Cyclopropylnitrenium Ions

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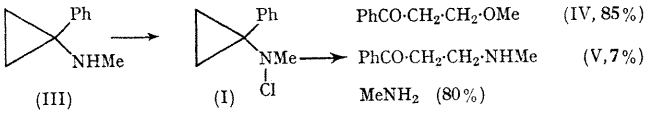
Summary Cyclopropylamines have been converted into the corresponding *N*-chloro-amines, which in polar solvents undergo solvolytic cleavage of the N–Cl bond in a heterolytic reaction leading to chloride anion and the nitrogen analogue of the cyclopropylcarbinyl cation.

THE cyclopropylcarbonium ion has received much attention because of its unusually fast rate of formation, interconversion with the cyclobutyl cation, and rapid relocation of isotopic labels.[1] As part of our investigations[2] of the nitrogen analogue of the carbonium ion, we have been studying the cyclopropylnitrenium ion.

We report that cations generated by heterolytic cleavage of the N-Cl bond of *N*-chlorocyclopropylamines rearrange

like cyclopropylcarbinyl cations. The *N*-chloro-*N*-methylcyclopropylamines (I) and (II) are among the most reactive *N*-chloro-amines we have studied. When *N*-methyl-1-phenylcyclopropylamine (III)[3] was treated with t-butyl



hypochlorite at dry ice–isopropyl alcohol temperatures in pentane, it was quantitatively converted into (I). The instability of (I) was demonstrated by the decomposition which occurred when the pentane solution was allowed to warm to room temperature. In addition to a large amount of intractable material, this decomposition in pentane gave 15% of (III), 3% of (V), and 4% of (VI) (of undetermined mechanistic origin). When the pentane solution was

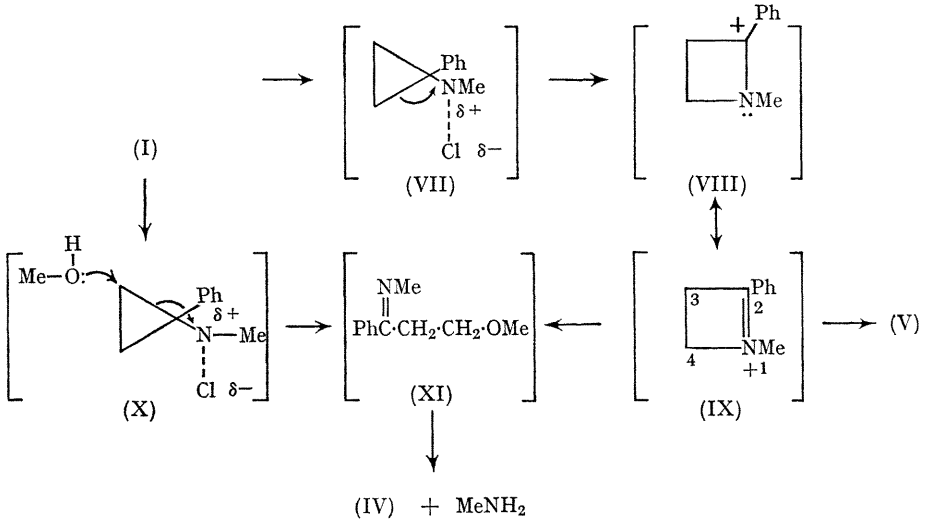
$$(PhCO\cdot CH_2\cdot CH_2)_2O$$
(VI)

diluted to five times its volume with methanol at −30° and then kept below 0° for 4 hr., (I) underwent complete solvolysis to give 85% of (IV), 7% of (V), and 80% of methylamine.†‡ We believe that the formation of (IV) and (V), which accounted for 92% of the starting material, occurred aqueous work-up would give (V). The formation of (V) requires a formal C → N migration of an alkyl group. In view of the tendency of alkyl groups to resist migration to anionic and radical centres it is most likely that the alkyl group in our case migrated with its bonding electron pair to an electron-deficient nitrogen centre.

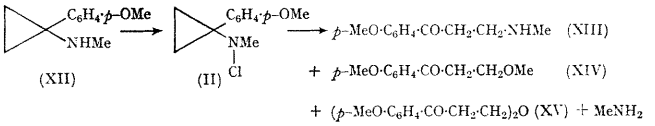
The formation of (IV) and methylamine can be explained in two different ways. Nucleophilic attack of methanol at C-4 of (IX) would lead to the imine (XI), which on hydrolysis would yield (IV) and methylamine. An alternative mechanistic path would involve a concerted loss of chloride and addition of methanol depicted by (X), which would lead directly to (XI). Both routes to (IV) require heterolytic cleavage of the N–Cl bond to give chloride anion and electron-deficient nitrogen intermediates.

When *p*-methoxyphenyl was used instead of phenyl as the aryl group (XII) and the amine function was converted into the *N*-chloro-amine (II) with t-butyl hypochlorite, the new *N*-chloro-amine was found to undergo a similar solvolytic rearrangement to yield (XIII) (11%); (XIV) (56%); (XV) (1%); and methylamine (66%). The routes to (XIII), (XIV), and methylamine are undoubtedly similar to those for the case where the aryl group is Ph. The history of (XV) is unknown.

The rearrangement of (I) and (II) in a manner similar to the analogous ring-cleavage of the cyclopropylcarbinyl cation extends the basis for a comparison of nitrenium ions and carbonium ions. The alkyl migrations observed in the



via heterolytic cleavage of the N–Cl bond to yield chloride anion and the nitrogen analogue of the cyclopropylcarbinyl cation. Just as a "classical" cyclopropylcarbinyl cation probably does not exist, so too, a cyclopropylnitrenium with a *unit* positive charge on nitrogen probably is not produced. We suggest that, as a partial positive charge starts to build up on nitrogen, cleavage of the cyclopropyl ring begins to occur as shown by (VII), to give (VIII), which, for purposes of discussing the formation of the observed products, can be considered in terms of its resonance structure (IX). Hydrolysis of (IX) during the rearrangements discussed above leave little doubt as to the intermediacy of an electron-deficient nitrogen species



either as a discrete intermediate or, more likely, as a crucial stage in the transition state of the reaction.

† Satisfactory analytical data have been obtained on all new compounds.

‡ All amines are isolated and characterized as their hydrochlorides or oxalates. Compounds (IV), (V), (XIII), and (XIV) were compared with independently synthesized authentic samples.

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[1] For a leading reference see D. Bethell and V. Gold, "Carbonium Ions," Academic Press, New York, 1967, pp. 266—271. See also R. Breslow, in "Molecular Rearrangements," ed. P. de Mayo, Interscience, New York, 1963, pp. 259—276.

[2] For references to published studies in this area, see P. G. Gassman, G. Campbell, and R. Frederick, *J. Amer. Chem. Soc.*, 1968, **90**, 7377.

[3] C. Kaiser, B. M. Lester, C. L. Zirkle, A. Burger, C. S. Davis, T. J. Delia, and L. Zirngibl, *J. Med. and Pharm. Chem.*, 1962, **5**, 1243.