Tetrahedron Letters No.10, pp. 761-764, 1971. Pergamon Press. Printed in Great Britain.

PENTACYCLODECANE CHEMISTRY. VII. SYNTHESIS AND ACETOLYSIS OF SYN- AND ANTI-6-METHYLPENTACYCLO[5.3.0.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]DEC-6-YL p-TOLUENESULFONATE. DEMONSTRATION OF THE ABSENCE OF STERIC OR STRAIN STEREOCHEMICAL CONTROL IN THE SOLVOLYSIS OF A 7-NORBORNYL SYSTEM[1]

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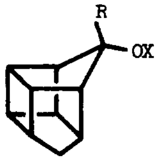
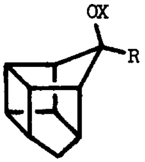
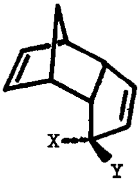
We present evidence that there are no inherent steric or strain effects in the 1,3-bishomocubyl system[1b] which could be responsible for the high degree (> 95%) of stereochemical retention observed in the solvolyses of the secondary tosylates 1 and 5.[1-2] The possibility that a steric or strain effect is responsible for the ca. 90% retention of configuration observed in solvolyses of the related 7-norbornyl esters[3,4] has been advanced[3] as an alternate explanation to σ-bridging.[4] The acetolysis of the tertiary tosylates 2 and 6 was undertaken as a test of these theories on the grounds that a steric or strain effect should still manifest itself or even be more pronounced in the tertiary system,[5] while bridging should be of less importance than in the secondary system.[6]



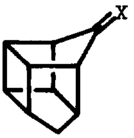
1 R = H, X = Ts
2 R = Me, X = Ts
3 R = Me, X = H
4 R = Me, X = Ac



5 R = H, X = Ts
6 R = Me, X = Ts
7 R = Me, X = H
8 R = Me, X = Ac



9 X,Y = O
10 X = OH, Y = Me



11 X = O
12 X = CH_2

Treatment of the dienone **9**[7] with methyllithium gave the *syn*-dienol **10**[8] (70%), which on irradiation in acetone solution (Corex filter) gave the *syn* tertiary alcohol **3**[9] (61%). Reaction of the ketone **11**[10] with triphenylmethylenephosphorane gave the olefin **12**[9] (92%), which on epoxidation with *m*-chloroperbenzoic acid followed by lithium aluminum hydride reduction gave a mixture of alcohols (93%): 56% *anti*-**7**, 44% *syn*-**3**. The *anti* alcohol **7**[9] was isolated by repeated crystallization. The tosylates **2**[9] and **6**[9] and acetates **4**[9] and **8**[9] were prepared by standard procedures.[11]

Preparative acetolysis of both tertiary tosylates **2** and **6** in either buffered or unbuffered acetic acid at 45° gave the *syn* acetate **4** as the major product along with smaller amounts of the *anti* acetate **8** (Table I). Analyses were carried out by integration of the acetoxy methyl resonances in the nmr spectrum (**4**, -2.02 ppm; **8**, -1.92 ppm, $CDCl_3$ solution). Both acetates **4** and **8** were completely stable under the reaction conditions at 45°. Both tosylates **2** and **6** solvolyze at about the same rate in unbuffered perdeuteroacetic acid at 34.5°, $k = 4.0 \pm 0.2 \times 10^{-4}$ sec^{-1} for **2**, $4.3 \pm 0.4 \times 10^{-4}$ sec^{-1} for **6**. *p*-Toluenesulfonic acid-catalyzed addition of

Table I. Product Distributions from Acetolyses of Tertiary 1,3-Bishomocubyl Tosylates and Acetic Acid Additions to Methylenepentacyclodecane

Starting material	Product distribution, % *syn*-**4**	*anti*-**8**	Total acetate yield, %
syn-**2**[a]	63	37	98
anti-**6**[a]	75	25	100
Olefin **12** + TsOH[b]	69	31	77
Olefin **12**[c]	63	37	76

[a] 45 ± 1° for 1 hr. [b] 45 ± 1° for 4 hr. with one equivalent of *p*-toluenesulfonic acid. [c] 100° for 168 hr. (83% conversion) without *p*-toluenesulfonic acid (no reaction at 45°).

acetic acid to the olefin 12 gave an acetate mixture whose composition was intermediate between those obtained in the solvolyses (Table I). The uncatalyzed addition gave a similar distribution.

The nearly equal acetate distributions from the isomeric tosylates 2 and 6 indicate that no inherent steric or strain effect is present in this system which could account for the high degree of stereospecificity observed in the secondary system.[1,2,12]

The 69:31 distribution of acetates 4 and 8, which was obtained from the acid catalyzed addition of acetic acid to the olefin 12 at 45°, probably is characteristic of the cationic intermediate(s) in the absence of the perturbing effect of the tosylate anion. The slight excess of inverted products from each tosylate is presumed to arise from a small net amount of rear side displacement. A discussion of the significance of the 69:31 acetate distribution, which is not that expected from the classical tertiary cation,[1b] is deferred to a later publication.

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