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283. Nucleophilic Reactions at Tertiary Carbon. Part 3. σ- and π-Routes to the 9-Decalyl Cation

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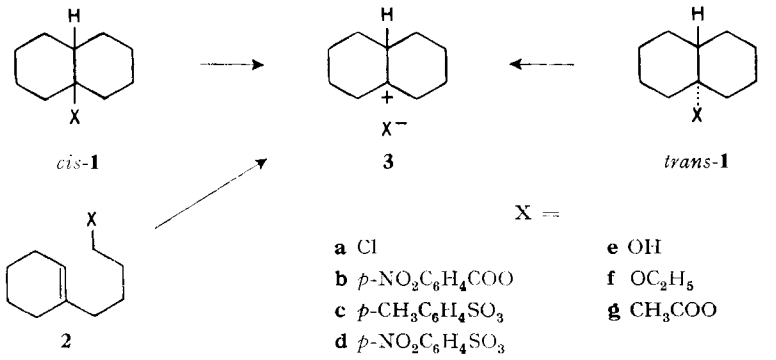
(28. IX. 73)

Summary. The generation of the 9-decalyl cation by solvolysis of *cis*- and *trans*-9-decalyl chloride (**1**) has been reinvestigated. The results of product, rate and isomerization studies implicate stereoisomeric ion pairs as intermediates, as in the case of the solvolysis of other stereoisomeric tertiary chlorides (Parts 1 and 2).

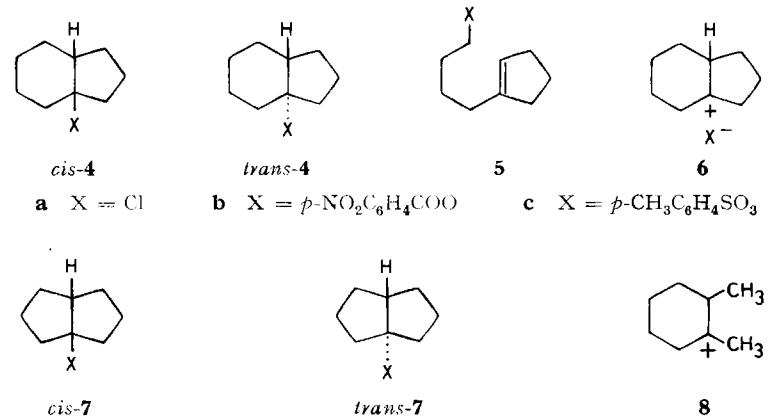
On the other hand, both symmetrically and unsymmetrically solvated 9-decalyl cations are indicated in the cyclization of 4-(cyclohexen-1-yl)butyl tosylate. No evidence was obtained that conformational isomers of the 9-decalyl cation play a role as product determining intermediates.

In an earlier communication [1] we described the generation of the 9-decalyl cation **3** by solvolysis of *cis*- and *trans*-9-decalyl chloride, *cis*- and *trans*-**1a** respectively, and by cyclization of 4-(cyclohexen-1-yl)butyl tosylate **2c** in 80% ethanol. Since different mixtures of products, namely olefins, alcohols and ethers, were obtained by these so-called σ- and π-routes [2] it was concluded that the intermediates were not identical.

Ion pairs which differ with respect to the location of the counter ion, *i.e.* the chloride ion in **3a**, were first considered. However, an explanation based solely on an encumbered carbenium ion was rejected in view of the relatively large difference of 1.4 kcal/mole between the free energies of the transition states for *cis*- and *trans*-**1a**.



This value was calculated from the reported equilibrium constant for the isomerization of the chlorides **1a** [3] and their rate constants. It was therefore suggested that this energy difference, which to a first approximation also reflects the relative stability of the intermediates, might be due to different conformations of the 9-decalyl cation **3** and that these conformers could therefore be considered as true intermediates in the solvolysis of certain tertiary halides [1].



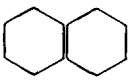
This view has been strongly advocated by *Fort et al.* [4] who solvolyzed the corresponding *p*-nitrobenzoates *cis*- and *trans*-**1b** in 60% acetone. These authors also studied the rate and products of *cis*- and *trans*-8-hydrindanyl *p*-nitrobenzoate (**4b**) and the corresponding derivatives of bicyclo[3.3.0]octane, *i.e. cis*- and *trans*-**7b**, and concluded that all three pairs of stereoisomers react by way of conformationally isomeric carbenium ions.

A different view was taken by us in an earlier communication [5] and in Part 2 [6] which describe the solvolysis of *cis*- and *trans*-8-hydrindanyl chloride **4a** and the cyclization of 4-(cyclopenten-1-yl)butyl tosylate **5c**. It was concluded that stereoisomeric ion pairs **6** are involved as intermediates in the solvolysis of *cis*- and *trans*-**4a** and an unsymmetrically solvated 8-hydrindanyl cation in the cyclization of **5c** [6].

Recently the generation of the 9-decalyl cation **3** by σ- and π-routes was also described by *Gream* [7]. This author acetolyzed the decalyl chlorides *cis*- and *trans*-**1a** as well as 4-(cyclohexen-1-yl)butyl *p*-nitrobenzenesulfonate **2d** and the corresponding chloride **2a**. On the basis of product analyses *Gream* suggested that ion pairs **3** involving *cis*- and *trans*-like conformers of the decalyl cation are involved and that the counter ion plays an important role in product formation. This viewpoint contrasts with that of *Fort* [4] but is in general agreement with our previous tentative interpretation [1][1]).

