282. Nucleophilic Reactions at Tertiary Carbon. Part 2. σ- and π-Routes to the 8-Hydrindanyl Cation

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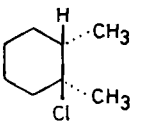
Summary. Stereoisomeric ion pairs are implicated as intermediates in the solvolysis of *cis*- and *trans*-8-hydrindanyl chloride **3**, whereas 4-(cyclopenten-1-yl)butyl tosylate **5** appears to cyclize by way of an unsymmetrically solvated 8-hydrindanyl cation. This follows from the solvolysis products and rates of these compounds in aqueous solvents.

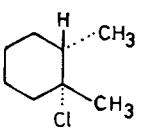
The rate and equilibrium constants of the chlorides **3** show that the transition state for the *trans*-isomer is more stable by 0.5 kcal than the one for the *cis*-isomer. By inference the intermediates differ by a similar amount of energy.

Experimental results are not explained satisfactorily by conformationally isomeric 8-hydrindanyl cations, as suggested in the literature.

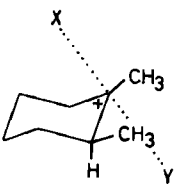
As described in Part 1 [1] the stereoisomeric ion pairs *cis*- and *trans*-**2** are implicated as intermediates in the solvolysis of *cis*- and *trans*-1-chloro-1,2-dimethylcyclohexane, *cis*-**1** and *trans*-**1**, respectively. This follows from the reaction products, the solvolysis rates and from the ground state free energies of these tertiary chlorides which show that the intermediate from *trans*-**1** is approximately 0.7 kcal more stable than the one from *cis* **1**. This energy difference was ascribed to the more efficient solvation of the *trans*-ion-pair **2**.



cis-**1**



trans-**1**



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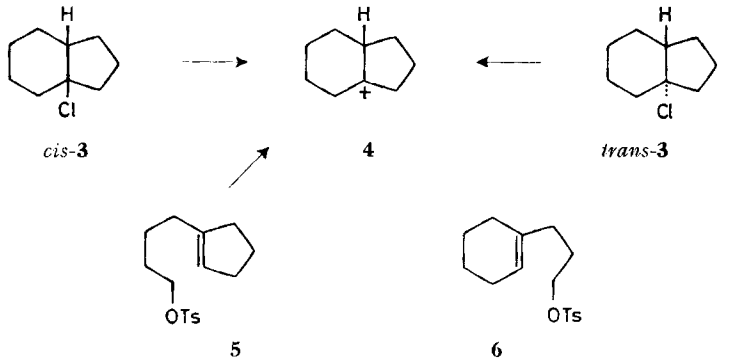
cis-**2** X = solvent, Y = Cl^-
trans-**2** Y = Cl^-, X = solvent

Support for this conclusion was sought by studying stereoisomeric tertiary chlorides with reduced conformational flexibility, as in *cis*- and *trans*-8-hydrindanyl chloride (**3**). These compounds have the additional advantage that their common cationic intermediate **4** should also be accessible by so called π-routes, *i.e.* by cyclization of 4-(cyclopenten-1-yl)butyl tosylate **5** or 3-(cyclohexen-1-yl)propyl tosylate **6**.

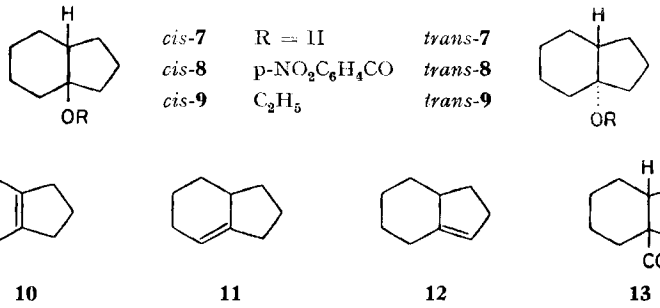
It was also anticipated that the stereoisomeric chlorides *cis*- and *trans*-**3** would be interconvertible and permit the determination of their relative ground state free energies by equilibration studies. These data coupled with the results of rate and product determinations should provide further insight into the nature of reactions at a tertiary carbon atom. As briefly reported [2] the results again implicate ion pairing and unsymmetrical solvation.



cis-**3** **4** *trans*-**3**

5 **6**

In view of the difficulties encountered in the purification of the labile tertiary chlorides *cis*- and *trans*-**3** esters of *cis*- and *trans*-8-hydrindanol (**7**) were also investigated. However, the *p*-nitrobenzoates *cis*- and *trans*-**8** proved to be unsatisfactory due to ester hydrolysis which accompanied solvolysis in aqueous media. *Fort et al.* [3] have recently described the rates and products of these *p*-nitrobenzoates in 60% aqueous acetone and have drawn conclusions from their results which are at variance with our work, as will be described below.



