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SOLVOLYSIS OF SPIRO[2.n]ALKYL-4 DINITROBENZOATES (1)

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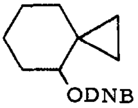
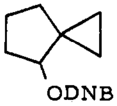
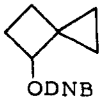
It now appears that cyclopropylcarbinyl derivatives solvolyze via an unrearranged cyclopropylcarbinyl cation as the initial intermediate (3). The questions which remain about the nature of the intermediate in cyclobutyl solvolyses made the examination of the following compounds of interest.



I



II



III

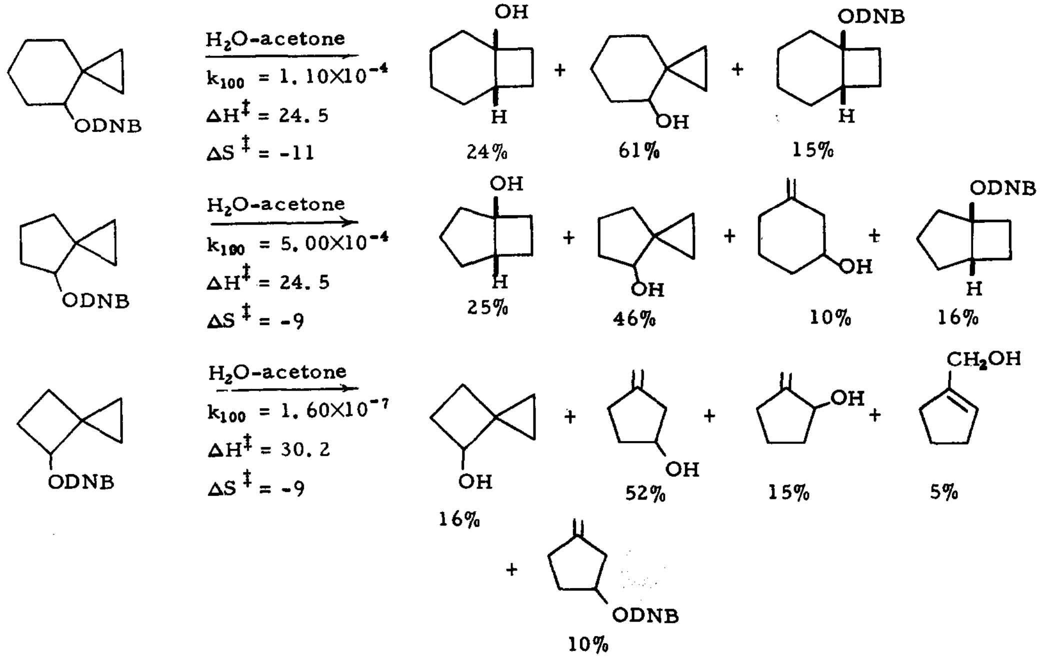
The solvolyses of the *p*-nitrobenzoates corresponding to I (4) and II (5) and the chloride corresponding to III (6) have been reported. However, no comparison of the three compounds using a single leaving group and solvent is available.

If in each case, the primary stabilization of the developing positive charge in the activated complex is the cyclopropylcarbinyl interaction, the reactivities of the compounds might be expected to correspond to the changes in energy resulting from the geometrical change from a tetrahedral to a trigonal arrangement. The ion formed from III would have the equivalent of two trigonal centers in the cyclobutane ring, and this ring should be planar. As a result of this and of the stabilization of the charge by the cyclopropane ring, no special rate acceleration due to the cyclobutane ring should be found.

