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The 2-Bicyclo[3,1,0]hexyl Carbonium Ion

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Reports of the intervention of the ion (I) in rearrangements,[1] and of its formation from bicyclo[3,1,0]hex-2-ene by protonation[2] prompt us to record our studies on the solvolysis of the epimeric 2-chlorobicyclohexanes (IIa and IIIa) and deamination of the corresponding 2-amino-derivatives (IIb and IIIb). The alcohols formed in these reactions and the rates of solvolysis confirm that the cation (I) is readily formed, relatively stable, and non-classical in nature.

Treatment of *endo*-bicyclohexan-2-ol (IIc; 7% *exo*-isomer) with thionyl chloride[3] gave a mixture of the corresponding *endo*- and *exo*-chlorides (respectively IIa and IIIa; ratio 2 : 1) contaminated with 4-chlorocyclohexene (12%).† Bromination, followed by distillation, removed the olefinic isomer, but the bicyclic chlorides rearranged to the less strained 4-chlorocyclohexene within 2 weeks at room temperatures[4] presumably by internal return from an ion-pair.[4] Preparative g.l.c. gave pure *endo*-chloride (IIa) and *exo*-chloride contaminated with 4-chlorocyclohexene which had the same retention time. The chlorides were stable at −40° or as dilute solutions in benzene.

Lithium aluminium hydride reduction of 2-oximinobicyclo[3,1,0]hexane yielded the *endo*-amine (IIb; hydrochloride m.p. 215°) as the major basic product (>90%), a stereochemical result in line with corresponding reduction of the 2-ketone.[5] The *exo*-amine (IIIb; hydrochloride m.p. 178—179°) was readily prepared from the mixture of bicyclic chlorides which after treatment with sodium azide gave the *endo*- and *exo*-azides (respectively IId and IIId) separable by g.l.c. The *exo*-epimer was then reduced with lithium aluminium hydride.

Deaminations were carried out by the method of Corey,[1b] and the alcohols, after extraction with ether, were analysed directly by g.l.c. Three alcohols were observed: in order of elution, *exo*-bicyclohexanol (IIIc), cyclohexen-4-ol, and *endo*-bicyclohexanol (IIc). N.m.r. analysis confirmed this result, and in addition showed about 2% of a second olefinic product, tentatively identified as cyclohexen-3-ol, which would have come under the first peak in the g.l.c. analysis. 4-Aminocyclohexene was also deaminated under the same conditions to prepare the cation (I).[1a]

For product analysis, solvolyses were carried out in 70% acetone in presence of calcium carbonate, 4-chlorocyclohexene was unaffected, permitting use of impure *exo*-chloride for comparison with the *endo*-isomer. The results of both solvolysis and deamination experiments are summarised in Table 1.

The yield and ratio of bicyclic alcohols formed is evidence of the 2-bicyclohexyl cation as an intermediate, partly shielded by the leaving group in the bicyclic series, and formed (to some extent) from diazotised 4-aminocyclohexene by homoallylic rearrangement. Formation of similar amounts of cyclohexen-4-ol in all reactions of the bicyclic precursors also suggests that the cation is non-classical with some positive character at C(5).

In a conductimetric rate-study, first-order

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† Analyses by combination of n.m.r. and g.l.c.: for n.m.r. of bicyclohexane derivatives see ref. 2.

TABLE 1

Starting product	Total yield of alcohol (%)	Product ratio			% *exo*-Epimer in bicyclic product
		(IIc)	(IIIc)	Cyclohexene-4-ol	
endo-Amine (IIb) ..	59	31	53	16	63
exo-Amine (IIIb) ..	34	34	50	16	60
4-Aminocyclohexene ..	20	18	25	38[a]	58
endo-Chloride (IIa)	70	29	59	12	67[b]
exo-Chloride (IIIa)[c] ..	—	35	51	14	59[b]

[a] Cyclohexen-3-ol (19%) also formed: low yield of alcohols due to formation of tars not noted in bicyclic series; [b] G.l.c. analysis only: after 24 hr. direct from reaction; [c] Contaminated with 35% 4-chlorocyclohexene: yield of alcohols not calculated.

kinetics were observed in the solvolysis of both *endo*- and impure *exo*-chlorides at 25° in 70% acetone. Only 87 ± 1% of the theoretical hydrochloric acid was generated in each case, and it was assumed that the remaining chloride had rearranged to less reactive species by internal return.‡ A check on the composition of the unreacted chlorides after one half-life showed slight interconversion of the two epimers, but this was hardly detectable in the runs over a period of five half-lives. Rate-constants were obtained from the expression:

$$kt = \ln\{[\mathrm{RCl}]/([\mathrm{RCl}] - [\mathrm{HCl}]/0{\cdot}87)\}$$

and are found in Table 2, together with rate constants for solvolysis of two related chlorides, for comparison, in the same solvent system.