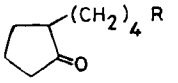
cis-**7**	R = H		*trans*-**7**
cis-**8**	p-$NO_2C_6H_4CO$		*trans*-**8**
cis-**9**	C_2H_5		*trans*-**9**

10 **11** **12** **13**

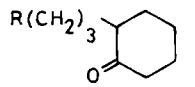
Results. – *Syntheses.* Stereoselective addition of HCl to $\Delta^{8,9}$-hydrindene (**10**) in ether at 0° afforded a mixture of 88% *trans*- and 12% *cis*-**3**. In liquid HCl at –98° or with HCl in methylene chloride at –78° a mixture of 87% *cis*- and 13% *trans*-**3** was obtained. Halodecarboxylation of *cis*-8-hydrindanecarboxylic acid (**13**) with lead tetraacetate and N-chlorosuccinimide yielded *cis*- and *trans*-**3** in the ratio 95:5 as reported elsewhere [4]. Thermal instability precluded the purification of the oily chlorides by gas liquid chromatography. Enriched mixtures of the stereoisomeric chlorides were therefore used. Configurations were assigned by spectral methods and by elimination to known hydrindenes, as described in the experimental part.

The olefins **10**, **11** and **12**, *cis*- and *trans*-8-hydrindanol (**7**) and the corresponding ethyl ethers (**9**) were required to identify the solvolysis products of the chlorides *cis*- and *trans*-**3** and the *p*-nitrobenzoates *cis*- and *trans*-**8**. These compounds were prepared as follows. Reduction of indane with lithium in ethylamine-dimethylamine gave $\Delta^{8,9}$-hydrindene (**10**) in 77% yield. Small amounts of isomeric olefins were removed by selective hydroboration and oxidation to alcohols. Pure $\Delta^{7,8}$-hydrindene

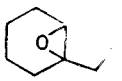
(**11**) and $\Delta^{1,8}$-hydrindene (**12**) were prepared by a *Wittig-Schöllkopf* cyclization reaction from 2-(4-bromobutyl)cyclopentanone (**14**) and 2-(3-bromopropyl)cyclohexanone (**16**), respectively, *via* the corresponding phosphonium salts **15** and **17**. The bromides



14 R = Br
15 R = $^{+}P(C_6H_5)_3$ $Br^{\ominus}$



16 R = Br
17 R = $^{+}P(C_6H_5)_3$ Br^{-}



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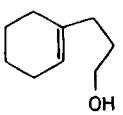
14 and **16** were known compounds [5]. Pure $\Delta^{8,9}$-hydrindene (**10**) was converted to the known epoxide **18** [6] from which *cis*- and *trans*-8-hydrindanol (**8**) were obtained by reduction with *Raney* nickel and with lithium aluminium hydride, respectively. The corresponding ethyl ethers *cis*- and *trans*-**9** were prepared from the lithium derivatives of the alcohols with ethyl iodide. The *p*-nitrobenzoates *cis*- and *trans*-**8** were obtained from the potassium salts of the alcohols *cis*- and *trans*-**7** with *p*-nitrobenzoyl chloride.

3-(Cyclohexen-1-yl)propyl tosylate (**6**) was prepared by tosylation of the known corresponding alcohol **19** [7]. The latter was also reduced and converted to 3-cyclohexylpropyl tosylate (**20**). 4-(Cyclopenten-1-yl)butyl tosylate (**5**) was synthesized from 2-(cyclopenten-1-yl)ethanol (**21**) [8]. Condensation of the tosylate **22** with sodium ethyl malonate afforded **23** which was hydrolyzed and decarboxylated to 4-(cyclopenten-1-yl)butanoic acid (**24**). The latter was reduced to the alcohol **25** and tosylated to **5**. Hydrogenation of **25** gave the saturated alcohol **26**, the tosylate **27** of which was required together with **20** for the determination of anchimeric π-participation in the ionization of **5** and **6**.



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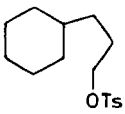

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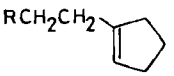
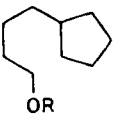


R =

21 OH
22 p-$CH_3C_6H_4SO_3$
23 $CH(COOC_2H_5)_2$
24 CH_2COOH
25 CH_2CH_2OH



26 R = H
27 R = p-$CH_3C_6H_4SO_2$

Solvolysis products. Mixtures consisting of 95% *cis*- and 5% *trans*-chloride and 89% *trans*- and 11% *cis*-chloride, respectively, were employed for the determination of solvolysis products and rates. Since these differed substancially for *cis*- and *trans*-**3**, the products and rate constants for the pure stereoisomers could be calculated from the data obtained with mixtures.