The question which remains to be decided is whether the cationic intermediates generated by different routes differ due to environmental factors, such as ion pairing or solvation, or due to conformational isomerism, or to both. Conclusive evidence cannot be derived from rate and product data alone. The relative energies of the ground and transition states should also be taken into account. Furthermore, the model compounds should show varying flexibility if the role of conformational isomerism is to be determined. The present article therefore follows our reports on the 1,2-dimethylcyclohexyl cation (**8**) [9] and the 8-hydrindanyl cation (**6**) [6].

Repetition of our work on *cis*- and *trans*-9-decalyl chloride (**1a**), utilizing an improved analytical technique, has provided more accurate data concerning the composition of the solvolysis products. Furthermore, a detailed study of the isomerization of the decalyl chlorides has failed to confirm the literature value for the equilibrium constant. Consequently, a reappraisal of the data became necessary.



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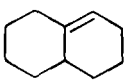

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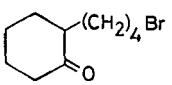

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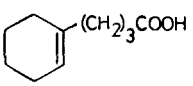

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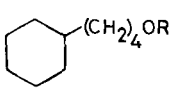

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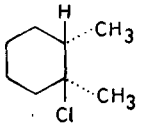
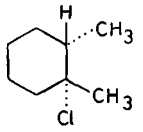
a R = H
b R = *p*-$CH_3C_6H_4SO_2$



cis-**14**



trans-**14**

Results. – *Syntheses. cis*- and *trans*-9-Decalyl chloride (**1a**) were prepared by addition of hydrogen chloride to $\Delta^{9,10}$-octalin (**9**). A modification [10] of the original procedure [3] yielded enriched mixtures of the stereoisomers which were obtained in pure form by preparative gas liquid chromatography. Configurations were assigned on the basis of spectral data and by conversion to the olefins **9** and **10** (see Experimental Part).

Pure samples of the olefins **9** and **10**, *cis*- and *trans*-9-decalol (**1e**) and the corresponding ethyl ethers **1f** were required to identify the solvolysis products of the chlorides *cis*- and *trans*-**1a**. $\Delta^{9,10}$-octalin (**9**) and the alcohols **1e** were prepared by known procedures. Reaction of the lithium derivates of the latter with ethyl iodide

[1]) Recently *Olah et al.* [8] have generated the 9-decalyl cation from various precursors in FSO_3H-SbF_5-SO_2ClF. The NMR. spectrum indicated the presence of only one cationic species.

yielded the corresponding ethyl ethers, *cis*- and *trans*-**1f**, respectively. $\Delta^{1,9}$-octalin **10** free of isomers was prepared by an intramolecular *Wittig-Schöllkopf* reaction from 2-(4-bromobutyl)-cyclohexanone (**11**). Reduction of the known 4-(cyclohexenyl)-butanoic acid (**12**) yielded the alcohol **2e** which was also hydrogenated to 4-cyclohexylbutanol (**13a**). Reaction of the alcohols **2e** and **13a** with *p*-toluenesulfonyl chloride afforded the tosylates **2c** and **13b**.

Solvolyses. – The solvolysis products of the chlorides *cis*- and *trans*-**1a** in 80% ethanol with and without 1.5 equiv. of silver nitrate, and in 50% acetone are listed in Table 1. Product composition was not affected by the presence of 1.2 equiv. of triethylamine. Table 1 also shows the cyclization products of 4-(cyclohexen-1-yl)-butyl tosylate **2c** in 80% ethanol, 50% acetone and in glacial acetic acid which were obtained in yields of 59%, 76% and 94%, respectively. Table 2 shows the ratios of elimination to substitution products E/S and of inversion to retention I/R for *cis*-**1a**, *trans*-**1a** as well as the *cis-trans* ratio of products from the tosylate **2c**.

Table 1. *Yields (in %) of solvolysis products from the chlorides* cis- *and* trans-**1a** *and the tosylate* **2c**

	Olefins		Decalols **1e**		Ethers **1f**	
	9	**10**	*cis*	*trans*	*cis*	*trans*
80% ethanol, 70° [a]						
cis-**1a**	43	44	4	5	2	2
trans-**1a**	68.5	28	1	1	1	0.5
tosylate **2c** [b]	32	42	8.5	5.5	10.5	1.5
80% ethanol + $AgNO_3$, 70°						
cis-**1a**	36	35	5.5	14	2.5	6.5
trans-**1a**	87.5	10	1	0.5	1	0
50% acetone, 40° [a]						
cis-**1a**	39	38	11.5	11.5		
trans-**1a**	71	25	2	2		
tosylate **2c** (90°) [c]	33	21	30	16		
abs. acetic acid, 110° [d]						
tosylate **2c** [e] [f]	33	64				

[a] In the presence of 1.2 equiv. triethylamine.
[b] 59% cyclization products beside 13% alcohol **2e**, 24% ether **2f** and 4% unidentified product.
[c] 76% cyclization products beside 21% alcohol **2e** and 3% unidentified product.
[d] In the presence of 2.0 equiv. sodium acetate.
[e] 94% cyclization products beside 3% acetate **2g** and 3% unidentified product.
[f] 0.5% of *cis*-acetate **1g** and 2.5% of *trans*-acetate **1g** were obtained. However, these eliminate to the olefins **9** and **10** under these conditions.

