Acetolysis of [4.2.2]Propellan-7-ylmethyl Tosylates

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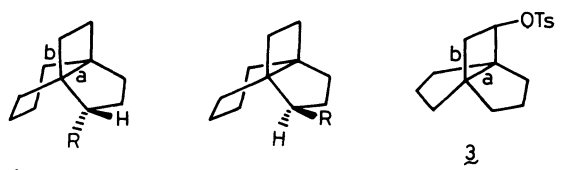
The acetolysis rates and products of [4.2.2]propellan-7-ylmethyl tosylates were determined in order to clarify the effect of the central and external cyclobutane bonds on the modes of the ring expansion of the cyclobutylmethyl moiety. Since the products obtained from the *endo* tosylate were the olefin and the acetate having 1,7-tetramethylenenorbornane skeleton, it is deduced that the ring expansion occurs selectively to afford [4.3.2]propellan-7-yl cation which is stabilized by the external cyclobutane bond. In contrast, the *exo* tosylate gave the products derived from both [4.3.2]propellan-7-yl and -8-yl cations which are subject to the participation of the external and central cyclobutane bonds, respectively.

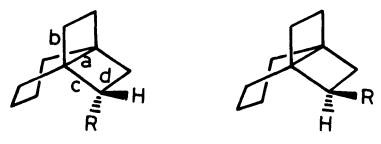
It has been documented that the solvolysis of cyclobutylmethyl derivatives proceeds with σ participation of the cyclobutane bond.[1] Since the ring expansion occurs so as to stabilize the ring-expanded cation, the specificity in the modes of the ring expansion is affected markedly by the geometry of the cyclobutylmethyl moieties, especially, involved in polycarbocyclic systems.[2] We have been interested in the solvolytic rearrangements of the propellane derivatives having one or two cyclobutane rings, [*m.n*.2]propellanes ($m \geq 3$, $n \geq 2$), such as [4.3.2]-propellan-7-yl tosylates (**1a**) and (**2a**),[3a,b] [3.3.2]-propellan-9-yl tosylate (**3**),[3c] [4.2.2]propellan-7-yl derivatives (**4a** and **5a**).[3d] In the above studies, it has been pointed out that the propellane derivatives undergo solvolysis with participation of the central (a) or external (b) bond of the cyclobutane ring depending on the ring size of the propellane framework and the stereochemistry of the leaving group. In this connection, we wish to report here the acetolysis of [4.2.2]propellan-7-ylmethyl tosylates (**4b** and **5b**) and emphasize that the central (a) and external (b) cyclobutane bonds which are remote from the cation center play an important role in the ring expansion of the cyclobutylmethyl moiety by 1,2-shift of the bond (c) or (d).

The tosylates **4b** and **5b** were prepared from the alcohols **4c** and **5c** which were obtained by the lithium aluminium hydride reduction of the corresponding methyl esters **4d** and **5d**.[4] In order to establish the *exo*/*endo* stereochemistry of **4b**—**d** and **5b**—**d** unambiguously, the unsaturated esters **6** and **7** were prepared by the ring contraction of the ketone **8**[5] in the manner similar to that of preparation of **4d** and **5d**.[4] The stereochemical assignment of **6** and **7** was based on the ^{1}H NMR spectra and the lanthanoide-induced shift in the ^{1}H NMR as follows: whereas the vinyl protons of **6** appeared as overlapping doublets (J=2 Hz) at δ 6.22 ($\Delta\delta$=0), those of **7** appeared at δ 6.03 (d, J=2 Hz) and 6.21 (d, J=2 Hz) ($\Delta\delta$=0.18). Moreover, in the lanthanoide-shifted NMR using Eu(dpm)$_3$, the S values[6] for the vinyl protons of **6** were 2.9 and 2.0 while those of **7** were 6.5 and 2.5. These results indicate clearly that the methoxycarbonyl group of **7** is located at exo direction which is nearer to the vinyl group. It is therefore deduced that **6** and **7** are the *endo* and *exo* isomers, respectively. Finally, catalytic hydrogenation of **6** and **7** with Pd/C gave the esters **4d** and **5d**, respectively, thus establishing the stereochemistry of **4b**—**d** and **5b**—**d**.



