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NUCLEOPHILICITY OF REMOTE CARBON-CARBON DOUBLE BONDS.
THE SIGNIFICANCE OF TRANSITION STATE COLINEARITY

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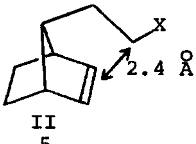
The recent report of an investigation of the solvolysis of β-(1,2,5,6-dibenzocycloheptatrien-7-yl)-ethyl tosylate (1) prompts us to present this preliminary account of our examination of the solvolytic behavior of the parent compound Ib and to comment on the bearing which these results have upon an understanding of the factors which influence the efficiency of nucleophilic double bond participation at primary carbon.

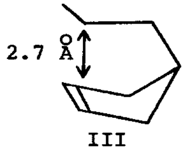
Although the ability of remote carbon-carbon double bonds to function as internal nucleophiles is now well established, little attention has been paid to the singularly enhanced efficiency apparent in participation by double bonds located in the 5,6-position relative to the site of displacement as compared to those found in the 4,5- or 6,7-positions (2). Comparison of the anchimeric assistance (k_U/k_S) which attends the solvolysis of model compounds II (3) and III (4) suggests that greater ground state proximity of double bond to site of displacement results in increased nucleophilic efficiency for double bond participation. Comparison of k_U/k_S for III and IV (2) demonstrates that the impact of such increased proximity can be more than offset by adverse torsional interactions inherent in the transition state for displacement at a primary propyl as opposed to a primary ethyl carbon atom (2). Consequently we have sought to combine the favorable aspects of displacement at primary ethyl carbon and the availability of a ground state conformation which places the double bond in close proximity to the site of potential displacement in constructing a model substrate for optimal nucleophilic participation by a 6,7-double bond. The solvolytic behavior of such a substrate should reveal whether 6,7-double bonds can participate as efficiently as 5,6-double bonds, and, if not, what the basis for their diminished nucleophilicity might be.

Cycloheptatriene and its simple 7-alkyl derivatives undergo rapid equilibration between two preferred boat conformations (5). Thus β-(7-tropyl)ethanol