First order rate constants for *cis*- and *trans*-**1a** were determined conductometrically in 80% ethanol and in 50% acetone in the presence of ca. 1.2 equiv. of triethylamine (Table 3). The rates were not affected by a change in the concentration of the base. The rate ratio of *cis*-**1a** and *trans*-**1a** is 1.15 in 80% ethanol and 1.39 in 50% acetone. In Table 4 the rates of the chlorides **1a** are compared with those of *t*-butyl chloride and of *cis*- and *trans*-1,2-dimethylcyclohexyl chloride (**14**).

Table 2. *Ratios of elimination to substitution products E/S and inversion to retention I/R for the chlorides* cis- *and* trans-**1a** *and the tosylate* **2c**

	E/S	I/R	*cis/trans*
80% ethanol			
cis-**1a**	6.7	1.2	
trans-**1a**	27.6	1.3	
tosylate **2c**	2.9	–	2.7
80% ethanol, $AgNO_3$			
cis-**1a**	2.5	2.6	
trans-**1a**	39	4	
50% acetone			
cis-**1a**	3.3	1	
trans-**1a**	24	1	
tosylate **2c**	1.2	–	1.9

Table 3. *First order rate constants for the chlorides* cis- *and* trans-**1a**, $c = 10^{-3}$ M[a])

	Temp (°C)	k (s^{-1})	$E^{\neq}$ (kcal)	$S^{\neq}$ (cal/degree)
cis-**1a**: 80% ethanol				
	62.00	3.23×10^{-4}		
	70.00	7.40×10^{-4}		
	78.00	1.64×10^{-3}		
	46.00	5.39×10^{-5} b)	23.8	−5.7
50% acetone	35.02	2.34×10^{-4}		
	45.30	7.27×10^{-4}		
	55.13	2.05×10^{-3}		
	46.00	7.89×10^{-4} b)	21.7	−6.9
trans-**1a**: 80% ethanol				
	61.86	2.53×10^{-4}		
	70.10	5.81×10^{-4}		
	78.07	1.21×10^{-3}		
	46.00	4.71×10^{-5} b)	22.6	−9.7
50% acetone	35.02	1.83×10^{-4}		
	45.30	5.21×10^{-4}		
	55.13	1.38×10^{-3}		
	46.00	5.67×10^{-4} b)	20.2	−12.2

a) Containing 1.2 equiv. of triethylamine.
b) Extrapolated.

Table 4. *Relative first order rate constants in 80% ethanol at 46°*

t-butyl chloride	*cis*-**14**	*trans*-**14**	*cis*-**1a**	*trans*-**1a**
1.00 [11]	0.52	0.55	0.46	0.40

First order rate constants for 4-(cyclohexen-1-yl)butyl tosylate **2c** and the saturated analogue **13b** were measured conductometrically in 80% ethanol and 50% acetone, and titrimetrically in glacial acid (Table 5). The rate enhancements with respect to the saturated tosylate are 2.16 in 80% ethanol, 5.35 in 50% acetone and 40.3 in glacial acetic acid.

Greene & Lowry [3] isomerized the chlorides **1a** in concentrated aqueous hydrochloric acid with zinc chloride and reported an equilibrium mixture of 11% *cis*- and 89% *trans*-**1a** after 6 days at 46°. Careful repetition of this experiment consistently led to a *cis*/*trans* ratio of 28:72 (Table 6), however equilibrium ratios were quite dependent on the solvent system. Table 6 also lists the derived differences of ground state free energy ΔG. The following discussion is based on an average ΔG value of 0.9 kcal/mol.

Table 5. *First order rate constants for the tosylates* **2c** *and* **13b**

	Temp. (°C)	k (s^{-1})	$E^{\neq}$ (kcal)	$S^{\neq}$ (cal/degree)
50% acetone[a])				
2c	71.9	2.07×10^{-4}		
	80.0	4.60×10^{-4}		
	87.9	8.37×10^{-4}		
	110.0	4.79×10^{-3} [b])	19.8	−19.6
13b	71.9	4.00×10^{-5}		
	80.0	8.43×10^{-5}		
	87.9	1.60×10^{-4}		
	110.0	8.96×10^{-4} [b])	20.8	−15.4
80% ethanol[a])				
2c	75.0	1.32×10^{-5}		
13b	75.0	6.12×10^{-4}		
abs. acetic acid[c])				
2c	110.0	7.03×10^{-4}		
13b	110.0	1.74×10^{-5}		

[a]) Containing 1.5 equiv. of triethylamine.
[b]) Extrapolated.
[c]) Containing 2.0 equiv. of sodium acetate.

Table 6. *Ratio of* cis- *and* trans-**1a** *at equilibrium* (46 °C)

	cis-**1a**/*trans*-**1a**	ΔG (kcal)
20% $ZnCl_2$ in 36% aqueous HCl	28:72	0.60
HCl-saturated CCl_4-$ZnCl_2$	25:75	0.70
HCl-saturated 80% ethanol	18:82	0.96
HCl-saturated 95% ethanol	13:87	1.21

Discussion. – Solvolysis of the *cis*- and *trans*-9-decalyl chlorides (**1a**) and cyclization of 4-(cyclohexen-1-yl)butyl tosylate (**2c**) in 80% ethanol and 50% acetone lead to the same products, namely olefins, alcohols and ethers, but in varying amounts (Table 1). This is also documented by the ratio of elimination to substitution products E/S which is much larger for *trans*- than for *cis*-**1a** (Table 2). Furthermore, almost equal amounts of $\Delta^{9,10}$ and $\Delta^{1,9}$-octalin are formed from *cis*-**1a**, whereas far more elimination to $\Delta^{9,10}$-octalin occurs from *trans*-**1a**.

