2.8	26.2	32.9	38.1
			5			0	59.0	1.8	39.2
			10	79		0	60.4	0	39.6

[a] S, 98% sulfuric acid in *n*-pentane; A, aluminum chloride in dichloromethane. [b] The material balance consisted of pentane insoluble polymeric substances.

Scheme I



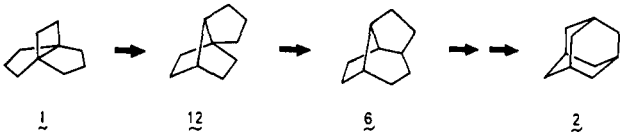
7 13 14 15 16 6

[a] Ph_3PCH_2; 71%. [b] (i) B_2H_6, (ii) H_2O_2; 80%. [c] (i) CrO_3, (ii) CH_2N_2; 55%. [d] Na, Me_3SiCl; 38%. [e] HCl; 100%. [f] Zn, HCl; 78%. [g] N_2H_4; 39%.

decane product in a 25% yield (run 1).[8] The structure of **6** was deduced mainly on the basis of its ^{13}C NMR spectrum ($CDCl_3$) which is comprised of five peaks at 47.00 (d), 40.32 (d), 31.51 (t), 26.69 (t), and 24.80 (t) ppm, indicative of the C_2 symmetry of the assigned structure. Further confirmation has been obtained by comparing the GLC retention time and mass and ^{13}C NMR spectra of **6** with those of an authentic sample independently synthesized from *cis*-bicyclo[3.3.0]octane-2,6-dione (**7**)[9] as outlined in Scheme I.[10] Similarly, the hydride-transfer reduction of the endo propellanol (*endo*-**4**) under similar conditions furnished only **6** in a 32% yield,[8] and, after a prolonged reaction time, gradual isomerization of **6** to **2** presumably catalyzed by sulfuric acid was observed (run 2). Moreover, the similar reduction of the propellene **5** proceeded slowly to afford **6** and **2** (run 3).[8] The isomerization of **6** to **2** was also effected by aluminum chloride with high efficiency (run 4). These facts seem to support that the adamantane rearrangement of the [3.3.2]propellane system readily takes place along the pathway involving the intermediate **6**. However, in every case, any intermediates formed in the course of the rearrangement pathway both from [3.3.2]propellanes to **6** and from **6** to **2** could not be detected.

Previously we reported on the synthesis of the olefin **8** and the alcohol **9**, having the 1,7-trimethylenenorbornane skeleton, by means of the acetolysis of [3.3.2]propellane tosylates (*exo*-**10**) and (*endo*-**10**).[4c] Moreover, we have found that the buffered formolysis of the endo tosylate (*endo*-**10**) afforded the formate **11** (mp 41–43 °C) as a sole product in an 80% yield. These results suggest that the isomerization of [3.3.2]propellanes to **6** would involve the intervention of 1,7-trimethylenenorbornane (tricyclo[4.2.2.0^{1,5}]decane) (**12**), though **12** has not been identified in the above reactions. Accordingly, the isomerization behavior of the alcohol (**9**)[4c] and the hydrocarbon **12** under the strongly acidic conditions was examined. **9** was more conveniently accessible by lithium aluminum hydride reduction of the formate (**11**) (98%). Dehydration of **9** with thionyl chloride in pyridine followed by diimide reduction of **8** afforded **12**[2h,11] (mp 33–34 °C) in a 36% yield. Hydride-transfer reduction of **9** with H_2SO_4/*n*-pentane gave only **6** in a 27% yield in analogy with the cases of *exo*-**4** and *endo*-**4** (run 5).[8] More interestingly, when **12** was subjected to $AlCl_3$-catalyzed rearrangement in dichloromethane at 15 °C (run 6), it disappeared thoroughly within 5 min and, instead, three tricyclodecanes, that is, **2**, **6**, and *exo*-tetrahydrodicyclopentadiene (**3**), appeared.