The products obtained in 80 vol.% ethanol and in 68.6 vol.% dioxane in the presence of 1.2 molar equivalents of triethylamine at 40° are listed in Table 1. In the

absence of base the product composition varied with time since even traces of acid convert trans-8-hydrindanol (**7**) and the olefins **11** and **12** into $\Delta^{8,9}$-hydrindene (**10**). Product composition in 80% ethanol was altered in the presence of silver oxide. The ratio E/S of elimination (olefins) to substitution products (alcohols, ethers) and the ratio of inversion to retention I/R of the substitution products are shown in Table 2.

4-(Cyclopenten-1-yl)butyl tosylate **5** reacted in 80% ethanol and 50% acetone in the presence of triethylamine to yield 43.5% and 67%, respectively, of hydrindane derivatives (Tables 1 and 2) beside the non-cyclized alcohol **25** and the corresponding ethyl ether. In acetic acid buffered with sodium acetate cyclization was quantitative.

Table 1. *Yields (in %) of solvolysis products from the chlorides* cis- *and* trans-**3** *and the tosylate* **5**

	olefins			alcohols **7**		ethers **9**	
	10	**11**	**12**	*cis*	*trans*	*cis*	*trans*
80% ethanol[a]							
cis-**3** (40°)	57	4	20	2	2.5	5	9.5
trans-**3** (40°)	42.5	1.5	46.5	6	0.5	2	1
5 (78°)[b]	36[c]		17	18	7	19	3
80% ethanol, Ag_2O							
cis-**3** (40°)	29	1.5	11	3	10	9	36.5
trans-**3** (40°)	76	1	11	7	1	4	0
68.6% dioxane[a]							
cis-**3** (40°)	52	3.5	21.5	8	15	–	–
trans-**3** (40°)	32	2	60.5	3	2.5		
50% acetone[a]							
5 (100°)[d]	30[c]		8.5	44.5	17	–	–

[a] Containing 1.2 molar equiv. triethylamine.
[b] Yield of cyclization products 43.5%.
[c] The olefins **10** and **11** were not separated.
[d] Yield of cyclization products 67%.

Table 2. *Ratios of elimination to substitution products E/S and inversion to retention I/R for the chlorides* cis- *and* trans-**3** *and the tosylate* **5**

	E/S	I/R	*cis/trans*
80% ethanol			
cis-**3**	4.3	1.7	
trans-**3**	9.5	5.3	
tosylate **5**	1.1	–	3.7
80% ethanol, Ag_2O			
cis-**3**	0.7	3.9	
trans-**3**	7.3	11	
68.6% dioxane			
cis-**3**	3.3	1.9	
trans-**3**	17	1.2	
50% acetone			
tosylate **5**	0.6	–	2.6

However, only olefins were obtained, namely 93% of a mixture of **10** and **11** and 7% of **12**. 3-(Cyclohexen-1-yl)propyl tosylate (**6**) did not undergo cyclization to hydrindane derivatives. In 50% acetone 93% of the corresponding alcohol (**6**, OH instead of OTs) were obtained beside two other unidentified products.

Table 3 lists the reaction products of the *p*-nitrobenzoates *cis*- and *trans*-**8** in 80% ethanol and 50% acetone in the presence of 1.5 molar equiv. of triethylamine.

Table 3. *Yields (in %) of reaction products from the* p-*nitrobenzoates* cis- *and* trans-**8**

	olefins			alcohols **7**		ethers **9**	
	10	**11**	**12**	*cis*	*trans*	*cis*	*trans*
80% ethanol[a])							
cis-**8** (110°)	54	8	32	2	2	1	1
trans-**8** (110°)	19	4	72	1.5	1.5	1.5	0.5
50% acetone[a])							
cis-**8**	46.5	6	33.5	7.5	6.5	–	–
trans-**8**	19	4	68	4	5	–	–

[a]) Containing 1.5 molar equiv. triethylamine.