It is especially noteworthy that in 80% ethanol both chlorides **1a** yield substitution products with slight predominance of inversion over retention, as shown by the I/R ratios in Table 2. In 50% acetone this ratio is one[2][3]. Furthermore, silver ion tends to accentuate the difference between the relative amounts of products and the I/R ratios (Tables 1 and 2)[4]. Finally, larger amounts of *cis*-decalols **1e** and the corresponding *cis*-ethers **1f** are formed by cyclization of **2c** than by solvolysis of the chlorides **1a**.

Preparative solvolyses therefore clearly show that the three compounds *cis*-**1a**, *trans*-**1a** and the tosylate **2c** react by way of different intermediates.

The rate constants for the chlorides **1a** are normal as shown by their close agreement with those of *t*-butyl chloride and 1,2-dimethylcyclohexyl chloride (Table 4). Furthermore, *cis*-**1a** reacts slightly faster than *trans*-**1a** and this is due a less negative activation entropy (Table 3)[5].

The reaction rates for 4-(cyclohexen-1-yl)butyl tosylate (**2c**) in 80% ethanol, 50% acetone and glacial acetic acid are accelerated by factors of 2.16, 5.35 and 40.3, respectively, when compared to the saturated analogue **13b** (Table 5). This shows that participation of the olefinic double bond in the ionization step increases as the nucleophilicity of the solvent decreases. This is also borne out by the yields of cyclization products which increase in the same order (*cf.* footnotes in Table 1).

Equilibration of the chlorides **1a** shows that the *trans* isomer is more stable than the *cis* isomer by 0.60 to 1.21 kcal/mol depending on the solvent system. On the basis of an average value of 0.9 kcal for this difference of ground state free energies and the almost identical activation free energies the transition state for *trans*-**1a** is also approximately 0.9 kcal more stable. This is illustrated in Fig. 1. Making the usual assumption, *i.e.* that intermediates in SN1-E1 reactions resemble the transition states for their formation [12], it follows that the intermediate from the *trans*-chloride is approximately 0.9 kcal more stable than that from the *cis*-chloride.

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[2] Our results are quite different from those reported by *Fort et al.* [4] for the 9-decalyl *p*-nitrobenzoates (**1b**) in 60% acetone. It is especially striking that these authors obtained only *trans*-decalol from *trans*-**1b**, *i.e.* substitution with complete retention of configuration. This fact coupled with our observations on the 8-hydrindanyl *p*-nitrobenzoates (**4b**) [6] strongly indicate that ester hydrolysis competes with the S_N1-E1 reaction.

[3] *Gream*'s results for acetolysis of *cis*- and *trans*-**1a** [7] also differ substancially from ours, particularly with respect to the ratio of $\Delta^{9,10}$ to $\Delta^{1,9}$-octalin, which according to this author, varies with time because of isomerization in this solvent. In addition *Gream* observed predominant retention of configuration in the acetates from the *trans*-chloride **1a**. This observation is hard to reconcile with an ion pair intermediate.

[4] The reasons for this are discussed in Part 1 [9].

[5] According to *Fort* [4] the rate difference between *cis*- and *trans*-*p*-nitrobenzoates **1b** is entirely due to the activation enthalpy term which contrasts with our results for the chlorides.

Conclusions regarding the nature of these intermediates cannot be drawn without considering the results of our studies of the pairs of stereoisomeric chlorides described in the preceding papers [6] [9], *i.e.* the *cis*- and *trans*-8-hydrindanyl chlorides (**4a**) and the *cis*- and *trans*-1,2-dimethylcyclohexyl chlorides (**14**). A comparison of these results reveals striking similarities:

a) Different amounts of the same products are formed from each stereoisomer, elimination products outweighing substitution products in 80% ethanol.

b) Substitution products (alcohols and ethers) have predominantly inverted configuration.

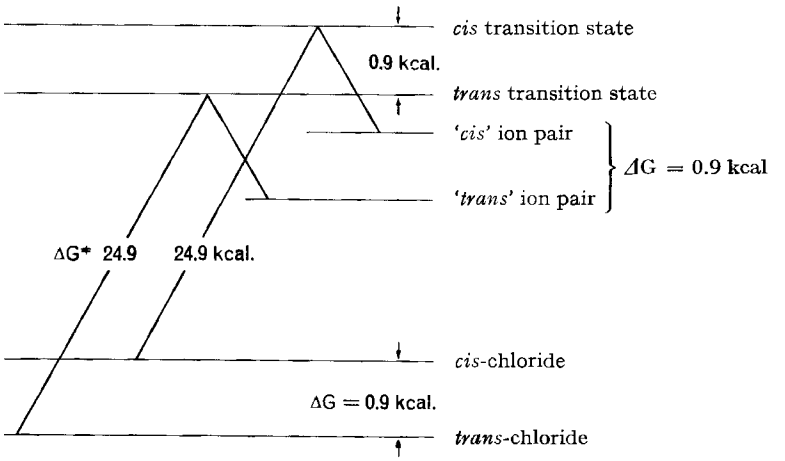
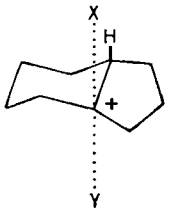


Fig. 1. *Free energy diagram for* cis- *and* trans-*9-decalyl chloride*

c) The transition states for the *trans*-chlorides are more stable than those for the *cis*-chlorides and, by inference, also the cationic intermediates regardless of the relative ground state energies.

d) The entropies of activation are consistently more negative for the *trans*-chlorides than for the *cis*-chlorides.



