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THE 8-HYDRINDANYL CATION

K. Becker, A.F. Boschung and C.A. Grob
Institut für Organische Chemie, Universität Basel

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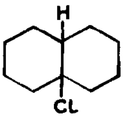
From a study of reaction rates and products of cis and trans 9-decalyl chloride, 1 and 2 respectively, in 80 % ethanol and from the equilibrium constant of isomerisation of the two chlorides it was concluded that they ionise to different conformers of the 9-decalyl cation 3 and that these should be regarded as true intermediates in solvolysis 1). Fort and Hornish who studied the corresponding p-nitrobenzoates reached a similar conclusion 2).



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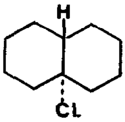

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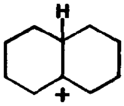

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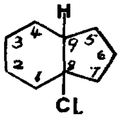

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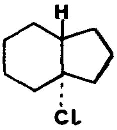

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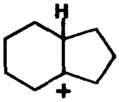


6

The 8-hydrindanyl (1-bicyclo[4.3.0]nonanyl) cation 6, however, possesses less conformational flexibility due to the rigidity of the cyclopentane ring. Ionisation of cis and trans 8-hydrindanyl chloride, 4 and 5 respectively, should therefore lead to nearly equivalent carbonium ions 6. Support for this view has now been obtained from a study of the rates, products and the isomerisation of the chlorides 4 and 5 3).

The equilibration constant for cis-trans isomerisation $\underline{4} \rightleftharpoons \underline{5}$ in aqueous HCl at 46° was 5.25 in favour of the cis isomer $\underline{4}$ [4]. This corresponds to a difference in ground state free energy ΔG of 1.06 kcal (Fig. 1). On the other hand, in 80 % ethanol at 46°, the trans isomer $\underline{5}$ reacted 10.7 times as fast as the cis isomer $\underline{4}$ (Table 1). This ratio corresponds to a difference in activation free energy $\Delta\Delta G^{\neq}$ of 1.50 kcal.

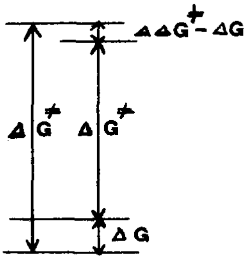
Table 1. First-order rate constants in 80-vol. % ethanol [a], 46°.

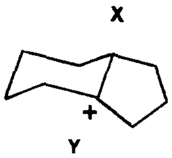
	cis chloride $\underline{4}$	trans chloride $\underline{5}$	$(CH_3)_3C\text{-}Cl$
$k \times 10^3$ (s^{-1})	1.42	15.14	0.117
k_{rel}	12.1	129	1

a) containing 1 to 5 molar equiv. of triethylamine.

The transition state energies of $\underline{4}$ and $\underline{5}$ therefore differ by $\Delta\Delta G^{\neq} - \Delta G$ = 0.44 kcal (Fig. 1) as compared to a value of 1.4 kcal for cis and trans 9-decalyl chloride, $\underline{1}$ and $\underline{2}$ respectively [1]. Since carbonium ions resemble the transition states of their formation it follows that the ion pair intermediates $\underline{7}$ are also of similar energy.

Fig.1

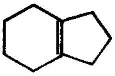
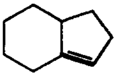
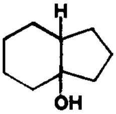
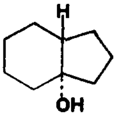




$\underline{7a}$ X = Cl^-, Y = solvent
$\underline{7b}$ X = solvent, Y = Cl^-
$\underline{7c}$ X = solvent, Y = TsO^-

These ion pairs must differ with respect to the position of the chloride ion which is located on the convex side $\underline{7a}$ of the 8-hydrindanyl cation derived from the cis chloride $\underline{4}$ and on the concave side $\underline{7b}$ in the one from the trans chloride $\underline{5}$. Since the carbonium ion centre is more accessible to solvent on its convex side the somewhat lower transition state energy of the trans chloride $\underline{5}$ may be attributed to tighter solvation in $\underline{7b}$. This is in agreement with the more negative activation entropy of the trans chloride 5 5). As shown in Table 1 the 8-hydrindanyl chlorides 4 and 5 react considerably faster than tert. butyl chloride, possibly as a result of steric acceleration.

Table 2. Solvolysis products in 80-vol. % ethanol a)

				
cis chloride 4	60 b)	18	6 (3) c)	10 (3) c)
trans chloride 5	51 b)	39	2.5 (6)	1.5 (0.5)
tosylate 8 d)	35.5 b)	16.5	18.5 (19)	7 (3)

a) containing 1.5 molar equiv. of triethylamine.

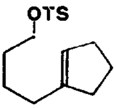
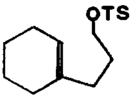
b) the $\Delta^{8.9}$-hydrindene fraction contained ca. 10 % of the $\Delta^{1.8}$ isomer.

c) yield of ethyl ether in parentheses.

d) yield of cyclised products 44 %.

Solvolysis of 4 and 5 leads to different amounts of the same products, as listed in Table 2, namely $\Delta^{8.9}$, $\Delta^{1.8}$ and $\Delta^{7.8}$ hydrindene, cis and trans 8-hydrindanol and the corresponding ethyl ethers 4). Substitution occurs with retention and with inversion of configuration, the latter process dominating considerably in the case of the trans chloride 5. This again indicates unsymmetrical solvation of the 8-hydrindanyl cation as in 7a and 7b.

Table 3. k_u/k_s values in:

		80 % ethanol	50 % acetone	abs. CH_3COOH
8		1.81	3.15	24.8
9		0.86	0.82	0.84

The 8-hydrindanyl cation 6 is also generated in the solvolysis of 4-(cyclopenten-1-yl)-butyl tosylate 8. The ratios k_u/k_s of the first-order rate constants for the unsaturated tosylate 8 (k_u) and its saturated analogue (k_s) in various solvents are listed in Table 3. These ratios clearly demonstrate anchimeric assistance to cyclisation. They increase as the nucleophilicity of the solvent decreases. The cyclisation products (Table 2) are the same as those formed in the solvolysis of the chlorides 4 and 5. However, cis-8-hydrindanol and the corresponding ether are present in larger amounts than the trans isomers. This suggests an encumbered carbonium ion 7c as the product-determining intermediate.

By contrast, no hydrindane derivatives are formed from 3-(cyclohexen-1-yl)-propyl tosylate 9 and no anchimeric assistance from the double bond is apparent from the k_u/k_s ratios in Table 3. Models confirm that participation of the olefinic π-orbital is precluded in this molecule for steric reasons.

In summary, it appears that reactions of the 8-hydrindanyl chlorides 4 and 5 and of the tosylate 8 are governed by environmental factors, such as ion-pairing and unsymmetrical solvation, rather than by different geometries of the 8-hydrindanyl cation 6).

References

1) A.F. Boschung, M. Geisel and C.A. Grob, Tetrahedron Letters 1968, 5169.

2) R.C. Fort and R.E. Hornisch, Chemical Communications 1968, 11.

3) These chlorides were prepared by addition of HCl to $\Delta^{8.9}$hydrindene. In CH_2Cl_2 at -78° the cis isomer 4, in ether at -5° the trans isomer 5 was formed preferentially.

4) determined by g.l. chromatography.

5) $\Delta S^{\neq}$ for 5 -12 e.u.; for 4 -4.9 e.u.

6) Professor R.C. Fort Jr. has kindly informed us of the results of a study of the 8-hydrindanyl p-nitrobenzoates prior to publication.