Table 4. *First order rate constants for the chlorides* cis- *and* trans-**3**, $c = 10^{-3}$ M[a])

	Temp. (°C)	k (s^{-1})	$E^{\neq}$ (kcal)	$S^{\neq}$ (cal/degree)
cis-**3**				
80% ethanol	29.73	2.18×10^{-4}		
	39.88	7.39×10^{-4}		
	49.86	2.11×10^{-3}		
	46.00	1.42×10^{-3} [b])	21.9	– 4.9
68.6% dioxane	30.08	1.52×10^{-4}		
	40.02	4.70×10^{-4}		
	50.03	1.33×10^{-3}		
	46.00	8.82×10^{-4} [b])	21.2	– 8.3
trans-**3**				
80% ethanol	20.00	1.16×10^{-3}		
	29.73	3.44×10^{-3}		
	39.88	8.55×10^{-3}		
	46.00	1.55×10^{-2} [b])	18.3	– 11.4
68.6% dioxane	20.07	7.56×10^{-4}		
	30.08	2.14×10^{-3}		
	40.02	5.51×10^{-3}		
	46.00	9.56×10^{-3} [b])	18.2	– 13.0

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

Kinetics. First order rate constants for *cis*- and *trans*-**3** were determined conductometrically in the presence of *ca.* 1.2 molar equiv. of triethylamine (Table 4). These were not affected by a change in the concentration of base. In 80 vol.% ethanol and

68.6 vol.% dioxane and at 46° *trans*-**3** reacts *ca.* 11 times as fast as *cis*-**3**. Both chlorides show the enhanced S_Ni-E1 reactivity of cyclopentyl derivatives, such as 1-methylcyclopentyl chloride, as shown by the comparison with *t*-butyl chloride in Table 5.

Table 5. *Relative first order rate constants in 80 vol.% ethanol* (46°C)

t-butyl chloride	1-methylcyclopentyl chloride	*cis*-**3**	*trans*-**3**
1.0 [9]	42 [10]	12	132

First order rate constants for the reaction of the *p*-nitrobenzoates *cis*- and *trans*-**8** in 50 vol.% acetone and 80 vol.% ethanol are listed in Table 6. The *trans*-isomer

Table 6. *First order rate constants for the* p-*nitrobenzoates* cis- *and* trans **8**, $c = 10^{-3}$ M[a])

	Temp. (°C)	k (s^{-1})	E≠ (kcal)	S≠ (cal/degree)
cis-**8**				
50% acetone	80.0	8.07×10^{-5}	24.3	−10.9
	87.9	1.72×10^{-4}		
	95.0	3.20×10^{-4}		
80% ethanol	105.0	1.98×10^{-4}		
trans-**8**				
50% acetone	71.9	1.18×10^{-4}		
	80.0	2.72×10^{-4}	24.6	−7.4
	87.9	5.80×10^{-4}		
80% ethanol	105.0	6.00×10^{-4}		

[a]) Containing 1.5 equiv. of triethylamine.

reacts faster than the *cis*-isomer by a factor of 3.4 in the former solvent and 3.0 in the latter[1]).

The rates of 4-(cyclopenten-1-yl)butyl tosylate (**5**) and of 3-(cyclohexen-1-yl) propyl tosylate (**6**) are compared with those of the saturated analogues **27** and **20** in Table 7. The rate ratios are summarized in Table 8.

It is apparent from Table 8 that in the case of the cyclopentenylbutyl tosylate **5** ionization is assisted by the olefinic bond in all solvents and that π-5,6 participation increases as the nucleophilicity of the solvent decreases. Conversely, no π-4,5 participation is noticeable in the case of the cyclohexenylpropyl tosylate **6** the rate of which s depressed due to the –I effect of the olefinic bond.

Isomerization. The same conditions were used to isomerize the chlorides *cis*- and *trans*-**3** as were described in Part 1 [1]. However, the equilibrium ratios were more dependent on the solvent system than in the case of the 1-chloro-1,2-dimethylcyclo-

[1]) *Fort et al.* [3] obtained a ratio of 3.8 in 60% acetone.

Table 7. *First order rate constants for the tosylates* **5** *and* **27**, **6** *and* **20**

	Temp. (°C)	k (s^{-1})	$E^{\neq}$ (kcal)	$S^{\neq}$ (cal/degree)
50% acetone[a]) **5**	71.9	1.78×10^{-4}		
	80.0	3.39×10^{-4}	18.51	– 24.3
	87.9	5.89×10^{-4}		
	110.0	2.63×10^{-3} [b])		
27	80.0	8.78×10^{-5}	20.10	– 22.5
	87.9	1.68×10^{-4}		
	95.0	2.82×10^{-4}		
	110.0	8.33×10^{-4} [b])		
6	80.0	6.66×10^{-5}	20.85	– 20.9
	87.9	1.36×10^{-4}		
	95.0	2.23×10^{-4}		
	110.0	6.96×10^{-4} [b])		
20	80.0	9.05×10^{-5}	20.00	– 22.7
	87.9	1.73×10^{-4}		
	95.0	2.89×10^{-4}		
	110.0	8.50×10^{-4} [b])		
80% ethanol[a])				
5	95.0	5.26×10^{-4}		
27	95.0	2.91×10^{-4}		
6	95.0	2.41×10^{-4}		
20	95.0	2.80×10^{-4}		
abs. acetic acid[c])				
5	110.0	4.45×10^{-4}		
27	110.0	1.78×10^{-5}		
6	110.0	1.53×10^{-5}		
20	110.0	1.84×10^{-5}		