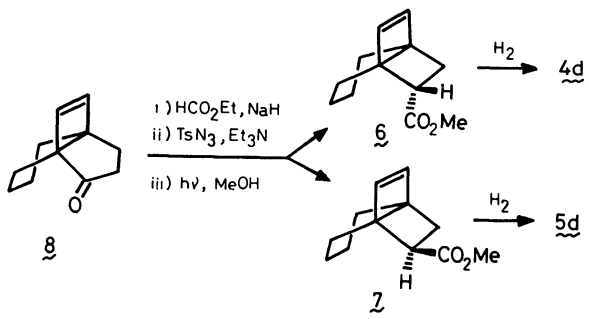
1a R = OTs
1b R = OAc
1c R = OH

2a R = OTs
2b R = OAc
2c R = OH



4a R = OTs
4b R = CH_2OTs
4c R = CH_2OH
4d R = CO_2Me
4e R = CH_2OAc

5a R = ODNB
5b R = CH_2OTs
5c R = CH_2OH
5d R = CO_2Me
5e R = CH_2OAc



The kinetic data for the acetolysis of **4b** and **5b** were summarized in Table 1. As shown in Table 1, the *endo* tosylate **4b** undergoes acetolysis at a rate slightly greater than that of the *exo* one **5b**, but the difference is rather small.

The acetolysis products from **4b** and **5b** after 10 half-lives were separated by column chromatography on silica gel and the subsequent preparative GLC separation. The combined yields of the products were almost quantitative and the distribution of the products were listed in Table 2 together with that from [4.3.2]-propellan-7-yl tosylates (**1a** and **2a**). The structures of the acetates **1b** and **2b** were established by the identity in GLC, ^{1}H NMR, and IR spectra with authentic

Table 1. Kinetic data for acetolysis of **4b** and **5b**

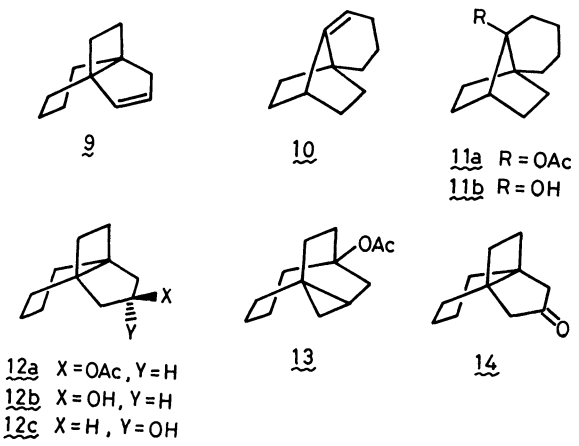
Tosylate	Temp °C	k[a] s^{-1}	$\Delta H^{\neq}$ kcal mol^{-1}	$\Delta S^{\neq}$ e.u.	k_{rel}
4b	60.0	7.50×01^{-5}			
	70.0	2.24×10^{-4}	23.8	−6.1	6.2
	80.0	6.11×10^{-4}			
5b	70.0	3.62×10^{-5}	22.0	−5.2	1.0
	90.0	2.97×10^{-4}			

a) Average of at least duplicate measurements and the deviations are within 6%.

Table 2. Product distribution from acetolysis of **4b**, **5b**, **1a**, and **2a**

Tosylate	Products (%)								
	1b	**2b**	**9**	**10**	**11a**	**12a**	**13**	**A**[a]	**B**[a]
4b	8	—	6	62	20	—	—	4	—
5b	—	—	3	15	10	11	30	20	11
1a[b]	48	—	—	39	9	—	—	4	—
2a[b]	—	10	5	44	28	—	—	7	6

a) Unidentified tertiary acetate. b) Ref. 3a.



