PENTACYCLODECANE CHEMISTRY. IV. SYNTHESIS AND ACETOLYSIS OF syn- AND anti-PENTACYCLO-[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]DEC-6-YL TOSYLATES. NEW EVIDENCE FOR BRIDGED CARBONIUM IONS (1)

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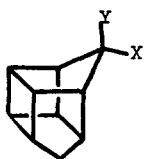The Dow Chemical Company, Midland, Michigan 48640

The rearrangement of a pentacyclodecyl cation (1,1-bishomocubyl) has recently been reported (2). Rearrangement of a related pentacyclodecyl system [1,3-bishomocubyl → 1,4-bishomocubyl (3)] occurred on treatment of a perchlorodiketone with phosphorus pentachloride (4), probably via a carbonium ion mechanism (5). In view of the general interest in the carbonium ion rearrangements of these strained polycyclic systems we wish to report the synthesis of syn-, 3, and anti-pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-6-ol, 6, (1,3-bishomocubyl systems) and the acetolysis of their tosylates, 4 and 7. We also would like to point out that these solvolysis reactions are best explained by invoking bridged carbonium ion intermediates.
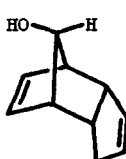
The syn-alcohol, 3, was synthesized by the acetone photosensitized ring closure (6) of endo, syn-tricyclo[5.2.1.0^{2,6}]deca-3,8-dien-5-ol, 1, (7) in 20% yield, m.p. 175-176° (8-10).

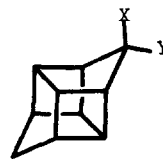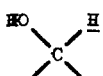|				
1 X=OH, Y=H	3 X=OH, Y=H	10	11 X=OH, Y=H	
2 X=H, Y=OH	4 X=OTs, Y=H		12 X=OTs, Y=H	
	5 X=OAc, Y=H		13 X=OAc, Y=H	
	6 X=H, Y=OH		14 X,Y=O	
	7 X=H, Y=OTs			
	8 X=H, Y=OAc			
	9 X,Y=O			

The nmr spectrum of $\underline{3}$ was in agreement with the assigned structure (Table I). The mass

TABLE I. NMR DATA FOR PENTACYCLODECANOLS, 3, 6, 11[a]

Compound	HO\C/H /C\	H|C /|	O-H	H\C/H /C\
$\underline{3}$	-4.04[b,c](0.95)[d]	-3.2 to -2.4[e]$(-)$[f]	-2.28[g]$(-)$[f]	-1.66[h], -1.39[h](2.1)
$\underline{6}$	-4.28[i] (1.0)	-3.0 to -2.5[e](7.9)	-2.07[g](1.1)	-1.62[j], -1.21[j](2.0)
$\underline{11}$	-4.07[c] (1.0)	-3.1 to -2.3[e](8.0)	-2.13[g](1.0)	-1.38[g] (2.0)

[a]$CDCl_3$ solution. [b]Ppm from internal TMS (δ). [c]Broad singlet. [d]Relative peak areas in parentheses. [e]Multiplet. [f]Total relative area, 9.0. [g]Singlet. [h]Unsymmetrical doublet, $J = 11.2$ cps. [i]Triplet, $J = 1.4$ cps. [j]Unsymmetrical doublet, $J = 11.1$ cps.

spectrum gave a parent peak at m/e 148 and a cracking pattern characteristic of the assigned structure (11).

Irradiation (6,8) of either endo, anti-tricyclo[5.2.1.0^{2,6}]deca-3,8-dien-5-ol, $\underline{2}$, or endo, syn-tricyclo[5.2.1.0^{2,6}]deca-3,8-dien-10-ol, $\underline{10}$, (7) in acetone solution gave the anti-alcohol, $\underline{6}$, m.p. 164-166°, in 31% and 29% yields respectively. The nmr (Table I), infrared, and mass (11) spectra were consistent with the assigned structure.

The tosylates, $\underline{4}$, m.p. 64.5-65.5°, and, $\underline{7}$, m.p. 78-78.5°, prepared by the method of Tipson (12), gave infrared, nmr, and mass spectra which were consistent with the assigned structures. The acetates, $\underline{5}$ and $\underline{8}$, liquids, also exhibited the expected spectral properties.

A mixture of alcohols, $\underline{3}$ and $\underline{6}$, m.p. 173-174°, obtained by lithium aluminum hydride reduction (1) of pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-6-one, $\underline{9}$, (13) was shown by nmr to consist of 80% syn-$\underline{3}$ and 20% anti-$\underline{6}$ (14). Equilibration (15) of the alcohols, $\underline{3}$ and $\underline{6}$, starting from the anti-isomer, $\underline{6}$, at 120° gave a mixture of 37% syn-$\underline{3}$ and 63% anti-$\underline{6}$ as analyzed by nmr. The equilibration and hydride reduction results are in agreement with predictions based on molecular models which indicate that non-bonded interactions of a substituent in the syn position are greater than in the anti position (16).