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

Table 8. *Rate ratios of unsaturated and saturated tosylates in different solvents*

rate ratios of tosylates	80% ethanol 95°	50% acetone 80°	acetic acid 110°
5/**27**	1.8	3.9	25
6/**20**	0.86	0.74	0.84

Table 9. *Ratio of* cis- *and* trans-**3** *at equilibrium* (46°C)

	cis-**3**/*trans*-**3**	ΔG (kcal/mol)
20% $ZnCl_2$ in 36% hydrochloric acid	5.25	1.06
HCl/saturated CCl_4/$ZnCl_2$	4.26	0.93
HCl/saturated ether	5.66	1.10
HCl/saturated ether/20% BF_3	3.76	0.84
HCl/saturated 95% ethanol	5.66	1.10

hexanes (**1**). The measurements and the derived differences of ground state free energy ΔG are listed in Table 9. *Cis*-**3** is more stable than *trans*-**3** by an average ΔG value of 1.0 $\pm$ 0.1 kcal/mol.

Discussion. – As shown in Table 1 different amounts of the same products are formed from *cis*- and *trans*-**3**. This also applies to the cyclization products of cyclopentenylbutyl tosylate **5** in 80% ethanol. The large differences in product composition are strikingly revealed in the rations of elimination to substitution products, which are invariably highest for *trans*-**3** (Table 2). Furthermore, in all solvents substitution products are formed with predominant inversion and, with the exception of 68.6% dioxane, inversion is more pronounced in the products from trans-**3** (Table 2). This trend is accentuated in the presence of silver ion[2]). Different intermediates are therefore involved in the solvolysis of the stereoisomeric *cis*- and *trans*-chlorides **3** and in the cyclization of the tosylate **5**.

The isomerization experiments indicate that *cis*-**3** is more stable than *trans*-**3** by 1.0 $\pm$ 0.1 kcal/mol (Table 9). Furthermore, *trans*-**3** reacts eleven times as fast as *cis*-**3** in 80% ethanol and in 68.6% dioxane (Table 4). This corresponds to a difference in the free energies of activation $\Delta G^{\neq}$ of 1.5 kcal. As shown in Fig. 1 the transition state for *trans*-**3** is therefore 0.5 kcal more stable than the one for *cis*-**3**. Assuming that intermediates resemble the transition states of their formation it follows that the first intermediate from *trans*-**3** is also more stable by approximately 0.5 kcal than the one from *cis*-**3** (Fig. 1). This is somewhat less than the free energy difference of 0.7 kcal found for the intermediates from *cis*- and *trans*-1-chloro-1,2-dimethylcyclohexane (**1**) [1].

The simplest and most convincing explanation for the energy difference of approximately 0.5 kcal between the intermediates from *cis*- and *trans*-**3** and for the predominantly inverted configuration of the substitution products is the formation of stereoisomeric ion pairs which differ with respect to the location of the counter chlo-

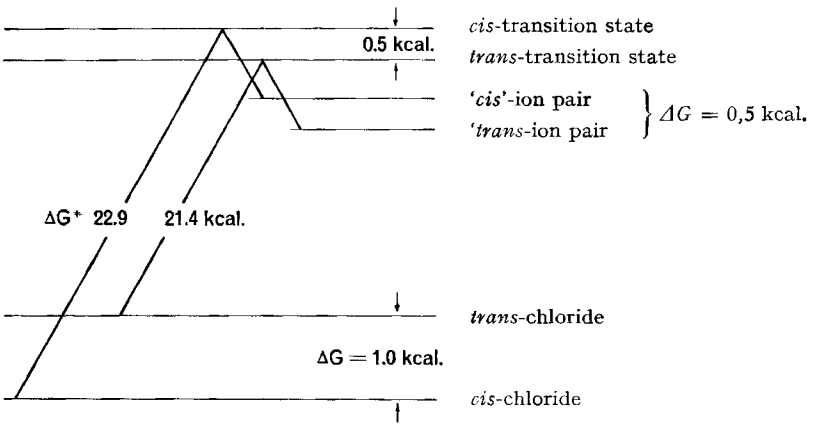
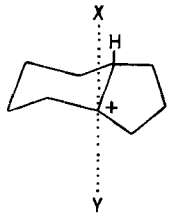


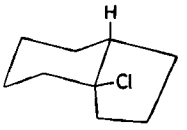
Fig. 1. *Free energy diagram for* cis- *and* trans-*8-hydrindanyl chlorides*

[2]) For an explanation see Part 1 [1].