9 **10** **11a** R = OAc, **11b** R = OH

12a X = OAc, Y = H
12b X = OH, Y = H
12c X = H, Y = OH

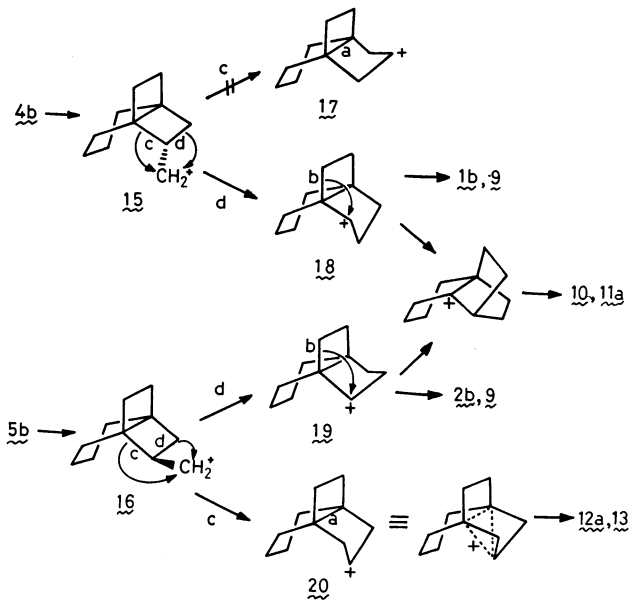
13 **14**

samples which were prepared by the acetylation of the alcohols **1c** and **2c**[3a] with acetic anhydride and pyridine. Similarly, [4.3.2]propell-7-ene (**9**) and tricyclo-[5.2.2.$0^{1,6}$]undec-5-ene (**10**) were identified with the respective authentic materials.[3a] The structure of the acetate **11a** was confirmed by the lithium aluminium hydride reduction to the alcohol **11b**.[3a] The structure of [4.3.2]propellan-8-yl acetate **12a** was determined by the following chemical transformations: the lithium aluminium hydride reduction of **12a** followed by Jones' oxidation of the resulting alcohol **12b** gave propellan-8-one (**14**). The authentic sample of this ketone was obtained by the hydroboration-oxidation of the olefin **9** and the subsequent Jones' oxidation of the major alcohol **12c**.[7] The structure of the acetate **13** having tricyclo[4.3.2.$0^{1,8}$]undecane skeleton was elucidated on the basis of the spectroscopic data as well as mechanistic considerations. Although the two remaining acetates (unidentified **A** and **B**) were characterized to be tertiary acetates, the structures of them were not elucidated as yet.[9] In every case, the absence of unrearranged acetates **4e** and **5e** was checked by GLC and ^{1}H NMR spectra.

In contrast to the kinetic results, the product study of the acetolysis revealed clearly the effect of the cyclobutane bonds (a) and (b) on the modes of the ring expansion. As shown in Scheme 1, the ring expansion of the propellanylmethyl cations **15** and **16** would take place by 1,2-shift of the bond (c) or (d) to afford the [4.3.2]propellan-8-yl cations **17** and **20** or the [4.3.2]-propellan-7-yl cations **18** and **19**, respectively. It should be noted that one of each pair of the ring-expanded cations has boat conformation of the bicyclo[3.2.0]-heptane moiety (**17** and **19**) and the other has chair conformation (**18** and **20**). Since it has been shown that the magnitude of the long-range interaction of strained σ bond to carbonium ion centers is greatly dependent on the orientation of the participating bond and the p orbital of the cation center,[10] it is reasonable to consider that the cation **20** having chair conformation is subject to the long-range interaction (edge participation) of the central cyclobutane bond (a),[11] while the cation **17** having boat conformation is not stabilized by the participation of the bond (a). On the other hand, both [4.3.2]propellan-7-yl cations **18** and **19** are subject to the σ participation of the external cyclobutane bond (b).[3a] Moreover, the degree of the interaction may be almost independent of the conformation of the bicyclo-[3.2.0]heptane moiety, because it has been found that the σ participation is relatively insensitive to the chair/boat conformational change in bicyclo[3.2.0]hept-2-yl cations.[12]

