Tetrahedron Letters No. 34, pp. 3193 - 3196, 1971. Pergamon Press. Printed in Great Britain.

PROTONATED NORCARANE (BICYCLO [4.1.0] HEPTANE) AS AN INTERMEDIATE IN THE THERMAL DECOMPOSITION OF CYCLOHEXYLMETHYL AND CYCLOHEPTYL CHLOROFORMATES AND IN THE DEAMINATION OF THE CORRESPONDING CYCLOALKYLAMINES

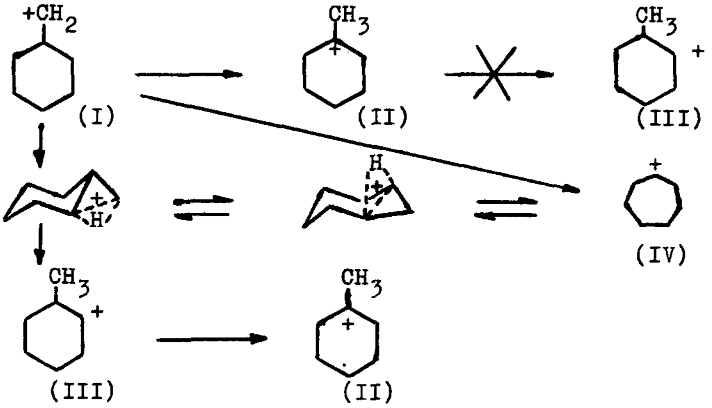
W.E. Dupuy, H.R. Hudson, and P.A. Karam
Department of Chemistry, The Polytechnic
of North London, Holloway Road,
London N7 8DB

(Received in UK 14 July 1971; accepted for publication 20 July 1971)

The formation of protonated cyclopropane intermediates has been postulated in a number of carbonium ion rearrangements,[1] and a protonated bicyclic intermediate (protonated bicyclo [3.1.0] hexane) has been thought to account for rapid isomerization and proton equivalence in the cyclopentylmethyl cation in SbF_5/SO_2ClF solution.[2] In certain reactions of acyclic compounds, cyclopropane or one of its derivatives has been isolated as a reaction product,[1,3] although the amount of substitution product which arises via the protonated cyclopropane intermediate is usually small, being 6% in the nitrous deamination of n-propylamine[4] and only 0.6% in the deamination of isobutylamine.[5] We now report the presence of norcarane (bicyclo [4.1.0] heptane) among the hydrocarbon products obtained during the pyrolytic decomposition of cyclohexylmethyl chloroformate and of cycloheptyl chloroformate, and during the reaction of cyclohexylmethylamine or cycloheptylamine with nitrous acid (Table 1). The similarity in the rearrangements which occur in chloroformate decompositions and in nitrous acid deaminations has also been noted in acyclic systems.[6] Norcarane was positively identified in the present work by g.l.c. on four different columns (including silver nitrate - ethylene glycol which increases the retention times for olefins[7] but not for saturated hydrocarbons), by g.l.c. - mass spectrometry,[8] and by recording the ^1H n.m.r. spectrum of the combined hydrocarbons with the aid of a computer of average transients; the latter revealed a series of peaks characteristic of cyclopropane derivatives[9] in the region 9 - 10.2 τ and identical to those for an authentic sample of norcarane, prepared by the method of Simmons and Smith.[10]

It appears likely that the protonated species is a reaction intermediate which leads to the formation of those 5 to 10% of rearrangement products which would not be expected to result from simple 1,2-shifts in carbonium ions in kinetically controlled processes (Scheme I).

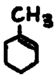
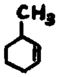
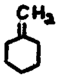
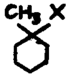
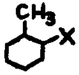
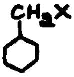
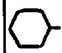
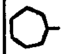
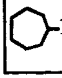
SCHEME I



SCHEME II

Whilst the cyclohexylmethyl cation (I) can yield the more thermodynamically stable 1-methylcyclohexyl cation (II) by a 1,2-hydride shift, further rearrangement of the latter to the less stable 2-methylcyclohexyl cation (III) clearly does not occur, since 1-methylcyclohexyl chloroformate (prepared from the alkoxide[11] and decomposed in situ at 20°) yielded 1-methylcyclohexyl chloride as the only substitution product. The tertiary alkyl products, furthermore, do not undergo isomerization after formation. Similarly, the observed ring contraction of the cycloheptyl cation (IV) would require the initial unlikely formation of the primary cyclohexylmethyl cation if classical carbonium ion intermediates were involved; subsequent rearrangement would then be expected to yield tertiary rather than secondary halide or alcohol as the major rearrangement product. The 2-methylcyclohexyl cation can, however, result directly from opening of the protonated norcarane (Scheme I). Formation of the primary cyclohexylmethyl substitution products might be due to a concerted ring opening and nucleophilic attack by halide ion or water on the protonated norcarane (Scheme II).

TABLE I

Reactants	Volatile Product Composition (% by weight)									
										
							trans	cis		
-CH_2OCOCl[a]	4.9	2.4	0.1	5.0	0.4	23.4	2.8	1.1	24.6	22.8[b]
-CH_2NH_2 + HNO_2[c]	9.1	6.8	0.8	4.2	1.1	29.5	1.2		22.2	25.1
-OCOCl[d]	traces	0.2	-	31.2	0.9	0.5	1.4	0.3	1.4	63.9
-NH_2 + HNO_2[e]	0.1	0.7	-	28.7	3.6	0.4	0.9		traces	62.8[f]

[a] 150°/200 hr. [b] 12.4% bis(cyclohexylmethyl) carbonate obtained.

[c] In H_3PO_4.[12] [d] 150°/30 hr. [e] In H_3PO_4.[12] [f] 2.8% unidentified

We thank the University of London Central Research Fund for a grant (to H.R.H.) for the purchase of a Perkin-Elmer F.11 chromatograph.

REFERENCES

1) C.J. Collins, Chem. Rev., 69, 543 (1969).
2) M. Saunders and J. Rosenfeld, J. Amer. Chem. Soc., 91, 7756 (1969).
3) G.M. Fraser and H.M.R. Hoffmann, Chem. Comm., 561 (1967).
4) G.J. Karabatsos, C.E. Orzech, Jnr., J.L. Fry, and S. Meyerson, J. Amer. Chem. Soc., 92, 606 (1970).
5) G.J. Karabatsos, Nelson Hsi, and S. Meyerson, J. Amer. Chem. Soc., 92, 621 (1970).
6) P.W. Clinch and H.R. Hudson, Chem. Comm., 925 (1968); J. Chem. Soc. (B), 747 (1971).
7) E. Gil-Av, J. Herling and J. Shabtai, J. Chromatog., 1, 508 (1958).
8) R.E. Winters and J.H. Collins, J. Amer. Chem. Soc., 90, 1235 (1968).
9) J.W. Emsley, J. Feeney and L.H. Sutcliffe, "High resolution N.M.R. spectroscopy," Vol. 2, Pergamon Press (1966), p. 690; P.K. Freeman, F.A. Raymond and M.F. Grostic, J. Org. Chem., 32, 24 (1967); K.B. Wiberg and W.J. Barttey, J. Amer. Chem. Soc., 82, 6375 (1960); R.S. Boikess, M. Mackay and D. Blithe, Tetrahedron Letters, 401 (1971).
10) H.E. Simmons and R.D. Smith, J. Amer. Chem. Soc., 81, 4256 (1959).
11) A.R. Choppin and J.W. Rogers, J. Amer. Chem. Soc., 70, 2967 (1948).
12) R. Kotani, J. Chem. and Eng. Data, 11, 248 (1966).