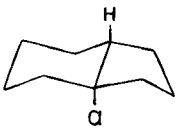
ride ion, as in *cis*- and ***trans*-28**. Nucleophilic attack of the solvent at the backside of the cationic centre competes effectively with the displacement of the chloride ion by solvent to produce the symmetrically solvated carbenium ion **29**. Inversion therefore outweighs retention.



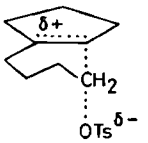
cis-**28** X = Cl^-, Y = solvent
trans-**28** X = solvent, Y = Cl^-
29 X = Y = solvent



cis-**30**



trans-**30**



31

Inspection of models indicates that the best conformation for the cation is one in which the planar and rigid five-membered ring is attached equatorially to the chair form of the cyclohexane ring. This conformation is produced directly when *cis*- and ***trans*-3** ionize in their most stable conformations *cis*-**30** and *trans*-**30**. Due to its curvature the cation is more accessible to solvent on the convex side. This explains the much higher inversion ratio for the *trans* ion pair **28** and its tighter solvation as reflected in the more negative activation entropy $\Delta S^{\neq}$ for *trans*-**3** (Table 4)[3].

Cyclization of 4-(cyclopenten-1-yl)butyl tosylate (**5**) in 80% ethanol leads to alcohols and ethers with predominant *cis* configuration (*cis*/*trans* ratio 3.7) (Tables 1 and 2). The intermediate cannot be represented as a contact ion pair because the tosylate anion is generated remote from the cationic center, as shown in **31**. Furthermore, the predominance of *cis* products is not readily explained by a symmetrically solvated cation **29**, even though solvent attack should be faster on the less hindered convex side of the cationic center. However, solvation of this center would be expected to commence on the opposite side of the incipient carbon to carbon bond in the transition state **31**. This unsymmetrical solvation should favor the formation of *cis* products.

Furthermore, the elimination to substitution ratio is much lower than that observed in the products from the σ-route, *i.e.* from the *cis*- and *trans*-chlorides **3** (Table 2)[4]. This again points to a cationic intermediate which is different from the one from *cis*- and *trans*-**3**. It is noteworthy that a bridged species would qualify as the transition

[3] An apparent exception is observed in the solvent 68.6% dioxane. In this case the inversion to retention ratio is higher for *cis*-**3**, *i.e.* 1.9, than for *trans*-**3**, *i.e.* 1.2 (Table 2). This finding can be ascribed to the special ability of dioxane to react with carbenium ions to form oxonium ions which are attacked by water to yield alcohols with overall retention of configuration [11]. This double inversion process would, for steric reasons, more likely occur with the *trans* ion pair **28**, where X is dioxane.

[4] This has been shown to be typical for secondary cations generated by σ- and π-routes [12].

state for the cyclization of the tosylate **5** but not as an intermediate for product formation since this should lead exclusively to *cis* alcohol **7** and *cis* ether **9** [13].

The rate data in Tables 7 and 8 show that the olefinic double bond does not participate in the ionization of 3-(cyclohexen-1-yl)propyl tosylate **6**, as is also borne out by the absence of hydrindanyl derivatives in the products and by models which reveal that π-4,5 participation should be very weak for stereoelectronic reasons.

An alternative explanation for the results reported in this paper was mentioned earlier [2] and involves intermediate carbenium ions which differ with respect to conformation. This possibility was rejected, however, since predominant inversion of substitution products is more convincingly explained by stereoisomeric ion pairs. Moreover, all conformations for the intermediate cation other than the one depicted in **28** require a boat or twist form for the cyclohexane ring. Such conformations would differ in energy by more than 0.5 kcal[5]) and therefore do not qualify as intermediates.