As shown in Table 2, the *endo* tosylate **4b** gave the olefin **10** and the acetate **11a** having 1,7-tetramethylene-norbornane skeleton as the major products (total of **10** and **11a**; 82%) along with small amounts of [4.3.2]-propellane derivatives **1b** and **9** and unidentified **A**. Since these products except for **9** were obtained from the acetolysis of *endo*-[4.3.2]propellan-7-yl tosylate (**1a**), it is deduced that the ring expansion of the *endo* cation **15** occurs through 1,2-shift of the bond (d) selectively to afford the propellan-7-yl cation **18** which is stabilized by σ participation of the external cyclobutane bond (b). Interestingly, in the case of the *exo* tosylate **5b**, two new acetates **12a** and **13** derived from the propellan-8-yl cation **20** were formed in considerable amounts (total of **12a** and **13**; 41%) together with the products **9**, **10**, **11a**, unidentified **A**, and **B** which are derived from the propellan-7-yl cation **19**. Since while the cation **19** is stabilized by the σ participation of the external cyclobutane bond (b), the cation **20** is stabilized by the long-range interaction of the central cyclobutane bond (a), the ring expansion of the *exo* cation **16** occurs nonstereoselectively through 1,2-shift of the bond (c) as well as that of the bond (d).

It is thus deduced that the modes of the ring expansion of the propellan-7-ylmethyl cations (**15** and **16**) are critically governed by the *exo*/*endo* geometry of the cyclobutylmethyl moiety because the chair/boat conformation of the bicyclo[3.2.0]heptane moiety of the ring-expanded [4.3.2]propellan-7-yl and -8-yl cations (**17**—**20**) is dependent on the above geometry of **15** and **16**.



Scheme 1.

Experimental

All melting and boiling points are uncorrected. IR spectra were recorded on a JASCO IR-G spectrometer. Mass spectra were taken by using a Hitachi RMU-6E spectrometer. ^1H NMR spectra were obtained on a JEOL JNM-PS-100 spectrometer in CCl_4 solutions by using Me_4Si as an internal standard. Analytical GLC was carried out on a Hitachi 163 gas chromatograph (10% FFAP and 5% SE-30 columns) and preparative GLC separation was undertaken on a Varian Aerograph 920 gas chromatograph.

*Methyl [4.2.2]Propellane-7-carboxylates (**4d** and **5d**).* The esters **4d** and **5d** were prepared as described previpusly[4] and were separated by careful chromatography on silica gel with 2% ether–petroleum ether eluent.

4d: IR 1730, 1220, 1190, 1170, 1065 cm^{-1}; MS *m/e* (rel intensity) 194 (M^+, 55), 135 (84), 91 (100), 79 (94); NMR δ 1.12—2.58 (m, 14H), 3.20 (t, J=8 Hz, 1H), 3.64 (s, 3H). Found: C, 74.18; H, 9.41%. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34%.

5d: IR 1730, 1195, 1175, 1050 cm^{-1}; MS *m/e* (rel intensity) 194 (M^+, 60), 135 (100), 91 (90), 79 (90); NMR δ 1.10—2.72 (m, 14H), 3.08 (t, J=9 Hz, 1H), 3.64 (s, 3H). Found: C, 74.11; H, 9.29%. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34%.

*[4.2.2]Propellan-7-ylmethanols (**4c** and **5c**).* A solution of 3.0 g (15.5 mmol) of **4d** in 100 ml of ether was added dropwise to a suspension of 587 mg (15.5 mmol) of lithium aluminium hydride in 50 ml of ether and the mixture was stirred at room temperature for 1 h. Water was added carefully followed by 1 mol dm^{-3} HCl and the organic layer was separated. The aqueous layer was extracted with ether and the combined organic layer was washed with sodium hydrogencarbonate solution and water and then dried (Na_2SO_4). Evaporation of the solvent gave 2.4 g (93%) of **4c** as viscous oil, whose analytical sample was obtained by preparative GLC. In a similar manner, **5c** was prepared from **5d** in a 99% yield.