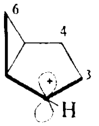
TABLE 2

Solvolysis rates in 70% *aqueous acetone*

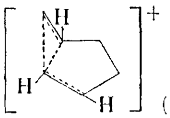
Compound	Temp.	Rate constant
endo-Chloride (IIa) ..	25°	$2{\cdot}67 \times 10^{-4}$
endo-Chloride (IIa) ..	10	$3{\cdot}94 \times 10^{-5}$
exo-Chloride (IIIa) ..	25	$1{\cdot}75 \times 10^{-4}$
Chlorocyclopentane[a] ..	50	8×10^{-8}
3-Chlorocyclopentene ..	0	$1{\cdot}32 \times 10^{-2}$

[a] Rate followed for 5% reaction only.

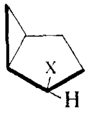
Cyclopropane participation in the case of the bicyclic chlorides (IIa and IIIa) is clearly indicated by the enhanced rates relative to that for chlorocyclopentane. Furthermore, as there are marked differences between the stereoelectronic situations for the *endo*-chloride (IIa) and the *exo*-chloride (IIIa) in the initial stages of ionisation, the simplest interpretation of the low $k_{endo} : k_{exo}$ ratio (1·52) is that considerable carbon–chlorine bond stretching has occurred in both transition-states which are stabilised by bishomoallylic resonance[5b] and resemble the final cation (IV). If participation were homoallylic or bicyclobutonium in type,[5] we should expect a larger $k_{endo} : k_{exo}$ ratio as the 1,5-bond which would exclusively assist ionisation of the *endo*-chloride is alkyl-substituted whilst the 1,6-bond affecting the *exo*-chloride is not.§



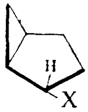
(I)



(IV)



(II)



(III)

(a) X = Cl (c) X = OH
(b) X = NH_2 (d) X = N_3

Compared with the bicyclic chlorides, 3-chlorocyclopentene solvolyses quickly [1370 times faster than the estimated rate for the *endo*-chloride (IIa), at 0°, corresponding to a $\Delta\Delta G$‡ of about 4·0 kcal./mol.] showing that the double bond is more effective than the cyclopropyl group in activating the α-chloro-group, when the latter is in a five-membered ring. In contrast, simple cyclopropylcarbinyl derivatives have been reported[6] to solvolyses 10—30 times faster than the corresponding allyl derivative ($\Delta\Delta G$‡ ~ 1·5 kcal./mole).

It is not possible to account for this reversal of rate-order (corresponding to $\Delta\Delta G$‡ ~ 5·5 kcal./mol.) in quantitative terms involving delocalisation

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‡ G.l.c. analysis of unsaponified material (pentane extract) showed at least nine peaks in the region expected for C_6-chlorides. The residues for *endo*- and *exo*-chlorides differed slightly, so no definite conclusion can be drawn as to whether the respective ion-pairs reach geometrical equivalence prior to isomerisation.

§ A less likely possibility is that stereoelectronic differences between the two ionisations fortuitiously balance the effect of alkylation of the 1,5-bond. Further investigation of this point is being carried out by use of 5- and 6-methyl-2-bicyclo[3,1,0]hexyl derivatives.

energies, torsional and bond-angle strains[7] at the present time. We suggest, however, that the main reason should be sought in the different effect of the extra ring-strain (due to the five-membered ring) on the two types of electron delocalisation. Thus, for the bicyclic chlorides, the ideal bisected conformation required for bishomoallylic resonance[5b] is difficult to achieve, and the energy of the transition state will be raised because of this. On the other hand, the transition state for 3-chlorocyclopentene should be lower in energy if ring strain leads to bond-shortening and increased π-overlap in the developing allyl cation.

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