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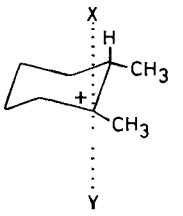


16

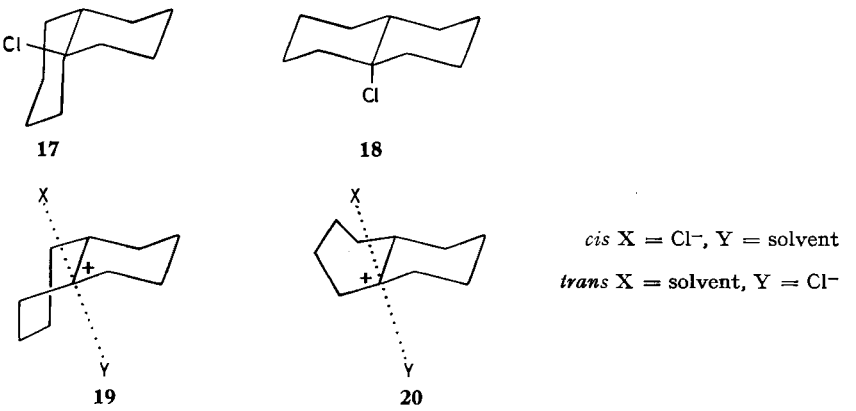
cis X = Cl^-, Y = solvent

trans X = solvent, Y = Cl^-

The results of our studies of the 8-hydrindanyl chlorides (**4a**) and the 1,2-dimethylcyclohexyl chlorides (**14**) were satisfactorily rationalized on the basis of intermediate stereoisomeric ion pairs, *cis*- and *trans*-**15** and *cis*- and *trans*-**16**, respectively, which differ with respect to the location of the counter ion. These ion pairs are

attacked by solvent somewhat faster than they are converted to symmetrically solvated cations **15** and **16**, where X and Y are solvent molecules. Substitution products, *i.e.* alcohols and ethers, therefore have predominantly inverted configuration. Furthermore, solvation is less hindered and therefore tighter in the *trans* ion pairs **15** and **16** which accounts for the fact that the activation entropies are more negative in the case of the *trans*-chlorides **4a** and **14** and that the inversion to retention ratios of their products are higher.

It was not necessary to consider conformational isomers of the 8-hydrindanyl and 1,2-dimethylcyclohexyl cations since conformations other than **15** and **16** are too



17 **18** **19** **20**

unstable to qualify as true intermediates, especially in the former case. On the other hand the most stable conformers **17** and **18** of *cis*- and *trans*-9-decalyl chloride ionize directly to the *cis* and *trans* ion pairs **19** and **20**, respectively. If reaction with solvent were faster than conformational equilibration then product formation would be influenced by the conformation of the cation and by the counter ion.

This suggestion was made previously [1] in order to explain the relatively high energy difference of *ca.* 1.4 kcal between the intermediates of *cis*- and *trans*-**1a**, which was calculated from an erroneous equilibrium constant for these chlorides. This energy difference is now shown to be 0.60 to 1.21 kcal and is close to the values obtained for the intermediates from the 8-hydrindanyl chlorides (**4a**) and the 1,2-dimethylcyclohexylchlorides (**14**), *i.e.* 0.4 and 0.7 kcal, respectively [6] [9]. It is therefore no longer necessary to invoke conformational isomers of the decalyl cation. Stereoisomeric ion pairs in conformational equilibrium also qualify as intermediates.

The two probable conformations for the cations in **19** and **20** have twist or half chair rings connected to a chair form[6]). However, the *'transoid'* conformation **20** should be more stable than the *'cisoid'* conformation **19** for the same reasons that the *trans*-chloride **18** is more stable than the *cis* isomer **17**. The incipient *cis* ion pair **19** from the *cis*-chloride **17** should therefore change into its conformer *cis*-**20**, whereas the *trans* ion pair **20** is formed directly from the *trans*-chloride **18**.

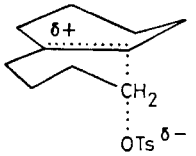
Cis and *trans* ion pairs **20** containing a common cation would explain the almost identical inversion to retention ratios observed in the substitution products of the

[6]) As deduced from models with planar cationic centers.

two chlorides (Table 2). If the *'cisoid'* ion pair **19** were the product determining intermediate a lower ratio would be expected for the *cis*-chloride **17** because the cation in **19** is much less accessible to solvent from the concave side.

However, it is reasonable to assume that the transition state for the ionization of the *cis*-chloride **17** resembles the *'cisoid'* ion pair **19**, because the Δ ($\Delta G - \Delta G^{+}$) value of *ca.* 0.9 kcal (Fig. 1) is slightly larger than for the other systems, *i.e.* **4a** and **14**. This assumption is supported by the activation entropy for **17** which is less negative than for the *trans*-chloride **18**. This indicates that solvation is less tight in the transition state due to steric hindrance on the concave side of the *cis*-decalyl system.

Noteworthy features in the cyclization of 4-(cyclohexen-1-yl)butyl tosylate (**2a**) are the much lower elimination to substitution ratios than those observed for chloride solvolysis and the preponderance of *cis* over *trans* alcohols and ethers (Table 2). The same trend was observed in the formation of hydrindanyl derivatives by the σ and π-routes [6].