4c: IR 3300, 1010 cm^{-1}; MS *m/e* (rel intensity) 166 (M^+, 2), 93 (73), 91 (84), 79 (100); NMR δ 1.00—2.32 (m, 15H), 2.51 (quintet, J=8 Hz, 1H), 3.57, 3.60 (2d, J=6, 8 Hz, 2H). Found: C, 79.26; H, 11.01%. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92%.

5c: IR 3300, 1030, 1000 cm^{-1}; MS *m/e* (rel intensity) 166 (M^+, 5), 93 (77), 91 (80), 79 (100); NMR δ 1.10—2.64 (m, 16H), 3.64, 3.67 (2d, J=7, 8 Hz, 2H). Found: C, 79.37; H, 11.03%. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92%.

*[4.2.2]Propellan-7-ylmethyl Tosylates (**4b** and **5b**).* To a solution of 919 mg (5.54 mmol) of **4c** in 60 ml of pyridine cooled in an ice bath 2.11 g (11.1 mmol) of *p*-toluenesulfonyl chloride was added portionwise and the solution was allowed to stir for 1 h and then to stand in a refrigerator for 3 d. The mixture was poured onto water and extracted with ether. The extract was washed with 1 mol dm^{-3} HCl, sodium hydrogencarbonate solution, and water and then dried (Na_2SO_4). Evaporation of the solvent gave 1.66 g (94%) of **4b** as a white solid, which was purified by recrystallization from petroleum ether. Similarly, **5b** was prepared from **5c** in a 93% yield.

4b: Mp 68—69 °C; IR 1595, 1355, 1165, 935 cm^{-1}; NMR δ 1.08—1.64 (m, 9H), 1.76—2.22 (m, 5H), 2.42 (s, 3H), 2.63 (quintet, J=8 Hz, 1H), 3.96 (2d, J=7, 9 Hz, 2H), 7.25 (d, 2H), 7.68 (d, 2H). Found: C, 67.32; H, 7.53; S, 9.93%. Calcd for $C_{18}H_{24}O_3S$: C, 67.46; H, 7.55; S, 10.01%.

5b: Mp 34—35 °C; IR 1595, 1355, 1165, 940 cm^{-1}; NMR δ 1.10—2.32 (m, 14H), 2.40 (s, 3H), 2.58 (quintet, J= 8 Hz, 1H), 3.99 (2d, J=6, 8 Hz, 2H), 7.20 (d, 2H), 7.60 (d, 2H). Found: C, 67.32; H, 7.54; S, 9.93%. Calcd for $C_{18}H_{24}O_3S$: C, 67.46; H, 7.55; S, 10.01%.

*Methyl [4.2.2]Propell-9-ene-7-carboxylates (**6** and **7**).* To an ice-cooled suspension of 480 mg of 50% sodium hydride (10 mmol) and 0.05 ml of ethanol in 20 ml of ether was added dropwise a mixture of 1.64 g (10.1 mmol) of the propellanone **8**[5] and 1.10 g (15 mmol) of ethyl formate and the mixture was stirred at room temperature for 3 h and then allowed to stand overnight. Water was added and the organic layer was separated which was washed once with water. The combined aqueous layer was washed with ether and then acidified with 1 mol dm^{-3} HCl. The oil separated was taken up in ether and the extract was washed with saturated sodium chloride solution. Evaporation of the solvent gave 1.5 g (78%) of the α-hydroxymethylene derivative of **8** as a pale yellow solid which was used without purification: IR 3040, 1690, 1600, 1200, 930, 780, 740 cm^{-1}.