Scheme II



1 12 6 2

As described earlier, **6** readily isomerized to **2** to result in a mixture of **2** and **3** in a ratio of 3:2.[12] The formation of **3** in this reaction may be due to the generation of a stable 2-norbornyl type cation by relatively random hydride abstraction with the Lewis acid compared with the case of the hydride-transfer reduction.[11] Thus, 1,7-trimethylenenorbornane system showed essentially the same isomerization behavior as that of [3.3.2]propellane system. From the above results, it is deduced that the isomerization of [3.3.2]propellanes to **6** occurs via **12**. Consequently, it is indicated that the adamantane rearrangement of the [3.3.2]propellane system follows the route [3.3.2]propellane → **12** → **6** → **2** (Scheme II).[14] Thus an entry of a propellane ring system into

(8) The material balance was consisted of pentane insoluble polymeric substances which are not investigated.

(9) Cantrell, T. S.; Strasser, B. L. *J. Org. Chem.* **1971**, *36*, 670.

(10) Alternatively, the authentic sample of **6** was prepared by the catalytic hydrogenation of the corresponding triene (lumibullvalene, Vedejs, E.; Steiner, R. P. *J. Chem. Soc., Chem. Commun.* **1973**, 599) over Pd/C.

(11) Jaggi, F. J.; Ganter. C. *Helv. Chim. Acta* **1980**, *63*, 214.

(12) Our result is somewhat different in full detail from that of the $AlBr_3$-catalyzed rearrangement of **12** in CS_2 reported very recently by Schleyer et al.[2h] Namely, (i) considerable amounts of the intermediate (**6**) accumulated (maximum concentration; 33%), (ii) the ratio of **2**:**3** was 3:2 (2:3 with $AlBr_3$), and (iii) other intermediates such as 4-homobrendane[13] and protoadamantane were not detected under the present reaction conditions. However, concerning the mechanistic pathway from **12** to **2**, both results led to the same conclusion.

(13) We are grateful to Dr. Inamoto for providing a sample of this compound.

"adamantaneland" was elucidated.

Experimental Section

Melting points and boiling points are uncorrected. Infrared spectra were recorded on a JASCO IR-G spectrometer. ^1H NMR spectra were obtained on a JEOL JNM-PS-100 spectrometer in CCl_4 and ^{13}C NMR spectra on a JEOL JNM-FX-60S spectrometer in $CDCl_3$ with the use of Me_4Si as an internal standard. Mass spectra were measured with a Hitachi RMU-6E spectrometer. Analytical GLC was carried out on a Hitachi 163 gas chromatograph: column A, 10% FFAP; column B, 5% SE-30; column C, 20% DC-550. Preparative GLC separation was conducted on a Varian Aerograph 920 gas chromatograph with the use of column A or B.

Materials. The propellanols *exo*-**4** and *endo*-**4**[5] and the propellene **5**[4c] were prepared as described previously. The propellane **1** was prepared by the Wolff–Kishner reduction of the corresponding propellanone[5] (38% yield) which showed ^{13}C NMR signals at δ 27.72 (t, 2 C), 30.99 (t, 2 C), 39.25 (t, 4 C), and 55.27 (s, 2 C). The alcohol **9**[4c] and the hydrocarbon **12** were prepared from the formate **11** as described below.

Formolysis of the *endo*-Tosylate (*endo*-10). A solution of 7.0 g (22.8 mmol) of *endo*-**10**[4c] and 3.4 g (50 mmol) of sodium formate in 350 mL of formic acid was heated at 60 °C for 10 h. The solution was poured into water and extracted with ether. The ether extract was washed with aqueous sodium carbonate solution and water and then dried over Na_2SO_4. After evaporation of the solvent, the residue was distilled under reduced pressure [80–82 °C (2 mmHg)] to give 3.2 g (80%) of **11** as a clear oil which solidified on standing.

An analytical sample was obtained by preparative GLC (column A): mp 41–43 °C; IR 1710, 1170 cm^{-1}; MS *m/e* (relative intensity) 180 (M^+, trace), 134 (88), 119 (52), 106 (85), 105 (100), 91 (91); ^1H NMR δ 1.10–2.70 (m, 15 H), 7.92 (s, 1 H). Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 72.92; H, 8.82.