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Cyclization of the tosylate **2c** cannot lead to a contact ion pair because the tosylate ion is liberated at a point remote from the incipient cationic center as shown in **21**[7]). On the other hand, a symmetrically solvated cation alone, such as **20** (X = Y = solvent) does not account for the preponderance of *cis* products since it should yield *trans* products with equal ease. However, solvation of the cationic center will tend to develop on the opposite side of the newly formed carbon to carbon bond and thereby favor the production of *cis*-decalyl derivatives. Both symmetrically and unsymmetrically solvated cations are therefore indicated as product determining intermediates for the π-route to the decalyl cation.

To summarize the results of our study of the 1,2-dimethylcyclohexyl, the hydrindanyl and the decalyl systems, the cationic intermediates generated by different routes are satisfactorily described as stereoisomeric ion pairs and unsymmetrically solvated cations. Furthermore, no evidence for conformationally isomeric cations, as suggested earlier [1] and as claimed by *Fort* [4], was found, nor for ion pairs involving *cis*- and *trans*-like conformers of the decalyl cation, as suggested by *Gream* [7].

It should be added that *Fort* drew his conclusions from a comparison of observed and predicted rates, the latter being based on estimated ground state energies of stereoisomeric pairs of compounds. These estimates include several arbitrary assumptions concerning the contributions of the leaving group to the total energy of the compound and a complete neglect of entropy terms. It is, therefore, not surprising that *Fort*'s calculated differences of ground state energies for the decalyl and hydrindanyl systems differ considerably from the observed free energy differences reported in this and the previous paper [6].

[7]) *Closson & Gray* [13] have given good reasons to assume that solvolytic cyclization of 5-hexenyl derivatives occurs in a chair-like conformation of the incipient cyclohexane ring.

Fort bases his claim that ion pairs play a minor role as intermediates from decalyl and hydrindanyl *p*-nitrobenzoates on the observation that no isomerization of starting material takes place during the reaction. This is also the case with the corresponding chlorides, which are only isomerized in the presence of catalysts, as shown above. However, failure to detect ion pair return in nucleophilic solvents, such as aqueous ethanol and acetone, does not exclude their intermediacy, especially if reaction of the cations with solvent is a diffusion-controlled process, as assumed by *Fort* [4]. There is therefore no reason to disregard the fundamental role of ion pairs and selective solvation in controlling reactions at tertiary carbon.

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Experimental Part

Melting points (m.p.) were determined on a *Kofler* Block and are corrected; boiling points (b.p.) are not corrected. Apparatus for IR. and NMR. spectroscopy and for gas liquid chromatography (GLC.) were the same as described in Part 1 [9]. Result for IR. are given in cm^{-1}, for NMR. in ppm.

Syntheses. – cis-*9-Chlorodecalin* (*cis*-1-chlorobicyclo[4.4.0]-decane) (**1a**). 0.30 g $\Delta^{9,10}$-octalin (**9**) [14] were added dropwise to *ca.* 5 ml dry condensed HCl at – 98°[8]) with stirring. The mixture was kept at – 98° for 20 min, then quenched with 20 g ice and 20 ml pentane. The pentane solution was washed with cold saturated aqueous $NaHCO_3$ and ice/water, dried over $CaCl_2$ and evaporated. GLC. (4% SE 30, 100°) showed quantitative transformation into a mixture of 64% *cis*- and 36% *trans*-chloride **1a**. Preparative GLC. (20% Carbowax 20M, 100°) gave pure *cis*-chloride. – IR. (CS_2): 638, 752 (C-Cl, expected for *cis*-**1a** 650–700 [16]). – NMR. (CCl_4): 1.1–2.2 (*m*).

trans-*9-Chlorodecalin* (trans-1-chlorobicyclo[4.4.0]decane) (**1a**). Addition of HCl to $\Delta^{9,10}$-octalin (**9**) in ether at 0° gave a mixture of 98% *trans*-chloride and 2% *cis*-chloride, b.p. 42–45°/0.4 Torr. Pure *trans*-**1a** was isolated by preparative GLC. – IR. (CS_2): 540, 740 (C-Cl, expected for *trans* **1a** 540–580 [16]). – NMR. (CCl_4): 1.1–2.0 (*m*).

All *trans*-9-decalyl compounds have shorter retention times on GLC. than the corresponding *cis*-9-decalyl compounds. The following results of bimolecular elimination of HCl with ethanolic potassium hydroxide support these assignments [17].

Elimination of HCl from cis- *and* trans-*9-chlorodecalin* (**1a**) was carried out as described in Part 1 [9]. The *cis*-chloride gave 90% $\Delta^{1,9}$-octalin (**10**) and 10% $\Delta^{9,10}$-octalin (**9**). The *trans*-chloride gave 80% $\Delta^{9,10}$-octalin (**9**) and 20% $\Delta^{1,9}$-octalin (**10**).

$\Delta^{1,9}$-*Octalin* (bicyclo[4.4.0]decene-1(2)) (**10**). 2.04 g (8.75 mmol) 2-(4-bromobutyl)cyclohexanone (**11**) [18] and 2.30 g (8.75 mmol) triphenylphosphine were heated in 20 ml dry ether 20 h at 100°. The glass-like phosphonium bromide (2.70 g, 62%) was washed with dry ether, dissolved in 10 ml dimethylsulfoxide and added to a solution of dimethylsulfoxide anion in 10 ml dimethylsulfoxide as described for $\Delta^{1,8}$-hydrindene in Part 2 [6]. Distillation gave 192 mg (26%) $\Delta^{1,9}$-octalin (**10**), b.p. 80°/17 Torr, free of isomers. – IR. (CCl_4): 3040 (=C–H), 1448, 1310, 925, 674. – NMR. (CCl_4): 5.30 (1H, *m*) =CH; 1.3–2.4 (15H, *m*) CH, CH_2.