p-Toluenesulfonyl azide (1.56 g, 7.9 mmol) was added dropwise to a solution of 1.5 g of the above hydroxymethylene ketone and 1.6 g (15.8 mmol) of triethylamine in 6 ml of dichloromethane cooled in an ice–salt bath (−5—−10 °C). The mixture was stirred at that temperature for 2 h. A solution of 530 mg (9.5 mmol) of potassium hydroxide in 6 ml of water was added and the mixture was stirred at room temperature for 15 min. The organic layer was separated and the aqueous layer was extracted with dichloromethane. The combined extract was washed with potassium hydroxide solution and water and then dried (Na_2SO_4). Evaporation of the solvent gave 1.5 g of the crude diazo ketone as a dark red oil (IR 3040, 2070, 1660, 1320, 780 cm^{-1}), which was dissolved in 100 ml of methanol and the solution was irradiated in a Pyrex vessel with a 500 W high-pressure mercury lamp for 22 h. Evaporation of the solvent followed by distillation at reduced pressure (bp 67—69 °C/133.3 Pa) gave 762 mg (50%) of a 1 : 2 mixture of **6** and **7** which were separated by chromatography on silica gel with 3% ether–petroleum ether eluent.

6: IR 3100, 3030, 1730, 1170, 760 cm^{-1}; MS *m/e* (rel intensity) 192 (M^+, 10), 133 (39), 105 (33), 91 (100); NMR δ 1.16—2.10 (m, 9H), 2.29 (dd, J=7, 12 Hz, 1H), 2.86 (dd, J=7, 8 Hz, 1H), 3.55 (s, 3H), 6.22 (d, J=2 Hz, 2H). Found: C, 74.70; H, 8.35. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39.

7: IR 3100, 3030, 1730, 1200, 790, 750 cm^{-1}; MS *m/e* (rel

intensity) 192 (M^+, 10), 133 (35), 105 (34), 91 (100); NMR δ 1.12—2.34 (m, 10H), 2.86 (dd, J=7, 10 Hz, 1H), 3.55 (s, 3H), 6.03 (d, J=2 Hz, 1H), 6.21 (d, J=2 Hz, 1H). Found: C, 75.16; H, 8.42%. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39%.

Hydrogenation of **6** *and* **7**. A sample of **6** (28 mg) and a catalytic amount of 5% Pd/C in 5 ml of ethanol was stirred under atmospheric hydrogen for 3 h. The catalyst was filtered off and the solvent evaporated to give 23 mg (82%) of **4b**. In a similar manner, hydrogenetion of **7** gave **5b** in a 96% yield.

Kinetic Measurements of Acetolysis of **4b** *and* **5b**. The rates of the acetolysis of **4b** and **5b** buffered with 2 equiv. of sodium acetate were measured by the titrimetric method as previously described.[3a] The results are summarized in Table 1.

Preparative Acetolysis of **4b** *and* **5b**. A solution of 1.47 g (4.59 mmol) of **4b** and 753 mg (9.18 mmol) of sodium acetate in 140 ml of acetic acid was heated at 80 °C for 23 h. The mixture was diluted with water and extracted with ether. The extract was washed with sodium hydrogencarbonate solution and water and then dried (Na_2SO_4). Evaporation of the solvent gave 751 mg (combined yield of the products; 98%) of a pale yellow oil. The products were analyzed by GLC (Table 2) and separated by chromatography on silica gel with ether–petroleum ether eluent followed by preparative GLC. Similarly, the acetolysis of 2.50 g (7.81 mmol) of **5b** gave 1.45 g of the products (combined yield; 94%) and the results are listed in Table 2.

1b: IR 1725, 1230, 1005, 955 cm^{-1}; MS *m/e* (rel intensity) 208 (M^+, trace), 148 (21), 120 (100); NMR δ 1.08—2.30 (m, 19H, s at 1.95), 4.86 (dd, J=4, 6 Hz, 1H). Found: C, 74.73; H, 9.97. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68.

2b: IR 1725, 1230, 1015 cm^{-1}; MS *m/e* (rel intensity) 208 (M^+, trace), 120 (100); NMR δ 1.10—2.24 (m, 19H, s at 1.96), 4.70 (t, J=8 Hz, 1H). Found: C, 74.58; H, 9.33. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68.

11a: IR 1725, 1230, 1160, 1125, 1000, 960 cm^{-1}; MS *m/e* (rel inrensity) 208 (M^+, 2), 148 (100), 120 (72); NMR δ 0.88—2.40 (m, 19H, s at 1.92), 3.65 (br t, J=3 Hz, 1H). Found: C, 75.01; H, 9.80. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68.

