

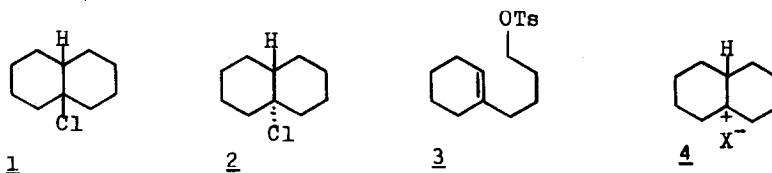
CONFORMERS OF 9-DECALYL CATION

A.F. Boschung, M. Geisel and C.A. Grob

Institut für Organische Chemie, Universität Basel

(Received in UK 2 September 1968; accepted for publication 16 September 1968)

Ionisation of *cis* and *trans* 9-chlorodecalin, 1 and 2 respectively ¹⁾, and anchimerically assisted cyclisation of 4-(cyclohexenyl)-butyl tosylate 3 lead to structurally identical carbonium ions 4. If the latter rapidly reach a state of conformational equilibrium identical products should result from solvolysis of all three compounds.



In fact different mixtures of products result from their reactions in 80% ethanol as shown in Table 1. Whereas only $\Delta^{1.9}$ and $\Delta^{9.10}$ -octalin are obtained from the *trans* chloride 2 *cis* and *trans* 9-decalol are formed also from the *cis* chloride 1 and the tosylate 3. The carbonium ion intermediates cannot therefore be identical.

TABLE 1
Solvolysis products in 80-vol.% ethanol ^{a)}

<i>cis</i> chloride <u>1</u>	51	42	5	2
<i>trans</i> chloride <u>2</u>	22	78	-	-
tosylate <u>3</u> ^{b)}	40.5	38.5	6.5	14.5

a) containing 1.2 molar equiv. of triethylamine

b) total yield of cyclised products 55%.

The different product compositions could be attributed to different locations of the counter ion X^- (Cl^- , TsO^-) in the ion pairs 4. However, formation of cis and trans 9-decalol from 1 and 3 militates against an explanation based solely on an encumbered ion pair.

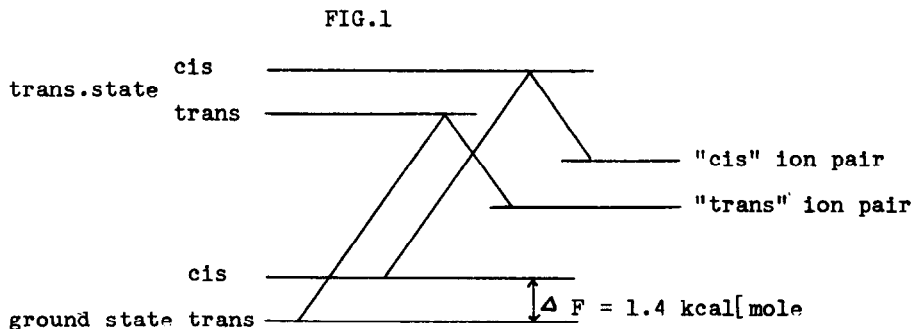
Consideration of ground state free energies and solvolysis rates of the tertiary chlorides 1 and 2 suggests an alternative explanation. The equilibrium constant $K = 9$ for the cis-trans isomerisation $1 \rightleftharpoons 2$ at $46^\circ C$ ¹⁾ corresponds to a difference in ground state free energy of 1.4 kcal/mole. On the other hand the solvolysis rates of cis and trans 9-chlorodecalin differ only slightly (Table 2), the cis chloride reacting faster by a factor of 1.35. The similarity of the rate constants of 1 and 2 and tert. butyl chloride demonstrates the absence of unusual steric effects.