$C_{10}H_{16}$ (136.24) Calc. C 88.16 H 11.84% Found C 88.38 H 12.02%

cis- *and* trans-*9-Decalol* (**1e**) were prepared by known methods [19].

cis-*9-Ethoxydecalin* (*cis*-1-ethoxybicyclo[4.4.0]decane) (**1f**) was prepared from *cis*-9-decalol (**1e**), butyllithium and ethyl iodide in hexamethylphosphortriamide as described for *cis*-1-ethoxy-1,2-dimethylcyclohexane in Part 1 [9]. Yield 14%, b.p. 140–142°. – IR. (CCl_4): 1450 (C–C), 1079 (C–O). – NMR. (CCl_4): 3.30 (2H, *q*) OCH_2; 1.10 (3H, *t*) CH_3; 1.7–1.1 (17H, *m*) CH, CH_2.

[8]) The cooling bath consisted of methanol and liquid nitrogen [15].

trans-*9-Ethoxydecalin* (*trans*-1-ethoxybicyclo[4.4.0]decane) (**1f**) was prepared similarly from *trans*-9-decalol (**1e**). Yield 13%, b.p. 133–135°. – IR. (CCl_4): 1455 (C—C), 1076 (C—O). – NMR. (CCl_4): 3.40 (2H, *q*) OCH_2; 1.20 (3H, *t*) CH_3; 2.0 (1H, *m*) CH; 1.9–1.0 (16H, *m*) CH_2.

$C_{12}H_{22}O$ (182.31) Calc. C 79.06 H 12.16% Found C 78.96 H 12.34%

cis-*9-Decalyl acetate* (*cis*-1-bicyclo[4.4.0]decyl acetate) (**1g**). 1.19 g (7.73 mmol) *cis*-9-decalol (**1e**) were dissolved in 12 ml hexane, treated with 4.0 ml solution of butyllithium in hexane (8.5 mmol) and refluxed for 5 h. 0.95 g (9.3 mmol) acetic anhydride were added dropwise at 0°, and the mixture stirred overnight. The resulting suspension was diluted with ether, washed with water, dried over $MgSO_4$ and evaporated. Chromatography over a column with silica gel (eluent 5% ether in petrol ether) followed by distillation gave 752 mg (50%) *cis*-9-decalyl acetate, b.p. 80–82°/0.02 Torr. – IR. (film): 1725 (C=O), 1367, 1240, 1140 (C—O). – NMR. (CCl_4): 1.1–1.7 (11H, *m*) CH_2; 1.93 (3H, *s*) CH_3; 1.7–2.2 (6H, *m*) CH, CH_2.

$C_{12}H_{20}O_2$ (196.29) Calc. C 73.43 H 10.27% Found C 73.39 H 10.08%

trans-*9-Decalyl acetate* (*trans*-1-bicyclo[4.4.0]decyl acetate) (**1g**) was made similarly from *trans*-9-decalol, yield 42%, b.p. 50–52°/0.01 Torr. – IR. (film): 1728 (C=O), 1367, 1230, 1152 (C—O). – NMR. (CCl_4): 0.8–2.1 (16H, *m*) CH_2; 1.97 (3H, *s*) CH_3; 2.4–2.9 (1H, *m*) CH.

$C_{12}H_{20}O_2$ (196.29) Calc. C 73.43 H 10.27% Found C 73.58 H 10.36%

4-(Cyclohexen-1-yl)butanol (**2e**). 23 g (0.137 mol) 4-(cyclohexen-1-yl)butanoic acid (**12**) [20] in 100 ml ether were added over 45 min to 7.3 g (0.54 mol) $LiAlH_4$ in 300 ml ether. The mixture was refluxed for 3 h, then hydrolysed carefully with 600 ml 15% sulfuric acid. The aqueous layer was extracted with ether. The etheral solutions were washed with 2N aqueous NaOH and water, dried over Na_2SO_4 and evaporated. Distillation gave 18.1 g (86%) 4-(cyclohexen-1-yl)butanol, b.p. 70–72°/0.09 Torr. – IR. (CCl_4): 3640, 3340 (OH), 1670 (C=C). – NMR. (CCl_4): 1.3–2.2 (14H, *m*) CH_2; 3.09 (1H, broad *s*) OH; 3.54 (2H, *t*) OCH_2; 5.36 (1H, broad *s*) =CH.

$C_{10}H_{18}O$ (154.25) Calc. C 77.86 H 11.76% Found C 78.20 H 11.93%

α-*Naphthylurethane*. White crystals from ligroin, m.p. 83–84.5°.

$C_{21}H_{25}NO_2$ (323.44) Calc. C 77.98 H 7.79 N 4.33% Found C 78.09 H 7.92 N 4.24%

4-Cyclohexylbutanol (**13a**). 1.54 g (10 mmol) 4-(cyclohexen-1-yl)butanol (**2e**) were hydrogenated over 150 mg 5% Pd/C in 25 ml ethanol. Distillation gave 1.30 g (87%) 4-cyclohexylbutanol, b.p. 68–69°/0.1 Torr. – IR. (CCl_4): 3640, 3400 (OH), 1040 (C—O).