12a: IR 1730, 1225, 1005 cm^{-1}; MS *m/e* (rel intensity) 208 (M^+, trace), 120 (92), 92 (100), 91 (95); NMR δ 1.36—2.20 (m, 19H, s at 1.92), 5.30 (t, J=8 Hz, 1H). Found: C, 74.72: H, 9.79%. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68%.

13: IR 3040, 1720, 1230, 1025, 1005 cm^{-1}; MS *m/e* (rel intensity) 208 (M^+, trace), 120 (100); NMR δ 0.20 (t, J=4 Hz, 1H), 0.52—0.90 (m, 2H), 1.20—2.48 (m, 17H, s at 1.84). Found: C, 75.09; H, 9.78%. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68%.

Unidentified **A**: IR 1725, 1230, 1005, 955 cm^{-1}; MS *m/e* (rel intensity) 208 (M^+, trace), 148 (40), 123 (100); NMR δ 1.10—2.20 (m, s at 1.86). Found: C, 74.94; H, 9.64. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68.

Unidentified **B**: Mp 53—54 °C; IR 1715, 1240, 1220, 1030, 1000, 930 cm^{-1}; MS *m/e* (rel intensity) 208 (M^+, trace), 148 (69), 120 (100); NMR δ 1.20—2.52 (m, s at 1.84). Found: C, 74.65; H, 9.58%. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68%.

*[4.2.2]Propellan-7-ylmethyl Acetates (***4e** *and* **5e**). A solution of 100 mg (0.60 mmol) of **4c** in 2 ml of acetic anhydride and 5 ml of pyridine was stirred at room temperature for 5 h. Water was added and the solution was extracted with ether. The extract was washed successively with 1 mol dm^{-3} HCl, sodium hydrogencarbonate solution, and water and then dried (Na_2SO_4). Evaporation of the solvent gave 113 mg (91%) of **4e** as colorless oil. Similarly, **5e** was prepared from **5c** in a 88% yield.

4e: IR 1730, 1220, 1010 cm^{-1}; MS *m/e* (rel intensity) 208 (M^+, 3), 148 (100), 133 (100), 120 (67), 119 (73), 91 (77); NMR δ 1.20—1.74 (m, 9H), 1.84—2.25 (m, 8H, s at 1.92), 2.60 (quintet, J=8 Hz, 1H), 3.97 (d, J=8 Hz, 2H). Found: C, 74.90; H, 9.74%. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68%.

5e: IR 1730, 1220, 1020 cm^{-1}; MS *m/e* (rel intensity) 208 (M^+, 2), 148 (95), 133 (100), 120 (73), 119 (72), 91 (71); NMR δ 1.12—2.76 (m, 18H, s at 1.91), 4.06 (d, J=8 Hz, 2H). Found: C, 74.73; H, 9.67%. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68%.

Preparation of Authentic Sample of **1b** *and* **2b**. The acetates **1b** and **2b** were prepared from **1c** and **2c**[3a] in 90—95% yields in a manner similar to that described for **4e** and **5e**. The authentic samples thus prepared were identical in all respects (IR, NMR, and GLC) with the samples obtained from the acetolysis.

Lithium Aluminium Hydride Reduction of **11a**. The reduction of **11a** was carried out as described for the preparation of **4c** and **5c** to give the alcohol **11b** in a 92% yield which was identical with the authentic material.[3a]

Conversion of **12a** *to [4.3.2]Propellan-8-one (***14**). The reduction of **12a** was undertaken as described above to afford the alcohol **12b** (95%).

12b: IR 3300, 1060 cm^{-1}; MS *m/e* (rel intensity) 166 (M^+, trace), 138 (100), 120 (57), 109 (55); NMR δ 1.10—2.08 (m, 16H), 3.46 (br s, 1H), 4.33 (t, J=6 Hz, 1H). *p*-Nitrobenzoate of **12b** was prepared in a usual manner: mp 93—94 °C. Found: C, 68.46; H, 6.67; N, 4.45%. Calcd for $C_{18}H_{21}O_4N$: C, 68.55; H, 6.71; N, 4.44%.

