

STEREOELECTRONIC EFFECTS ON CYCLOBUTYL PARTICIPATION. THE

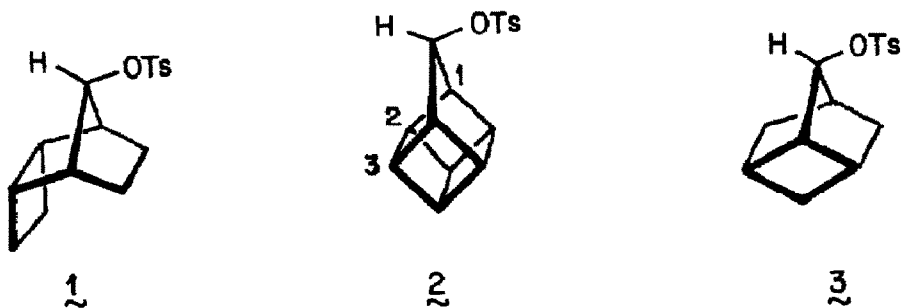
10-TETRACYCLO[5.2.1.0^{2,6}.0^{3,9}]DECYL CATION

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Summary: While the solvolysis of tosylate 5c proceeds very rapidly to generate 4 or its rapidly equilibrating classical alternative, the epimeric compound 6c proved to be unreactive; bond orientation effects are implicated.

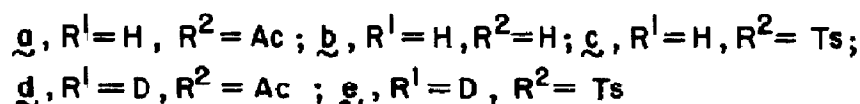
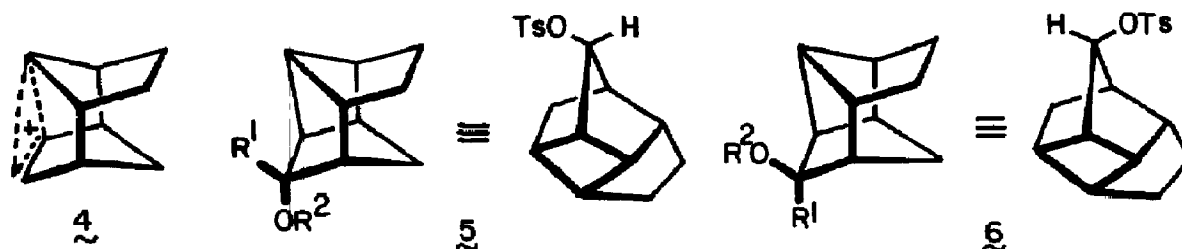
Whereas the level to which cyclopropane edge bond interaction can develop relative to remote carbonium ion centers has been intensively examined,¹ less attention has been accorded to neighboring cyclobutane rings. On the basis of the rate of acetolysis of 1 which is 10^{4-3} times faster than that of 7-norbornyl tosylate,² the level of anchimeric assistance provided by the cyclobutane ring is seen to be less than one-third that available to the cyclopropane



analog ($k_{rel} 10^{14}$).³ As regards the solvolysis of 2,⁴ carbonium ion formation is recognized to proceed with C₁-C₂ participation rather than with the C₂-C₃ edge bond which is pivotal to the enhanced reactivity of 1. This striking crossover has been attributed to the change in spatial relationship of the β-cyclobutyl group relative to the incipient carbonium ion.² Whatever the cause, this effect is seen to persist in less strained caged systems.⁵ The relative rate of acetolysis of 3 is 10^{3-1} , only one order of magnitude less than 1.⁶

We should now like to present evidence which establishes by means of a degenerate rearrangement involving the aesthetically pleasing 10-tetracyclo[5.2.1.0^{2,6}.0^{3,9}]decyl cation

(4) or its rapidly equilibrating classical ion pair equivalent that the rate enhancements observed for substrates of type 3 are attributable principally to cyclobutane edge bond delocalization, but with a strong kinetic dependence on bond geometries.



The synthetic route to the requisite epimeric tosylates began with acetate 5a as obtained in an earlier study.⁷ Conversion to tosylate 5c, mp 82-83°C,^a was achieved conventionally. Collins oxidation of 5b provided the related ketone, mp 121-123°C, whose reduction with sodium borohydride or lithium aluminum hydride returned principally 5b with lesser amounts (20 and 16% respectively) of 6b. Because this alcohol mixture proved difficultly separable, epimeric tosylate 6c, mp 53-54°C, was prepared by reaction of the mixture with *p*-toluenesulfonyl chloride in pyridine and selective acetolysis of 5c (HOAc, NaOAc, 117°C, 15 hr). Under these conditions, a readily separable two-component mixture of 5a and 6c was produced.