Nevertheless, *Fort et al.* [3] invoke conformationally isomeric carbenium ions to explain solvolysis rates and products of the *p*-nitrobenzoates **8** of *cis*- and *trans*-hydrindanol in 60% acetone. In this solvent *trans*-**8** reacted *ca* 3.8 times as fast as *cis*-**8** which is in good agreement with the ratio of 3.4 observed in 50% acetone (Table 6). However, these authors reported that *cis*-**8** underwent substitution with predominant retention of configuration as was also observed for *cis*- and *trans*-**8** in 50% acetone (Table 3). This result, which is very unusual for a S_Ni-reaction, and the low rate ratio for the *trans*- and *cis*-*p*-nitrobenzoates **8**, namely ca. 3.5 *versus* 11 for the *trans*- and *cis*-chlorides **3** strongly suggest that ester hydrolysis accompanies ionization to the 8-hydrindanyl cation. Conclusions derived from rates and products of *p*-nitrobenzoates are therefore unreliable, as will also be pointed out in the following communication [15].

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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 [1]. Results for IR. in cm^{-1}, for NMR in ppm.

Syntheses. – cis-*8-Chlorohydrindane* (*cis*-1-chlorobicyclo[4.3.0]nonane) (*cis*-**3**). a) *By halodecarboxylation of* cis-*8-hydrindanecarboxylic acid* (**13**). A mixture of 4.8 g (36 mmol) N-chlorosuccinimide in 10 ml dimethylformamide and 2 ml glacial acetic acid was degassed and heated under a stream of nitrogen to 50° until a clear solution resulted. 1.00 g (5.95 mmol) *cis*-8-hydrindanecarboxylic acid [16] and 2.80 g lead tetraacetate (85–90% in glacial acetic acid, 5.4–5.7 mmol) were added. After an induction period of *ca.* 1 min evolution of carbon dioxide started. The heating source was replaced by a cooling bath to maintain a reaction temperature of 50°[6]). After 5 min, when gas evolution had ceased, the reaction mixture was diluted with 20 ml water and extracted with pentane. The extracts were washed with cold 20% perchloric acid, cold saturated $NaHCO_3$ solution and ice/water. After evaporation in a vacuum rotary evaporator 860 mg (91%) colourless oil remained. The IR. spectrum of the crude product showed the presence of acetates (1735 and 1240 cm^{-1}). Separation on an aluminium oxide column (50 g, activity III) at –10° (eluent petrol ether b.p. 45–60°) gave 509 mg (54%) oily product consisting of 83% 8-chloro-

[5]) In the case of cyclohexanone, which is a good model for the cyclohexyl cation, the boat form is reported to be 3.3 kcal less stable than the chair form [14].

[6]) The temperature may rise to 120° if cooling is omitted and cause decomposition [4].

hydrindanes (**3**) (*cis*:*trans* = 95:5) and 17% hydrindenes **10**, **11** and **12** as shown by GLC. Distillation or separation by preparative GLC. caused decomposition of the thermally instable chlorides.

b) *By addition of HCl.* 0.50 g (0.41 mmol) $\Delta^{8,9}$-hydrindene (**10**) were added dropwise with stirring to 25 ml methylene chloride saturated with HCl at −78°. HCl was bubbled through the solution for 30 min at −78°. 30 g of ice were added, the mixture diluted with pentane and the organic layer washed with cold aqueous $NaHCO_3$ and ice/water, dried over $MgSO_4$ and evaporated at 0°. GLC (10% Carbowax 20 M on Chromosorb, 90°) showed a mixture of 87% *cis*- and 13% *trans*-8-chlorohydrindane (**3**). The crude product was purified by rapid column chromatography over aluminium oxide (activity III) at −10° to give 526 mg (82%) 8-chlorohydrindane containing 89% *cis*-**3** and 11% *trans*-**3**. A mixture of 87% *cis*- and 13% *trans*-8-chlorohydrindane is obtained by dropwise addition of $\Delta^{8,9}$-hydrindene (**10**) to condensed dry HCl without solvent. – IR. (film): 654, 780, 805 (C—Cl, expected [14] for *cis*-**3** 650–700). – NMR. (CCl_4): 1.1–2.5 (*m*).

$C_9H_{15}Cl$ (158.67) Calc. Cl 22.34% Found Cl 22.39%

trans-*8-Chlorohydrindane* (*trans*-1-chlorobicyclo[4.3.0]nonane) (*trans*-**3**). 0.50 g (0.41 mmol) $\Delta^{8,9}$-hydrindene (**10**) were added at 0° to 60 ml ethyl ether saturated with dry HCl. HCl gas was bubbled through the solution for 15 min at 0° After work-up and purification as above GLC. showed the presence of 91% 8-chlorohydrindane (**3**) (*trans*:*cis* = 88:12) and 9% olefins. In one experiment the ratio was 93% *trans* and 7% *cis*. – IR. (film): 545 (C—Cl, expected [17] for *trans*-**3** 540–580). – NMR. (CCl_4): 1.2–2.5 (*m*).