$C_{10}H_{22}O$ (156.27) Calc. C 76.86 H 12.90% Found C 77.04 H 12.94%

4-(Cyclohexen-1-yl)butyl p-*toluenesulfonate* (**2c**) was prepared from 4-(cyclohexen-1-yl)butanol (**2e**) and *p*-toluenesulfonyl chloride in pyridine as described for the *p*-toluenesulfonates in Part 2 [6]. Colourless crystals, from pentane at –35°, m.p. 5°. – IR. (CS_2): 3040 (ArH), 1370, 1180 (OSO_2). – NMR. (CCl_4): 1.1–2.2 (14H, *m*) CH_2; 2.44 (3H, *s*) CH_3; 3.92 (2H, *t*) OCH_2; 5.23 (1H, broad *s*) =CH; 7.22 and 7.65 (2H each, *d*) ArH.

$C_{17}H_{24}O_3S$ (308.44) Calc. C 66.21 H 7.85 S 10.39% Found C 66.22 H 7.82 S 10.20%

4-Cyclohexylbutyl p-*toluenesulfonate* (**13b**) was obtained from 4-cyclohexylbutanol (**13a**). Colourless needles, m.p. 41.5–42.5° from petrol ether. – IR. (CS_2): 3040 (ArH), 1370, 1178 (OSO_2).

$C_{17}H_{26}O_3S$ (310.46) Calc. C 65.78 H 8.44 S 10.33% Found C 65.56 H 8.30 S 10.16%

4-(Cyclohexen-1-yl)butyl chloride (**2a**). 2.0 g (13 mmol) 4-(cyclohexen-1-yl)butanol (**2e**) in 20 ml chloroform were added over 20 min to 2.8 g (24 mmol) thionyl chloride and 1.4 g (18 mmol) dry pyridine in 20 ml chloroform. The solution was refluxed for 3 h, then evaporated. The residue was dissolved in ether, washed with 5% aqueous K_2CO_3, dried over $MgSO_4$ and evaporated. Distillation gave 1.12 g (50%) 4-(cyclohexen-1-yl)butyl chloride, b.p. 45–46°/0.07 Torr. – IR. (CCl_4): 3050 (=CH), 1670 (C=C), 1445, 922, 655 (C—Cl). – NMR. (CCl_4): 1.3–2.2 (14H, *m*) CH_2; 3.50 (2H, *t*) CH_2Cl; 5.40 (1H, broad *s*) =CH.

$C_{10}H_{17}Cl$ (172.70) Calc. C 69.59 H 9.93 Cl 20.54% Found C 69.71 H 9.91 Cl 20.43%

4-(Cyclohexen-1-yl)butyl ethyl ether (**2f**). 290 mg (1.68 mmol) 4-(cyclohexen-1-yl)butyl chloride (**2a**) were added dropwise to a suspension of sodium ethylate (16.5 mmol, from 380 mg sodium and abs. ethanol) in 20 ml dimethylsulfoxide. The reaction mixture was stirred 16 h at room

temperature, then hydrolysed and acidified with 2N hydrochloric acid. The product was extracted with ether, the etheral solution washed with aqueous $NaHCO_3$ and water, dried, and evaporated. Chromatography over silica gel with petrol ether/ether and distillation gave 151 mg (38%) 4-(cyclohexen-1-yl)butyl ethyl ether, b.p. 100–102°/12 Torr. – IR. (CCl_4): 1125, 1108, 940. – NMR. (CCl_4): 1.12 (3H, *t*) CH_3; 1.1–2.1 (14H, *m*) CH_2; 3.30 (2H, *t*) OCH_2; 3.33 (2H, *q*) OCH_2; 5.3 (1H, broad *s*) =CH.

$C_{12}H_{22}O$ (182.31) Calc. C 79.06 H 12.16% Found C 79.23 H 12.27%

Preparative Solvolyses. – *9-Chlorodecalins* (**1a**). 0.01M solutions of 3.5 mg of the decalyl chlorides in 2 ml 80 vol. % ethanol (70°) or 50 vol. % acetone (40°) were solvolysed as described for 1-chloro-1,2-dimethylcyclohexane in Part 1 [9]. GLC. analyses (2.5% SE 52, 120° and 10% Carbowax 20M 137°) were carried out with the reaction solutions.

p-*Toluenesulfonates* **2c** *and* **13b**. 0.01M solutions of 31 mg tosylate in 10 ml 80 vol. % ethanol (3 h, 70°) or 50 vol. % acetone (3 h, 90°) containing 1.2 equiv. triethylamine were reacted and analysed as above. Acetolysis (3 h, 110°) was carried out in 0.01M solution containing 2.0 equiv. sodium acetate as in Part 2 [6]. It was shown that the *cis*- and *trans*-acetates **1g** are not stable under the reaction conditions.

cis-9-Decalyl acetate gave 40% $\Delta^{1,9}$-octalin (**10**) and 48% $\Delta^{9,10}$-octalin (**9**), only 12% acetate remained unchanged. *trans*-9-Decalyl acetate gave 27% $\Delta^{1,9}$-octalin (**10**) and 24% $\Delta^{9,10}$-octalin (**9**), 49% acetate were recovered. The octalins **9** and **10** were stable under the reaction conditions.

Equilibrations. – The reaction conditions for isomerization of the 9-chlorodecalins were described in Part 1 [9]. More unknown side products were produced than in the case of the 1-chloro-1,2-dimethylcyclohexanes. In 80% aqueous ethanol saturated with HCl 11% octalins and 2% side products were formed after 10 days. In 95% ethanol, 2% octalins and only traces of impurities were found.

The kinetic measurements were carried out as described in Part 1 [9] and 2 [6].

Elemental analyses were carried out by Mr. *E. Thommen*. The NMR. spectra were recorded by Mr. *K. Aegerter*.

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