TABLE 2

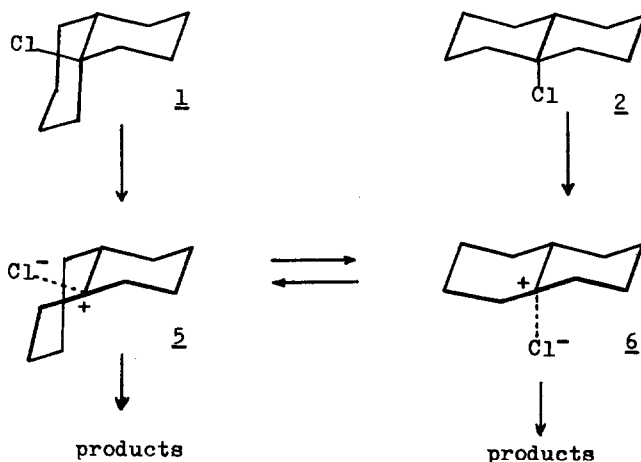
First-order rate constants in 80-vol.% ethanol ^{a)} at $70.0^\circ C$			
	cis chloride <u>1</u>	trans chloride <u>2</u>	$(CH_3)_3C-Cl$
$k \times 10^4 \text{ s}^{-1}$	7.66	5.68	15.1
k_{rel}	1.35	1	2.1

a) containing 1 to 5 molar equiv. of triethylamine

Since the reaction rates of 1 and 2 are almost identical and since their ground states differ by 1.4 kcal/mole the transition states of ionisation must also differ by approximately the same amount. Following the generally accepted rule, namely that carbonium ion intermediates resemble the transition states of their formation, one concludes that the energies of the carbonium ions derived from 1 and 2 also differ by approximately 1.4 kcal/mole, as shown in Fig. 1.



This energy difference could reflect the formation of different conformations of the 9-decalyl cation 4. In fact models show that replacement of the tetrahedral C-9 atoms in cis and trans 9-chlorodecalin by trigonal C-9 atoms results in two relatively rigid conformations 5 and 6. In these cations one ring adopts a chair the other a boat or twist conformation. Furthermore, the conformer 5 derived from the cis chloride 1 still possesses a large part of the non-bonding interactions which are responsible for the higher ground state free energy of this stereoisomer.



The most striking feature of a model of the 9-decalyl cation is the considerable energy barrier opposing interconversion of the conformers 5 and 6.*

* This resembles the familiar energy barrier to the chair-boat-chair interconversion of cyclohexane.

Subsequent reaction of these conformers leading to elimination and substitution products could therefore be faster than their interconversion to an equilibrium mixture in which the more stable "trans" conformer 6 would predominate. On this basis formation of products will be markedly influenced by the conformation of the cation in the ion pairs 5 and 6 and, to a lesser degree, by the departing chloride ion.

Products derived from the solvolytic cyclisation of 4-(cyclohexenyl)-butyl tosylate 3 resemble those obtained from the cis chloride 1 (Table 1). This suggests that the intermediate 9-decalyl cation adopts a cis-like conformation similar to 5. The rate ratios of the unsaturated tosylate 3 and its saturated analogue which are 2.16 in 80% ethanol, 5.2 in 50% acetone and 40.3 in acetic acid, clearly demonstrate the participation of the olefinic double bond in the ionisation process. Production of both cis and trans 9-decalol is in line with a mechanism involving a classical carbonium ion rather than a bridged one.

Conformers of tertiary carbonium ions should therefore be considered as true intermediates in the solvolysis of certain angular halides such as the 9-chloro-decalins and similar systems currently under investigation.*

* Two different 9-decalyl radicals were recently postulated to account for the decomposition products of cis- and trans-9-decalylcarbonyl hypchlorite ¹⁾ and of cis- and trans-tert.butyl 9-decalinpercarboxylate ²⁾.

REFERENCES

- 1) F.C. Greene and N.N. Lowry, J.Org.Chem. 32, 875 (1967); Dissertation Manfred Geisel, Basel (1968).
- 2) P.D. Bartlett, R.E. Pincock, J.H. Rolston, W.G. Schindel and L.A. Singer, J.Amer.chem.Soc., 87, 2590 (1965).