A slightly excess of Jone's reagent was added dropwise to a solution of 46 mg (0.28 mmol) of **12b** in 2 ml of acetone and the mixture was allowed to stir at room temperature for 20 min. After evaporation of the solvent, the residue was dissolved in water and extracted with ether. The extract was washed with sodium hydrogencarbonate solution and water and then dried (Na_2SO_4). Evaporation of the solvent gave 44 mg (96%) of **14** which solidified on standing.

14: IR 1730, 1160 cm^{-1}; MS *m/e* (rel intensity) 164 (M^+, 13), 136 (82), 108 (100); NMR δ 1.20—2.16 (m, 12H), 2.20 (s, 4H). Semicarbazone: mp 209—211 °C. Found: C, 65.12; H, 8.60; N, 18.94%. Calcd for $C_{12}H_{19}ON_3$: C, 65.12; H, 8.65; N, 18.99%.

Preparation of Authentic Sample of **14**. To a suspension of 1.0 g (6.8 mmol) of the olefin **9** and 87 mg (2.3 mmol) of sodium borohydride in 10 ml of tetrahydrofuran was added dropwise under nitrogen 0.344 ml (2.72 mmol) of boron trifluoride etherate and the mixture was stirred at room temperature for 1 h. 0.2 ml of water, 0.75 ml of 3 mol dm^{-3} sodium hydroxide solution, and 0.75 ml of 30% hydrogen peroxide solution were added successively with caution and the mixture was allowed to stand overnight. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was washed with saturated sodium chloride solution and dried (Na_2SO_4). Evaporation of the solvent gave 1.1 g (97%) of a mixture of the alcohols **1c**, **2c**, and **12c** in a ratio of 2 : 1 : 10 (by GLC). **12c** was separated by silica-gel chromatography with 20% ether–pertoleum ether eluent.

12c: IR 3250, 1035 cm^{-1}; MS *m/e* (rel intensity) 166 (M^+, trace), 138 (100); NMR δ 1.28—2.04 (m, 16H), 3.23 (br s, 1H), 4.50 (t, J=7 Hz, 1H). *p*-Nitrobenzoate: Mp 113—115 °C. Found: C, 68.18; H, 6.57; N, 4.42%. Calcd for $C_{18}H_{21}O_4N$: C, 68.55; H, 6.71; N, 4.44%.

Jones' oxidation of 640 mg (3.86 mmol) of **12c** as described for the oxidation of **12b** gave 632 mg (100%) of the ketone **14** which was identical with the sample prepared from **12a**.

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7) Though the *exo/endo* stereochemistry of the acetate **12a** and the alcohols **12b** and **12c** was not determined, it may be reasonable to assume that **12a** and **12b** are *exo* isomers and **12c** is *endo* isomer on the basis of the following considerations: (i) The mechanistic consideration for the formation of **12a** shown in Scheme 1 suggests that the attack of an acetate anion from *exo* side is preferred. (ii) Since we have found out that the *endo* side of [4.3.2]propellane system is less hindered compared with the *exo* side,[8] the hydroboration of the olefin **9** would be expected to give the *endo* alcohol **12c** as a major product by the attack of diborane from the less hindered *endo* side.

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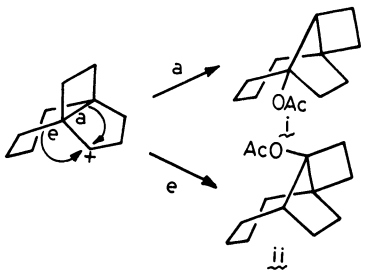
9) Possibly, the unidentified acetates **A** and **B** may be tricyclo[4.3.2.$0^{1,7}$]undecane derivatives such as (**i**) and (**ii**) derived by 1,2-shift of the bond (a) and (e), respectively.



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