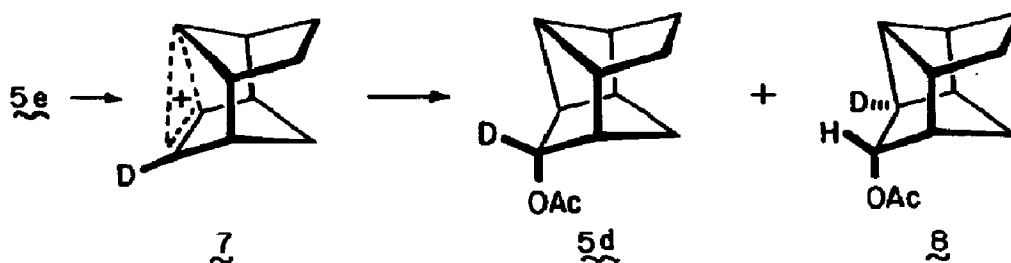
By means of a sequence involving $LiAlD(t\text{-}BuO)_3$ reduction of the ketone, tosylation of the resulting alcohol mixture, and recrystallization of this product from ether-hexane, there was delivered the important tosylate 5e. This substance was essentially 100% deuterated at the α -position, as determined by the total absence of the 1H NMR triplet ($J = 1.8$ Hz) at δ 4.82 (in $CDCl_3$) which is prominent in the spectrum of 5c.

Rates of acetolysis were measured on 5c and 6c at 112°C in buffered acetic acid (0.05 M in NaOAc) using standard titrimetric procedures. The ionization of 5c proved to be rapid, the rate constant being $2.08 \times 10^{-3} \text{ sec}^{-1}$. The solutions of 5c remained clear and colorless through 200 half-lives and acetate 5a was isolated as the sole product. In contrast, solutions of 6c turned dark brown rather rapidly and some solid gradually became deposited after 5-6 hr. While this behavior precluded exact titre determinations by the indicator method, it was possible to establish that the half-life of 6c at 112°C was 4-5 days. The high reactivity of 5c is

reflected in its $t_{1/2}$ of 5.6 min at this temperature.

Comparable buffered acetolysis of 5e delivered the deuterium labeled acetates 5d and 8 in high yield. The extent of isotopic rearrangement was determined from the area of the α -acetoxy ^1H NMR absorption at δ 4.73 relative to the acetoxy methyl singlet as reference standard. The key resonance of the isolated ester was seen to consist of a doublet ($J = 1.8$ Hz) of area 0.50 (± 0.03) instead of the customary triplet. This feature confirmed that only a 1,2-Wagner-Meerwein C-C shift had taken place.

The 50:50 distribution of 5d and 8, which is not due to prior scrambling within 5e or to subsequent equilibration of 5d, demands the intermediacy of bridged ion 7 or its equivalent of two rapidly equilibrating classical cations. The full retention of stereochemistry observed in the products are additionally supportive of this conclusion and rule out kinetic contributions



due to nucleophilic solvent assistance. A comparison of relative reactivities reveals that 5c is 3.3×10^5 times more reactive than 7-norbornyl tosylate. This factor indicates that 5c is more prone to ionization than 1 and 3, as well as the homocubyl derivative 2. These data unequivocally demonstrate effective and exclusive participation by the $\text{C}_1\text{-C}_2$ cyclobutane bond during the solvolysis of 5c. Because the cyclobutylcarbonyl rearrangement which accompanies the solvolytic generation of 4 or 7 delivers products of formally unrearranged structures, overall strain relief cannot be involved as a driving force to ionization. Rather, most, if not all, of the anchimeric assistance delivered in the solvolytic transition state must arise from participation of the cyclobutane ring. There may be some thermodynamic advantage to formation of a symmetric cation, but we shall leave it to the theoreticians to address this question.

The structural feature which distinguishes 5c from 6c is the orientation of the ethano bridge relative to the C-OTs bond. Both molecules are conformationally rigid. The vastly different solvolysis rates can be properly understood if the dihedral angle (θ) separating the

potentially anchimeric cyclobutane C-C bond and the impending tosylate ionization trajectory are given proper significance. In 5, a θ closely approximating 90° results in high reactivity; in 6, the alignment is poor and participation by the four-membered ring is essentially inoperative.

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References and Notes

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