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SYNTHESIS AND SOLVOLYTIC REACTIVITY OF EXO-TETRACYCLO$[3.3.0.0^{3,6}.0^{2,8}]$OCT-4-YL TOSYLATE

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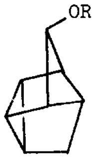
Participation by remote cyclopropane rings has been observed in many solvolysis reactions, (1) and in certain rigid polycyclic ring systems gives rise to large rate enhancements. Since rate accelerations both greater than (2) and less than (3) the corresponding unsaturated analogues have been found, it is of some interest to define further the structural requirements for such long range cyclopropane participation. We have synthesized exo-tetracyclo$[3.3.0.0^{3,6}.0^{2,8}]$oct-4-yl tosylate (**1**-OTs) in order to assess the effect of contracting the ring which bridges the bicyclo[3.1.0]hexyl moiety in **1**. Since the bicyclic, olefinic analogue, exo-bicyclo-[2.1.1]hex-2-en-5-yl methoxyacetate (**2a**, R = $COCH_2OCH_3$) is estimated to be 5 x 10^3 more reactive than derivatives of its homologue with a two carbon bridge, anti-norborn-2-en-7-ol (**2b**), (4) there was reason to expect substantial reactivity despite the constriction of the C-C bond angle at the carbinyl position.



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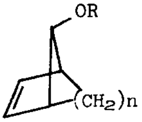

2a (n = 1)
2b (n = 2)

Diazoketone **4** (mp 41-42.5°, ν_{max} 2080 cm^{-1}) (5) was obtained in 75% yield from the hydroxymethylene derivative (42%) of tetracyclic ketone **3** (6) by the diazo transfer method. (7) Photolysis of **4** in aqueous dioxane followed reaction with methyl lithium affords an exo,endo mixture of methyl ketones (**6**) in 21% yield from **4**. A 3:1 mixture of the epimeric tetracyclic alcohols (**7**-OH and **1**-OH), separable by gas-liquid chromatography, is formed in 74% after Bayer-Villiger oxidation of **6** and lithium aluminum hydride reduction. Oxidation with chromium trioxide in pyridine leads to the interesting tetracyclic ketone **8** (58%, ν_{max} 1780 cm^{-1}). (8)

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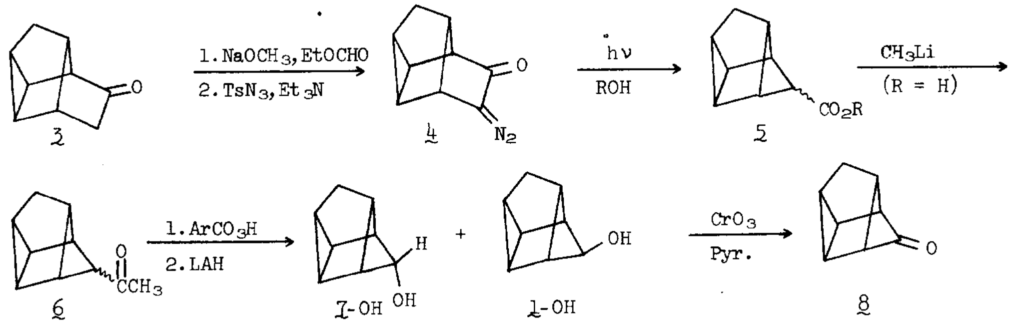
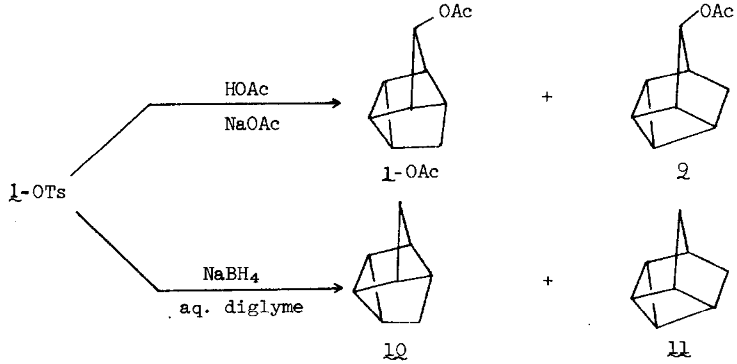
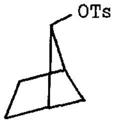


The isomeric alcohols were characterized as the p-nitrobenzoate esters (7-OPNB, mp 83.5-84.5°; 1-OPNB, mp 112-113.5°). The relative stereochemistry of the hydroxyl group is assigned on the basis of the coupling observed for the carbinyl protons (C<u>H</u>OH) in the nmr spectra of 7-OH (τ 5.92, quartet, J = 2.4 Hz) and 1-OH (τ 5.89, s).(7b,9) The additional splitting in the former results from long range coupling to the unique cyclopropane proton.(1)

The <u>exo</u> tosylate (1-OTs, mp 62-63.0°) undergoes smooth acetolysis to a 60:40 mixture of 1-OAc and 9. Although neither the isomeric acetates nor alcohols could be separated, the nmr spectral properties of the new acetate were readily inferred from the spectrum of the mixture and established that the compound must be tetracyclic (no vinyl protons). Solvolysis of 1-OTs in 65% aqueous diglyme containing sodium borohydride (10) affords a 36:64 mixture (17%) of the known tetracyclic hydrocarbons 10 and 11 which were identified by nmr spectral comparisons.(11) Since the conditions used in this reduction lead to carbonium ion intermediates which are intercepted by reaction with borohydride,(10) the identification of 11 confirms the structure assigned to the rearranged acetate, namely tetracyclo[3.2.1.$0^{2,4}$.$0^{3,6}$]oct-7-yl acetate (9).



The first order rate constant for solvolysis of 1-OTs in acetic acid containing 0.042 M sodium acetate is 2.05×10^{-5} sec^{-1} at 25.0° and 2.49×10^{-4} sec^{-1} at 44.9°. The acetolysis rate at 25° indicates considerable rate enhancement (10^6) when compared to the acetolysis rate of exo-bicyclo [2.1.1]hex-5-yl tosylate (12).(12) However, 1-OTs is distinctly less reactive than either 2a (by $\sim 10^{-5}$) or pentacyclo[$4.3.0.0^{2,4}.0^{3,8}.0^{5,7}$]non-9-yl p-nitrobenzoate (13) (by $\sim 10^{-1}$-10^{-3}). (1,13)



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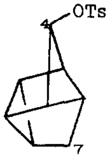
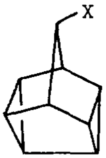


1-OTs



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25° k_{rel}	(1.0)	10^6	10^7-10^9

The reactivity of 1-OTs is clearly determined by a combination of several reinforcing and opposing factors. While the ring contraction alone should increase orbital overlap in the transition state as judged from the reactivity of 2a and its benzologue,(4) the methylene bridge (C-7) connecting the three and four-membered of 1 would appear to be counter-productive. The presence of this bond must increase the strain energy associated with the movement of the two equivalent cyclopropane carbons (C-1 and C-2) towards the incipient carbonium ion site at C-4, thus destabilizing the transition state and the resulting trishomocyclopropenyl cation intermediate.

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