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CONCERNING ION PAIRS AND HYDRIDE PARTICIPATION IN THE ACETOLYSIS OF CYCLOOCTYL TOSYLATE

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The occurence of 1,5-hydride migrations in the reactions of cyclooctyl derivatives has been well documented.[1] In the solvolysis of 1,2,2,8,8-pentadeutero-cyclooctyl brosylate Cope and coworkers found that there was 53% 1,5-hydride migration in acetic acid and 60% in formic acid.[2] Almost no 1,3-hydride shift was observed. cis-5-Methyl cyclooctyl tosylate[3] gave 90% 1,5-hydride migration. The trans-isomer, which has an unfavorable stereochemistry for 1,5-hydride migration, gave only 9% of 1,5- rearranged products. Allinger and coworkers found that acetolysis of cis-5-t-butylcyclooctyl tosylate gave 99% of the 1,5- rearranged product.[5] The trans-compound gave only 12% rearranged product. The rates of acetolysis were measured giving relative rate constants of 1:2.5:53 for trans-5-t-butylcyclooctyl, cyclooctyl, and cis-5-t-butylcyclooctyl tosylates, respectively. The larger rate of the cis-compound over the trans-compound was considered evidence for acceleration by hydride participation. Similarly, hydride participation was said to be minor in cyclooctyl tosylate itself. There should be a greater driving force for participation in the cis-5-substituted compound because of the insipient formation of a tertiary carbonium ion.

In order to assess the extent of hydride participation, the isotope effect in the solvolysis of a 5-deuterated cyclooctyl tosylate would be of interest. cis-Cyclooctene was perdeuterated by the method of Anet.[6] The deuterated cyclooctene was converted to the alcohol by hydroboration followed by basic peroxide oxidation. This alcohol was oxidized to a ketone with chromic acid, and the deuteriums alpha to the carbonyl were exchanged for protons by refluxing in aqueous potassium carbonate solution. The exchanged ketone was reduced with lithium aluminum hydride giving the d_{10} alcohol, 3,3,4,4,5,5,6,6,7,7-decadeuterocyclooctanol. The kinetics of the acetolysis at 35.8° of the tosylate of this d_{10} alcohol were followed

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titrimetrically. For comparison the d_5 tosylate, 1,2,2,8,8-pentadeuterocyclooctyl tosylate,[2] the d_1 tosylate, 1-deuterocyclooctyl tosylate, and the undeuterated cyclooctyl tosylate were solvolyzed under similar conditions. The results are summarized in the Table.

TABLE

Compound	$10^5 k_1$ sec^{-1}	Rel. Rate
d_0	11.6 ± 0.1	(1.00)
d_1	10.2 ± 0.1	1.13 ± .02
d_5	6.2 ± 0.4	1.84 ± .10
d_{10}	9.6 ± 0.3[a]	1.21 ± .03[a]

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[a] Corrected for incomplete deuteration.

The reaction could also be followed by pmr spectral measurements at 100 MHz. These rates were in agreement with the titrimetric rates. When the d_1-tosylate was solvolyzed, it was found that a signal characteristic of 1-protiocyclooctyl tosylate appeared with time. This signal (δ = 4.74 ppm) distinct from, but partially overlapping the signal from the 1-protiocyclooctyl acetate, could be integrated. This peak represented approximately 20% of the unreacted tosylate at one half-life. This was considered evidence for return from ion pair intermediates[7] which have undergone 1,5-hydride shift to rearranged organic tosylate. Furthermore, since the reaction was found not to exhibit a special salt effect with added lithium perchlorate and since the return to rearranged tosylate was still observed with added lithium perchlorate, it was concluded that there is no significant return to starting material from solvent separated ion pairs, and that significant hydride shift has occurred in the intimate ion pair or during the formation of an intimate ion pair.

The isotope effects observed for the d_1 and d_5 tosylates are of the expected magnitude for alpha and beta secondary isotope effects.[8] The kinetic isotope effect for the d_{10} compound (k_H/k_D = 1.21/1.00) is k_H/k_D = 1.02 per deuterium atom. Such an isotope effect could be solely due to a remote secondary isotope effect with no hydride participation. It agrees well, perhaps fortuitously well, with the value Prelog, found for the acetolysis of 5,5,6,6-tetradeuterocyclodecyl tosylate, k_H/k_D = 1.02 per deuterium atom. He suggested that this isotope effect is caused by a decrease in ground state steric strain (cf. ref. 1).

On the other hand, if this isotope effect is regarded as a primary isotope effect associated with participation, the fraction of hydride assisted ionization (f_Δ) can be calculated by assuming that the primary hydride participation isotope effect is 2.6.[9] The fraction (f_Δ) is calculated to be about one-fourth, which would mean that most of the hydride migration occurs after ionization.

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