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4-SPIRO[2.n]ALKYL CATIONS

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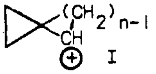
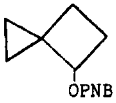
The 4-spiro[2.n]alkyl cations (I) represent a class of cations in which stabilization



I

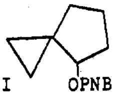
by bicyclobutonium type bridging (1) might be electronically as favorable as in the parent cyclopropylcarbinyl cation, since in each case the contributing cyclobutyl cation structure is stabilized by one alkyl group more than the contributing cyclopropylcarbinyl structure (3° and 2°, respectively in I; 2° and 1°, respectively, in bicyclobutonium ion itself). On the other hand, bicyclobutonium ion bridging in I should be subject to severe steric restrictions when n is small, and a study of the extra driving force provided by the 3-ring in the formation of I, as a function of n, could provide evidence for or against bicyclobutonium ion bridging.

Besides the present work, there are numerous data on rates of reactions leading to I (2). Missing until now have been satisfactory comparisons of the spirohexyl (II) and spiroheptyl (III) systems. The rates of the p-nitrobenzoates have been measured in 60% aqueous acetone, to obtain the first-order constants shown below the formulae. The rate for III is



II

ca $1.4 \times 10^{-7} \text{sec}^{-1}$ (94.82°)
$2.37 \times 10^{-5} \text{sec}^{-1}$ (148.5°)



III

$3.22 \times 10^{-4} \text{sec}^{-1}$ (94.82°)

in good agreement with the value 3.36×10^{-4} obtained by interpolation of the data of Krapc (2d). The relative values for II and III are also in good agreement with those of Wiberg an Hiatt (3).

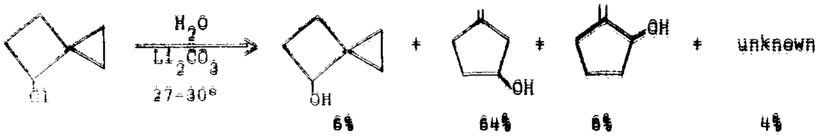
The most serious problem in interpretation of the rate constants obtained from II and other spirohexyl derivatives is the absence of an unambiguous standard for the unassisted solvolysis of a cyclobutyl derivative. We have previously (2a) proposed three empirical models for the relative rates of cyclopentyl and "classical" cyclobutyl solvolyses, namely the relative rates of the tertiary 1-methylcycloalkyl chlorides, the relative rates calculated from the heats of hydrogenation of methylenecyclopentane and methylenecyclobutane, and the relative rates of cyclopentyl chloride and 5-chlorospiro[3.2]hexane (IV). The rate ratios

IV V

of cyclopentyl to "classical" cyclobutyl from these three models are, respectively, 195, 31 and 567 at 95°. Additional support for the use of IV as a model for unassisted cyclobutyl is now found in the fact that the hydrolysis product in the presence of lithium carbonate is exclusively the unrearranged alcohol V.

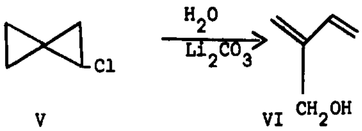
If the foregoing models for unassisted cyclobutyl solvolysis are used to compare the rates of spiro compounds II and III, it is seen that the rate enhancement due to the cyclopropane ring in III is 4 to 74 times that in II at 95°. This effect is in the direction expected for some steric restriction of bicyclobutonium ion formation in the case of II, but the effect is so small and the uncertainty of the models so great that no compelling argument for bicyclobutonium ion formation can be adduced.

The products of hydrolysis of 4-chlorospirohexane are as shown below:

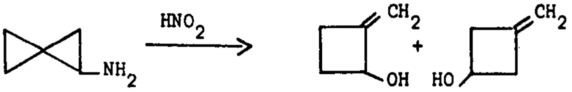


These are in good agreement with the similar study of Wiberg and Hiatt (3). The similarity to the array of products from the spiroheptyl system (3, 4) adds validity to the comparison of the rates of II and III.

Previously (2a), an attempt was made to compare the cyclopropyl participation in spiropentyl chloride (V) with that in 4-chlorospirohexane. The quantitative validity of the comparison, even assuming the accuracy of the models for unassisted rates, must now be questioned by the discovery that the exclusive product of hydrolysis of V is 2-hydroxymethylbutadiene (VI). The hydrolysis is thus like that of cyclopropyl chloride, giving ring opening to an



allylic cation, rather than like that of cyclopropylcarbinyl chloride. The rate is therefore a *maximum* for solvolysis with cyclopropylcarbinyl participation (with or without bicyclobutonium character). Interestingly, the deamination of spiropentylamine gives products quite in keeping with cyclopropylcarbinyl character of the cation (5).



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