The solvolysis rate data for tosylates (4 and 7) in unbuffered acetic acid are summarized in Table II (18).

TABLE II.   ACETOLYSIS RATES OF PENTACYCLODECYL TOSYLATES (4 and 7)

| Tosylate	Temp. (°C)	Rate Constant[a] (sec.$^{-1}$)	$\Delta H^{\ddagger}$ (kcal./mole)	$\Delta S^{\ddagger}$ (e.u.)
syn-4	120.0 ± 0.1	2.84 ± 0.12 x 10^{-4}	27.6[b]	-5.1[c]
	110.0 ± 0.1	1.10 ± 0.04 x 10^{-4}		
	25	2.7 x 10^{-9} [d]		
anti-7	130.0 ± 0.1	1.19 ± 0.01 x 10^{-4}		
	120.0 ± 0.1	4.90 ± 0.22 x 10^{-5}	27.2[e]	-9.7[f]
	25	5.5 x 10^{-10} [g]		

[a]Rate constants are an average of two runs at each temperature. Reasonably good first order kinetics were observed to 75-80% reaction. [b]± 3.0 kcal./mole. [c]± 7.6 e.u. [d]Calculated from data at higher temperatures. Uncertainty factor in this value is 3.6. [e]± 2.3 kcal./mole. [f]± 5.8 e.u. [g]Calculated from data at higher temperatures. Uncertainty factor in this value is 2.8.

Preparative acetolysis of the syn-tosylate, 4, in unbuffered acetic acid at 120° for 10 half-lives, followed by lithium aluminum hydride reduction of the acetate product (19) gave the alcohol, 3, with retained stereochemistry as the major product (94% overall yield). The nmr spectrum of the crude product showed no anti-isomer 6 by the lack of absorption at -4.28 ppm (it is estimated that presence of 5% of 6 would have been detected). G.c. analysis of the crude product showed a minor product (4% of the mixture by peak area integration) which by retention time was tentatively assigned the symmetrical alcohol structure, 11, (see below).

Acetolysis of the anti-tosylate, 7, in unbuffered acetic acid at 120° for 10 half-lives gave an acetate product which was reduced with lithium aluminum hydride to give an alcohol product (75% overall yield) which was shown by nmr and g.c. analysis on two columns to be a mixture of 85% pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decan-5-ol, 11, (1,4-bishomocubyl) and 15% anti-alcohol, 6. A pure sample of alcohol, 11, was obtained by recrystallization from pentane, m.p. 143-144°; reported m.p. 137-140° (2). The nmr spectrum of 11 (Table I)

was consistent with the assigned structure. Oxidation of the alcohol, <u>11</u>, with chromic

acid (20) gave pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decan-5-one, <u>14</u>, m.p. 119-122°; reported

m.p. 120-122° (2) and 123° (4b). The nmr spectrum was also in agreement with that previously

reported (2,21). Isolation of the tosylate from an incomplete acetolysis reaction of the

<u>anti</u>-tosylate, <u>7</u>, at 100° (<u>ca</u>. 40% solvolysis) and analysis by nmr (singlet at -1.40 ppm for

the methylene hydrogens) indicated the occurrence of <u>ca</u>. 30% internal return to the rearranged

pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]dec-5-yl tosylate, <u>12</u>. No evidence (nmr, infrared) for any

olefinic products was detected in the acetolysis of either tosylate, <u>4</u> or <u>7</u>.

The major product acetates, <u>5</u> and <u>13</u>, can be rationalized as arising via 1,2-alkyl

shifts (Scheme I) (22) and by substitution with retention of configuration. We suggest that
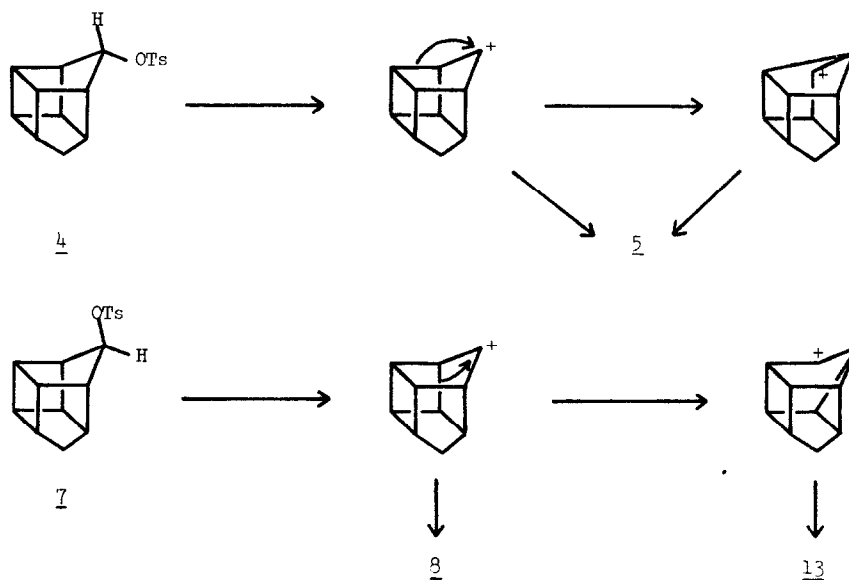
Scheme I