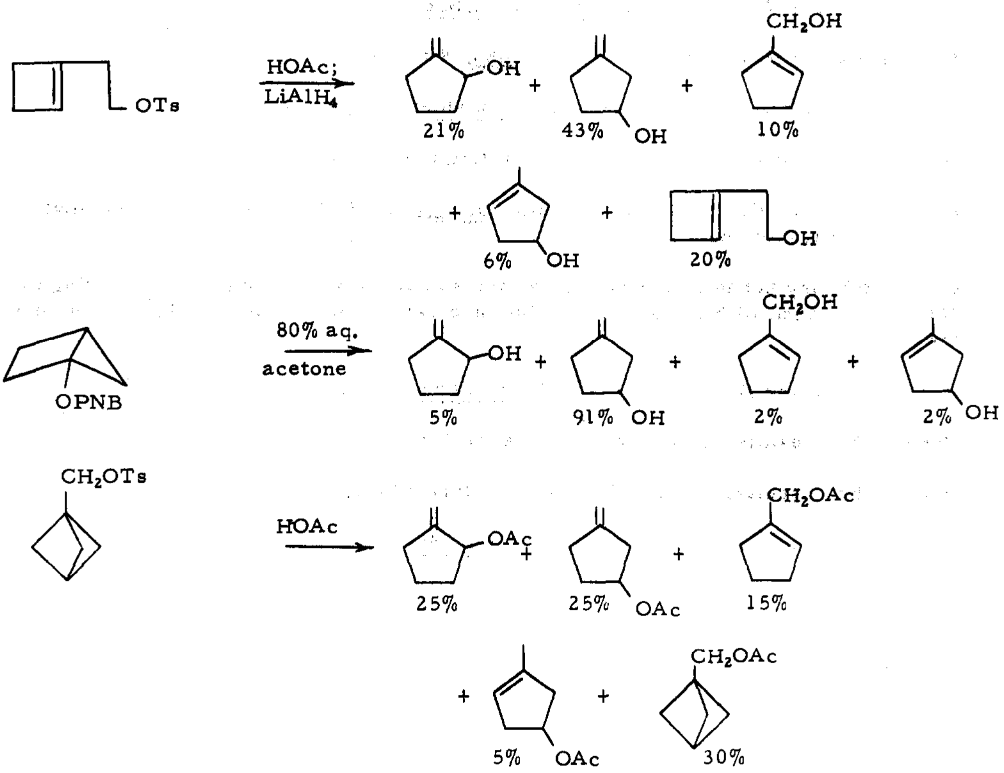
If this interpretation is correct, the reactivity order should be $\mathrm{II} > \mathrm{I} \gg \mathrm{III}$. If the reactivity of I is taken as normal, II would be expected to be more reactive because of the relief of torsional strain on going to the cation, and III would be expected to be the least reactive because of the large increase in strain on going to the cation. A dinitrobenzoate leaving group should be good for this comparison since a relative poor leaving group (as compared to tosyl) will lead to an activated complex relatively closer to the intermediate cation than would be the case with a better leaving group.

The expectation is born out by the data shown below for 80% aqueous acetone. The ratio of the reactivity of I and II is 1:5, similar to that observed in comparing cyclohexyl tosylate with cyclopentyl tosylate (7). The reactivity of III is 1/700 that of I. However, it still is 500 times more reactive than cyclobutyl dinitrobenzoate. If one assumes that relative rate of III corresponds to that of a normal unassisted solvolysis and compares this with the relative rate of solvolysis of cyclobutyl tosylate, one concludes that the latter has a rate acceleration of 8×10^3 (8). This is in good accord with our earlier estimate based on the use of the rate of borohydride reduction of cyclobutanone as a model (9).

The products of the solvolyses are shown below:



The products found with I and II are those expected based on the work of Hanack and Schneider (4) and of Closson and Kwiatkowski (5). The solvolysis of III leads to the same products as found in the solvolyses of 1-cyclobutenylethyl tosylate (10), bicyclo[1.1.1]pentyl-1-methyl dinitrobenzoate (11) and bicyclo[2.1.0]pentane-1-methyl p-nitrobenzoate (12).



All of these results appear best accommodated by assuming that the bicyclo[2.1.0]pentane-1-methyl cation is an intermediate. The details of these transformation will receive further consideration at a later time.

References

1. This investigation was supported by a grant from the National Institute of Health.
2. NIH Predoctoral Fellow, 1964-1967.
3. cf. K. B. Wiberg and A. J. Ashe, III, J. Am. Chem. Soc., **90**, 63 (1968); P. v. R. Schleyer and G. W. Van Dine, J. Am. Chem. Soc., **88**, 2321 (1966).
4. M. Hanack and H. J. Schneider, Ann., **686**, 8 (1965).
5. W. D. Closson and G. T. Kwiatkowski, Tetrahedron, **21**, 2779 (1965).
6. D. E. Applequist and J. A. Landgrebe, J. Am. Chem. Soc., **86**, 1543 (1964).
7. H. C. Brown and G. Ham, J. Am. Chem. Soc, **78**, 2735 (1956) found a cyclopentyl/cyclohexyl rate ratio of 14.
8. Cyclobutyl tosylate is 11 times as reactive as cyclohexyl tosylate.[7] Correcting for the 700:1 ratio found with I and III, one obtains a rate acceleration of 8×10^3 for cyclobutyl tosylate.
9. K. B. Wiberg and B. A. Hess, Jr., J. Am. Chem. Soc., **89**, 3015 (1967).
10. Unpublished results, J. E. Hiatt, this laboratory.
11. Unpublished results, V. Z. Williams, this laboratory.
12. W. G. Dauben and J. Wiseman, J. Am. Chem. Soc., **89**, 3545 (1967).