A solution of 2.90 g (16.1 mmol) of **11** in 100 mL of ether was added dropwise to the slurry of 0.6 g (16 mmol) of lithium aluminum hydride in ether (50 mL), and the mixture was stirred at room temperature for 1 h. Water was added, followed by careful addition of 1 N HCl, and the organic layer was separated. The aqueous layer was extracted with ether, and the combined organic layer was washed with water and dried. Evaporation of the solvent gave 2.50 g (98%) of **9** which was purified by sublimation [60 °C (2 mmHg)].

Dehydration of **9** by thionyl chloride and pyridine was carried out as described before[4c] to afford the olefin **8** (71%). A solution of 1.50 g (11.2 mmol) of **8**, 11.0 g of hydrazine hydrate, and 0.1 g of cupric sulfate in 30 mL of ethanol was stirred at room temperature for 10 h while air was bubbled through. The mixture was diluted with water and extracted with ether. The ether extract was washed with water and dried. After evaporation of the solvent, sublimation at 50 °C (20 mmHg) afforded 0.79 g (51%) of **12**: mp 33–34 °C; IR 2900, 1450 cm^{-1}; MS *m/e* (relative intensity) 136 (M^+, 13), 108 (100), 107 (48), 80 (47), 79 (33); ^1H NMR δ 1.00–2.40 (m); ^{13}C NMR δ 21.53 (t), 28.77 (t), 29.04 (t), 30.33 (t), 32.30 (t), 32.84 (t), 36.86 (d), 37.57 (t), 58.66 (s), 60.49 (d). Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.22; H, 11.78.

Hydride-Transfer Reduction of *exo*-4, *endo*-4,5, and 9. A solution of 1 mmol of the reactant in 5 mL of *n*-pentane was stirred vigorously with 2.0 g of 98% sulfuric acid at 15 °C. After completion of the reaction, the pentane solution was decanted and washed with aqueous sodium carbonate solution and water and then dried. After evaporation of the solvent, the products were sublimed [50 °C (20 mmHg)] and analyzed by GLC (columns B and C), and the results are summarized in Table I. A pure sample of 6 was obtained by preparative GLC (column B): IR 2900, 1450 cm^{-1}; MS *m/e* (relative intensity) 136 (100), 121 (40), 108 (58), 107 (36), 94 (56), 80 (73), 79 (51), 67 (53); ^1H NMR δ 1.00–2.20 (m); ^{13}C NMR δ 24.80 (t), 26.69 (t), 31.51 (t), 40.32 (d), 47.00 (d). Anal. Calcd for $C_{10}H_{16}$: C, 86.16; H, 11.84. Found: C, 88.05; H, 11.95.

Aluminum-Chloride-Catalyzed Rearrangement of 6 and 12. A solution of 1 mmol of the reactant in 10 mL of dichloromethane was stirred vigorously with 40 mg (0.3 mmol) of aluminum chloride at 15 °C. At appropriate intervals, the reaction was quenched by addition of water and analyzed by GLC (columns B and C) (Table I). The product identification was done by comparison of GLC retention times, mass spectra, and (sometimes) ^{13}C NMR spectra of the isolated product with those of the authentic samples.

Independent Preparation of 6. To 9.6 g (0.20 mol) of 50% sodium hydride was added dropwise 100 mL of dimethyl sulfoxide (Me_2SO) under nitrogen, and the mixture was heated at 75–80 °C with stirring for 45 min. The mixture was cooled with ice bath, and a solution of 71.4 g (0.20 mol) of triphenylmethylphosphonium bromide in 20 mL of Me_2SO was added dropwise. The mixture was stirred at room temperature for 10 min, and then a solution of 11.6 g (0.084 mol) of the dione **7**[9] in 50 mL of Me_2SO was added. The mixture was heated at 50 °C for 20 h and poured into water and then extracted with pentane. The pentane extract was washed with water, dried, and, passed through a short column of alumina. The solvent was evaporated and the residue distilled [74–76 °C (27 mmHg)] to give 8.0 g (71%) of the diene **13**:[15] IR 1640, 860 cm^{-1}.

