Evidence for C–C σ-Delocalisation in Simple Secondary Carbonium Ions; Secondary → Primary Rearrangements

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Summary Small yields of primary acetates are obtained in the acetolysis of typical secondary *N*-alkyl-*N*-nitrosoacetamides; they imply strongly endothermal rearrangements in the cationic intermediates, best explained by C–C σ-delocalisation or 'non-classicism.'

Apart from the cyclobutyl ⇌ cyclopropylmethyl system, a special case, there have been few reports[1] of reactions that can be formulated as involving cationic secondary → primary rearrangements during substitution reactions, and little discussion of their mechanism. Reutov and Shatkina[2] described, without indicating yield or method of identification, the formation of cyclopentylmethanol in the nitrous acid deamination of cyclohexylamine in water. We find that acetolysis of *N*-nitroso-*N*-cyclohexylacetamide,[3] prepared from recrystallized cyclohexylacetamide, gives a substitution product consisting of cyclohexyl acetate and cyclopentylmethyl acetate (99·05 : 0·95); the latter was identified by retention times differing by $<$ 0·25 and $<$ 0·5% on two different liquid phases, used at *ca.* 20,000 plates, from authentic ester. We have reported[4] the formation of skeletally rearranged esters (3% of substitution product, 2·5% overall) in the deamination of 4-*trans*-t-butylcyclohexylamine (but not of the *cis*-isomer) by various routes, along with 1·4—3·5% of a t-butylbicyclo[3.1.0]-hexane.† The acetate, earlier[4] denoted as 'W', is now identified as *trans*-3-t-butylcyclopentylmethyl acetate, through the synthesis of the *cis*- and *trans*-esters from 4- and 3-t-butylcyclohexanones by selenium dioxide–hydrogen peroxide oxidation to the corresponding ring-contracted acids,[5] lithium aluminium hydride reduction, and acetylation, and proof of g.l.c. inseparability from the latter acetate. The rearrangement, like exothermal and thermoneutral 1,2-alkyl shifts in carbonium ions, thus involves inversion of configuration at the reaction site.

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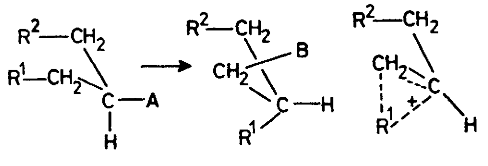
† The substituted bicyclohexane reacted with acetic acid only in the presence of toluene-*p*-sulphonic acid, and then gave no 'W.' Presumably bicyclo[3.1.0]hexane is formed from the cyclohexylamine derivative; it is also acetolysed to give a mixture of products which do not include cyclopentylmethyl acetate (R. T. Lalonde and L. S. Forrey, *J. Amer. Chem. Soc.*, **1963**, **85**, 3767).

In the acetolysis of cyclohexyl toluene-*p*-sulphonate the substitution product was found to contain $<$ 0·03% of the cyclopentylmethyl derivative; a trace probably was present. The non-volatile fraction, recovered after 16 half-lives,[6] was again acetolysed, and a 0—0·003% yield of the primary sulphonate (19 times less reactive)[6] was deduced from kinetic measurements. Axial and flexible conformers would be expected[7] to constitute the main reacting species and, lacking antiparallel C–C bonds, not to rearrange, whereas in the 2-adamantyl → protoadamantyl rearrangement, which is comparably endothermal,[8] the lower reactivity of the arenesulphonate intermediate did not prevent detection of protoadamantyl acetate.



(1) **(2)** **(3)**

If, as seemed likely, this rearrangement [(**1**) → (**3**) → (**2**)] is characteristic of any C_4 or C_5 chain in conformation (**1**), it should take place in the 1-ethylpropyl system, to the extent that this adopts a *gauche*, rather than an extended conformation. Nitrosation of carefully purified crystalline *N*-(1-ethylpropyl)acetamide and acetolysis gave a 99·7 : 0·3 mixture of (1-methylbutyl + 1-ethylpropyl) acetates and 2-methylbutyl acetate; pentyl, 3-methylbutyl, and 2,2-dimethylpropyl acetates would have been detected in 0·03% concentration in the substitution product, but were absent. Similarly, crystalline *N*-s-butylbenzamide gave, *via* s-butylamine, its acetyl derivative, and the nitrosoamide, a *ca.* 99·8 : 0·2 mixture of s-butyl and isobutyl acetates (the n-butyl acetate content was $<$ 0·05% of the substitution product). In simultaneous blank experiments, omitting only the nitroso-amide, no peaks were obtained at the same retention times as for the rearranged acetates.

We have argued[8] that the formation of two products in comparable yield (a factor of 10^2 or 10^3 should be considered small) is incompatible with their generation from two corresponding rapidly interconverting intermediates, if the equilibrium ratio of these is of the order of 10^6 or more and the (presumably) less reactive is known to react very rapidly. Here equilibrium between a secondary and a primary ion, some 70—80 kJ mol^{-1} apart in energy[9] (equilibrium coefficient *ca.* 10^{12}), would require a physically unrealistic difference of 10^9 or more in the reaction rates of two assumed 'classical' intermediates. Direct formation of a non-classical ion or protonated cyclopropane[9] (**3**), in which each of the carbon atoms that ultimately reacts with a nucleophile carries some charge, economically explains the facts; if this can happen with s-butyl$^+$ and cyclohexyl$^+$, there can be few secondary carbonium ions incapable of such C–C σ-delocalisation. However, species (**3**), generated only when the R–C and C–A bonds are initially antiparallel and probably having a lifetime comparable with the times of rotation around single bonds and of solvent reorganisation,[10] can usefully be thought of as an 'intermediate' only after careful consideration of the meaning of the term; if, as we believe, C–C σ-delocalisation in carbonium ions is more widespread than has been assumed in much recent controversy, it must in many cases be dissociated from the consequences (acceleration, control of stereochemistry, *etc.*) that it has been assumed to explain.

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