these results are best explained by postulating the bridged carbonium ions, <u>15</u> and <u>16</u>, as the

intermediates in these solvolyses of the tosylates, <u>4</u> and <u>7</u>, respectively, especially in the

case of <u>4</u> since the intermediate, <u>15</u>, is symmetrical (23).

The alternate rationalization of substitution with retention due to anion assistance

(24) does not appear to be applicable in the present case because of the relative instability
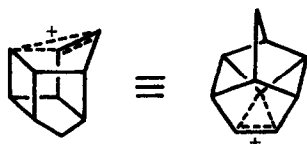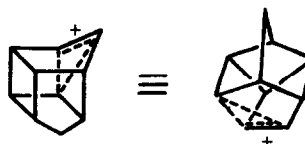
15   16

of the carbonium ion and the low basicity of the anion. Nor does the concept of rapidly equilibrating non-bridged ions (25) appear to give a reasonable explanation since one of the non-bridged ions from both tosylates is the same (assuming a planar sp^2 carbonium ion); thus the same products would be expected from either tosylate, and such is not the case. The only alternative would appear to be an equilibration between the two non-bridged cations at a rate which is faster than the C-6 carbon-hydrogen bending vibration, a situation which for all practical purposes is the same as a vibrating bridged ion.

Participation in the solvolysis is also indicated by the enhanced solvolysis rates as determined by comparison of the experimental rates with those calculated for unassisted solvolysis using the equation developed by Schleyer (26); the rate acceleration of the syn-tosylate, 4, is 1×10^4 and that of the anti-tosylate, 7, is 3×10^3 (28).

The details of this and related work will be presented later.

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1. Part III, W. L. Dilling and M. L. Dilling, Tetrahedron, 23, 1225 (1967).

2. W. G. Dauben and D. L. Whalen, J. Am. Chem. Soc., 88, 4739 (1966).

3. The numbering for the bishomocubane system of nomenclature refers to the shortest path along the edges of a cube between the positions of the two methylene bridges. Thus the five possible bishomobubanes are as follows:

   pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decane, 1,1-bishomocubane; pentacyclo[4.4.0.0^{2,5}.0^{3,9}.-0^{4,7}]decane, 1,2-bishomocubane; pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane, 1,3-bishomocubane; pentacyclo[4.4.0.0^{2,5}.0^{3,9}.0^{4,8}]decane, 1,3'-bishomocubane; pentacyclo[5.3.0.0^{2,6}.0^{3,9}.-0^{4,8}]decane, 1,4-bishomocubane.
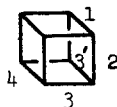
4. (a) P. E. Eaton, Ph.D. Thesis, Harvard University (1960); (b) G. W. Griffin and A. K. Price, J. Org. Chem., 29, 3192 (1964).

5. See M. S. Newman and L. L. Wood, Jr., J. Am. Chem. Soc., 81, 4300 (1959).

6. (a) G. O. Schenck and R. Steinmetz, Chem. Ber., 96, 520 (1963), have reported the acetone sensitized ring closure of endo-dicyclopentadiene to pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]-decane; (b) For other related ring closures see, W. L. Dilling, Chem. Rev., 66, 384 (1966).

7. R. B. Woodward and T. J. Katz, Tetrahedron, 5, 70 (1959).

8. Irradiations were carried out in acetone solution (10 g./140 ml.) with a 450 watt Hanovia medium pressure mercury arc lamp with a Corex filter. Reactions were followed by g.c. analysis of aliquots withdrawn periodically.

9. The alcohols, 3 and 6, and tosylates, 4 and 7, gave satisfactory elemental analyses.

10. Although the structural formulas in this paper show only one enantiomer, all the compounds capable of existing as optical isomers were actually racemic mixtures.

11. The mass spectral analyses were performed by Mrs. W. L. Dilling and co-workers. See ref. 1 for additional mass spectral data on this cage system.