To a mixture of 4.3 g (0.032 mol) of **13** and 1.0 g (0.026 mol) of sodium borohydride in 40 mL of tetrahydrofuran (THF) was added dropwise 4.5 g (0.032 mol) of boron trifluoride etherate, and the mixture was stirred at room temperature for 3 h. After successive addition of 2 mL of water, 10 mL of 3 N NaOH solution, and 10 mL of 30% H_2O_2 solution, the mixture was stand overnight. The organic phase was separated, and the aqueous layer was extracted with ether, and the combined organic phase was washed with saturated sodium chloride solution and dried. Evaporation of the solvent gave 4.3 g (80%) of a diol mixture (IR 3300, 1050, 1000 cm^{-1}) which was used without further purification.

To a solution of 4.3 g of the above diols in 100 mL of acetone was added with stirring a slight excess of Jones reagent at room temperature. After 2 h, acetone was evaporated and the mixture was diluted with water and extracted with ether. The ether extract was washed with water and dried. After evaporation of the solvent, the residue was dissolved in ether and treated with an excess of ethereal diazomethane to afford 3.1 g (55%) of the crude diester mixture which comprised of three isomers in a ratio percent of 25:15:60. The major isomer **14** was isolated by preparative GLC (column A); IR 1730, 1165 cm^{-1}; MS *m/e* (relative intensity) 226 (M^+, trace), 194 (92), 166 (100), 134 (85), 107 (62), 79 (68); ^1H NMR δ 1.20–2.20 (m, 8 H), 2.60–3.00 (m, 4 H), 3.62 (s, 6 H). Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.95; H, 8.22.

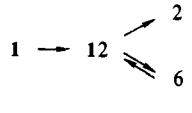
A solution of 2.5 g (0.011 mol) of the above diester mixture and 5.5 g (0.050 mol) of trimethylchlorosilane in 10 mL of toluene was added dropwise to 1.2 g (0.050 mol) of a sodium dispersion in 25 mL of toluene. The mixture was heated at reflux with vigorous stirring for 5 h and then cooled and filtered. The filtrate was evaporated and the residue distilled [108 °C (2 mmHg)] to afford 1.4 g (38%) of the silyl ether **15**: IR 1665, 1630, 1230, 1190, 820 cm^{-1}.

A solution of 1.4 g (0.0042 mol) of **15** and 0.3 mL of 1 N HCl and 5 mL of THF was stirred under nitrogen at room temperature for 10 h. The solution was poured into water and extracted with ether. The ether extract was washed with saturated sodium chloride solution and dried. Evaporation of the solvent gave 0.70 g (100%) of crude acyloin: IR 3450, 1700, 1090, 1030 cm^{-1}.

A mixture of 0.70 g (0.0042 mol) of the above acyloin and 0.8 g of zinc dust in 5 mL of acetic acid was heated at 75–80 °C with vigorous stirring, and to this was added, in three portions, 5.4 mL of concentrated HCl every 30 min. After being cooled, the mixture was diluted with water and extracted with ether. The ether extract was washed with aqueous sodium carbonate solution and water and dried. Evaporation of the solvent gave 0.49 g (78%) of the crude ketone **16** which was purified by preparative GLC (column A): mp 47–49 °C; IR 1700 cm^{-1}; MS *m/e* (relative intensity) 150 (M^+, 58), 106 (100); ^1H NMR δ 1.52–2.80 (m); ^{13}C NMR δ 23.78 (t), 24.17 (t), 29.56 (t), 32.23 (t), 41.26 (d), 43.60 (t), 46.52 (d), 47.95 (d), 58.61 (d), 215.12 (s). (Semicarbazone mp 189–191 °C). Anal. Calcd for $C_{11}H_{17}ON_3$: C, 63.74; H, 8.27; N, 20.27. Found: C, 63.45; H, 8.25; N, 20.21.

A solution of 99 mg (0.66 mmol) of **16**, 0.70 g of KOH, and 7 mL of 80% hydrazine hydrate in 7 mL of diethylene glycol was refluxed for 2 h. Excess hydrazine was distilled off, and the mixture was heated at 210 °C for 2 h. After being cooled, the mixture was neutralized with HCl and extracted with pentane. The extract was washed with water and dried. Evaporation followed by sublimation [50 °C (15 mmHg)] gave 36 mg (39%) of **6**.

(14) The experimental results are consistent with the proposed pathway; however, it is not proved experimentally. For example, a branch into a deadend is possible



(15) Shea, K. J.; Wise, S. *Tetrahedron Lett.* **1978**, 2283.