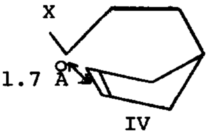
II

k_U/k_S 10^5



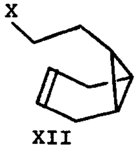
III

95



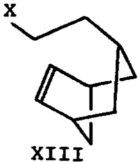
IV

ca. 1



XII

3



XIII

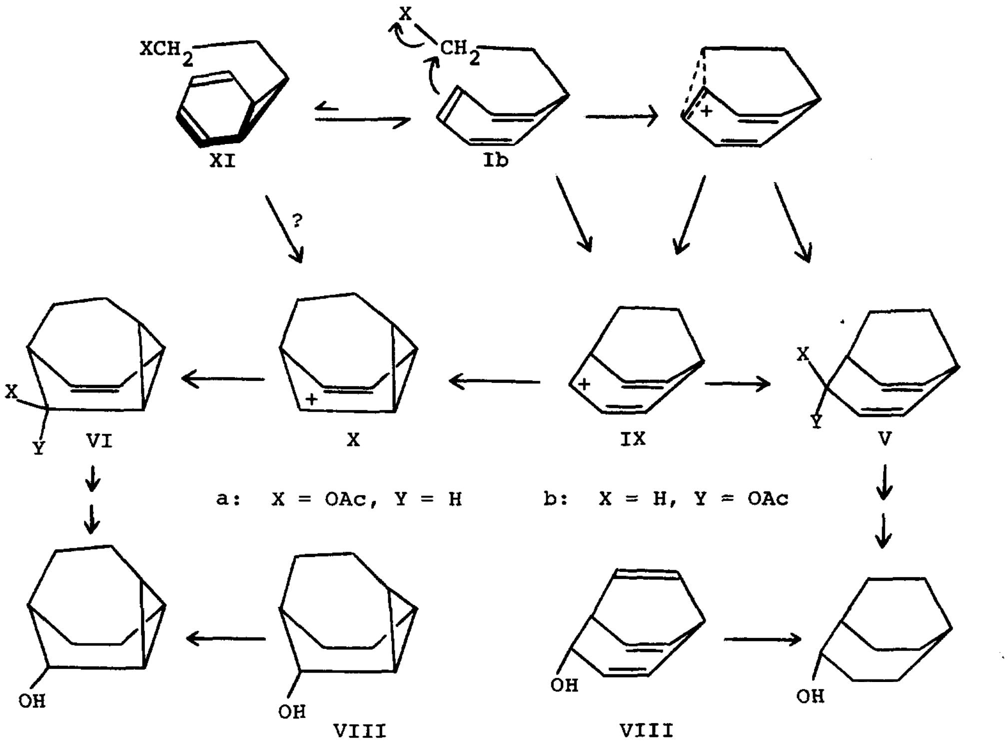
15

(Ia) has available a *ground state conformation* in which the primary carbon could potentially be located only 1.7 Å from the mid-point of the C-3,C-4 double bond. Of course, non-bonded interactions will distort this conformation in such a way as to increase this distance. It is important to note, however, that these non-bonded interactions involve only the primary carbon and its substituents and C-3 and C-4 and their hydrogen substituents; these *non-bonded interactions will be inherent in the transition state for any reaction which involves double-bond participation at primary carbon*. Thus an appropriate derivative of Ia would appear to be an even better potential substrate for solvolysis with nucleophilic double bond participation than II, in which the primary carbon and double bond are separated by *ca*. 2.4 Å in the ground state. For this reason, we have investigated the kinetics and products of acetolysis of β-(7-tropyl)-ethyl *p*-nitrobenzenesulfonate (Ib), prepared in the usual way (6) from the corresponding alcohol (Ia), which in turn was synthesized by $LiAlH_4$ reduction of 7-tropylacetic acid (7).

The acetolysis of Ib is cleanly first order through at least three half lives with k_1 (59.8°) = $1.56 \pm 0.03 \times 10^{-5}$ sec^{-1}, k_1 (75.0°) = $1.05 \pm 0.15 \times 10^{-4}$ sec^{-1}, and k_1 (100.2°) = $9.01 \pm 0.30 \times 10^{-4}$ sec^{-1} (ΔH = 24.3 ± 1.8 kcal/mole, ΔS = −7.6 ± 2.6 e.u.). Since rate constants for acetolysis of β-substituted ethyl *p*-nitrobenzenesulfonates are markedly insensitive to steric variations in the substituent, (2,6) the rate of acetolysis of β-cyclopentylethyl *p*-nitrobenzenesulfonate (8) may be utilized as an indication of the rate expected for Ib in the absence of *pi*-bond participation. Calculated in this way, k_U/k_S for Ib is found to be 16, a fact which clearly implies pronounced participation by the 6,7-double bond during acetolysis of Ib.

Product analysis confirms that the enhanced rate of acetolysis of Ib results from participation by the most remote double bond of the cycloheptatrienyl ring. The product consists of an approximately 1:1 mixture of bicyclic acetates Va, b and tricyclic acetates VIa, b (9), whose structures were inferred from their n.m.r. spectra and confirmed by saponification and catalytic hydrogenation to an alcohol identical to that obtained, respectively, by catalytic hydrogenation of VII (10, 11) and VIII (11, 12). Bicyclic acetate V is the product expected from simple 6,7-π-bond participation; tricyclic acetate VI may derive either from isomerization of an initially formed allylic cation (IX) to the cyclopropylcarbinyl cation X or through valence tautomerism of Ib to XI prior to ionization with subsequent 5,6-π-bond participation.

Taken together, the enhanced rate of reaction and the nature of the products generated by acetolysis of Ib establish that a 6,7-double bond can participate as an efficient nucleophilic neighboring group. The disparity in the nucleophilic efficiencies of the 5,6-double bond in II and the 6,7-double bond



in Ib must command attention, however, in light of the significantly greater proximity of the primary carbon and double bond in Ib than in II. At least three possible explanations for the relative nucleophilic inefficiency of double bond participation during solvolysis of Ib must be considered. First, the nucleophilicity of the π-bond may be reduced by *sigma* electron drain toward the neighboring *sp*^{2} hybridized carbon atoms which may be expected to be relatively more electronegative than the approximately *sp*^{3} hybridized carbon atoms which flank the double bond in II. Second, to the extent that the incipient cation derived from participation during acetolysis of Ib resembles the bicyclic allylic cation IX, it may suffer "bishomoconjugative destabilization". (12) Third, approach to colinearity of π-electron nucleophile, primary carbon, and potential leaving group may be more closely approximated or more readily achieved in the transition state for ionization of II than in that for Ib. The acetolysis of model compounds XII (14 and XIII (15) each of which has available a ground state conformation closely resembling that which prompted us to adopt Ib as a substrate for potential optimal π-bond nucleophilic participation, is less strongly accelerated than that of Ib itself. Since neither of the first two rationales offered above can readily accommodate this result, and since transition state colinearity as defined above would appear to be less readily achieved during solvolysis of XII than of Ib, we prefer the last of these explanations. The degree to which colinearity can be achieved in the transition state appears to be a factor whose extent in controlling the relative rates of solvolysis of a large number of compounds which undergo solvolysis with remote double bond participation has not as yet been fully appreciated. This thesis will constitute the theme of a more extensive forthcoming publication.

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