12. R. S. Tipson, J. Org. Chem., 9, 235 (1944).

13. R. C. Cookson, J. Hudec, and R. O. Williams, Tetrahedron Letters, No. 22, 29 (1960).

14. The alcohols could not be separated by g.c. (1) or by thin layer chromatography. The thin layer chromatographic analyses were performed by Dr. N. E. Skelly. The acetate derivative of the mixture showed only one peak by g.c.

15. The equilibration was carried out by the aluminum isopropoxide-acetone procedure of C. F. Wilcox, Jr., M. Sexton, and M. F. Wilcox, J. Org. Chem., 28, 1079 (1963).

16. The predominance of the syn alcohol in the hydride reduction apparently arises from steric-approach control (17). The strained nature of the sp^2 carbon atom in the ketone, 9, should lead to a transition state in the reduction which is close to the reactants.

17. Cf. H. O. House, "Modern Synthetic Reactions", W. A. Benjamin, Inc., New York, N. Y., 1965, pp. 28-32.

18. Rate measurements were made by the sealed ampoule technique according to S. Winstein, E. Grunwald, and L. L. Ingraham, J. Am. Chem. Soc., 70, 821 (1948).

19. The infrared spectrum of the crude acetate mixture from both tosylates, 4 and 7, showed no tosylate or alcohol bands. The nmr spectrum of the product from 4 showed only acetate absorption. See (a) C. W. Shoppee and G. A. R. Johnston, J. Chem. Soc., 3261 (1961); (b) C. A. Bunton and Y. F. Frei, J. Chem. Soc., 1872 (1951).

20. H. C. Brown and C. P. Garg, J. Am. Chem. Soc., 83, 2952 (1961).

21. The infrared and nmr spectra of the symmetrical alcohol, 11, and the nmr spectrum of the ketone, 14, were in agreement with the spectra of these compounds kindly provided by Professor W. G. Dauben. See ref. 2.

22. The intermediates shown in Scheme I are for illustration purposes only, and are not ment to represent what we believe to be their true geometry. Other products resulting from 1,2-shifts are possible, but these products have not been detected. See ref. 2.

23. For reviews of the bridged ion problem see: (a) A. Streitwieser, Jr., "Solvolytic Displacement Reactions", McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 126; (b) J. A. Berson, "Molecular Rearrangements", Part 1, P. deMayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p. 111; (c) P. D. Bartlett, "Nonclassical Ions", W. A. Benjamin, Inc., New York, N. Y., 1965; (d) G. D. Sargent, Quart. Rev., 20, 301 (1966); (e) B. Capon, M. J. Perkins, and C. W. Rees, "Organic Reaction Mechanisms, 1965", Interscience Publishers, New York, N. Y., 1966, p. 1; (f) H. C. Brown, Chem. Brit., 199 (1966); Chem. Eng. News, 45, No. 7, 86 (1967); (g) G. A. Olah, Chem. Eng. News, 45, No. 14, 77 (1967).

24. Cf. (a) H. L. Goering and S. Chang, Tetrahedron Letters, 3607 (1965); (b) H. L. Goering, R. G. Briody, and J. F. Levy, J. Am. Chem. Soc., 85, 3059 (1963); (c) H. Hart and H. S. Eleuterio, J. Am. Chem. Soc., 76, 1379 (1954).

25. (a) H. C. Brown, K. J. Morgan, and F. J. Chloupek, J. Am. Chem. Soc., 87, 2137 (1965); (b) H. C. Brown, R. Bernheimer, C. J. Kim, and S. E. Scheppele, J. Am. Chem. Soc., 89, 370 (1967).

26. P. v. R. Schleyer, J. Am. Chem. Soc., 86, 1854, 1856 (1964). The question of whether there is rate enhancement in these systems of course depends on the validity of Schleyer's equation (27). This equation appears to be best model for the systems under investigation at the present time. Further work is being pursued on this point.

27. See e.g. H. C. Brown, I. Rothberg, P. v. R. Schleyer, M. M. Donaldson, and J. J. Harper, Proc. Nat. Acad. Sci., 56, 1653 (1966).

28. These rate accelerations were calculated using the following parameters: syn-4; νc=o, 1760 (29) (ketone 9); ϕ, 60, 60; GS-TS, 0.4. anti-7; same as 4 except GS-TS, 0.3.

29. The precision carbonyl frequency measurements and calculations on the ketone, 9, in CCl$_4$ solution were made by Dr. W. J. Potts, Jr., and co-workers. The frequency used in the calculation has been corrected to a first approximation for Fermi resonance according to the method of Langseth and Lord (30). The mode in Fermi resonance with νc=o (1763 cm.$^{-1}$ most intense component observed) was assumed to be the first overtone of the band at 862 cm.$^{-1}$

30. Cf. R. Ryason and M. K. Wilson, J. Chem. Phys., 22, 2000 (1954).