$C_9H_{15}Cl$ (158.67) Calc. Cl 22.34% Found Cl 20.32%

All *trans*-8-hydrindanyl compounds have shorter retention times on GLC. than the corresponding *cis*-8-hydrindanyl compounds. The following results of bimolecular elimination of HCl with ethanolic potassium hydroxide support these assignments [18].

Elimination of HCl from cis- *and* trans-*8-chlorohydrindane* (**3**). 20 mg (0.13 mmol) of chloride mixtures rich in *cis*- or *trans*-chloride were heated with 0.5 ml 5 M ethanolic potassium hydroxide at 80° for 15 h. The mixture was diluted with 20 ml water and extracted continuously in a *Kutscher-Steudel* extractor with pentane. The pentane solution was analyzed by GLC. (2.5% SE 52, 70°). The olefins, which were shown to be stable under the conditions of the reactions, were identified by comparison with authentic samples (*vide infra*). The percent composition was corrected for olefins present in the initial chloride mixtures and extrapolated to pure *cis*- and *trans*-chloride. All experiments were repeated at least twice and gave the same results within ±2%. *cis*-Chloride yielded 49% $\Delta^{1,8}$-hydrindene (**12**), 39% $\Delta^{8,9}$-hydrindene (**10**) and 12% $\Delta^{7,8}$-hydrindene (**11**). *trans*-Chloride yielded 74% $\Delta^{8,9}$-hydrindene (**10**), 13% $\Delta^{1,8}$-hydrindene (**12**) and 13% $\Delta^{7,8}$-hydrindene (**11**).

$\Delta^{8,9}$-Hydrindene (bicyclo[4.3.0]nonene-1(6)) (**1c**). In analogy to a synthesis of $\Delta^{9,10}$-octalin [19], 18.9 g (0.16 mol) indane were reduced with a mixture of 100 ml ethylamine and 100 ml dimethylamine and 4.62 g (0.66 mol) lithium which was added in small portions at 0°. The mixture was stirred at 0° for 6 h. The amines were distilled off at room temperature and the residue hydrolysed with 200 ml water. The olefins were extracted with ether, the extracts washed with 2 N hydrochloric acid and water and dried over $MgSO_4$. Distillation gave 15.1 g (77%) crude hydrindene, b.p. 58–60°/15 Torr. GLC. showed the presence of *ca.* 15% impurities (other olefins and hydrindane).

A solution of diisoamylborane in tetrahydrofuran was prepared by dropwise addition of 8.4 g (59 mmol) freshly distilled boron trifluoride etherate in 15 ml tetrahydrofuran to a cooled mixture of 1.62 g (43 mmol) sodium borohydride and 8.0 g (113 mmol) 2-methyl-2-butene in 70 ml tetrahydrofuran. 15.1 g crude hydrindene were added and the solution stirred for 5 h at room temperature. The mixture was hydrolysed with 25 ml water and oxydized with 17 ml 30% hydrogen peroxide and 17 ml 3 M aqueous NaOH for 5 h at 45°. The organic layer was separated, washed with aqueous NaCl, dried over $MgSO_4$ and distilled. The olefin fraction was redistilled at 54°/13 Torr to give 9.3 g (48%) pure $\Delta^{8,9}$-hydrindene (**10**). – IR. (CCl_4): 2930, 2840 (C—H), 1682 (C=C), 1448, 1305, 1142 (C—C). – NMR. (CCl_4): 1.4–2.5 (*m*).

C_9H_{14} (122.21) Calc. C 88.45 H 11.77% Found C 88.46 H 11.55%

$\Delta^{7,8}$-Hydrindene (bicyclo[4.3.0]nonene-1(2)) (**11**). 9.44 g (43.1 mmol) 2-(4-bromobutyl)cyclopentanone (**14**) [5] and 11.3 g (43.1 mmol) triphenylphosphine were heated 24 h at 100° and 3 h

at 140°, then dried over phosphorous pentoxide. The glass-like hygroscopic phosphonium bromide **15** did not crystallize and was used without purification. It was dissolved in 50 ml dimethylsulfoxide and added with stirring under nitrogen to a solution of dimethylsulfoxide anion made from 1.08 g (45 mmol) sodium hydride and 20 ml dimethylsulfoxide. The red suspension was warmed to 80° for 10 min, when the reaction mixture was clear, and the olefin distilled off at 35–42°/12 Torr, diluted with pentane, washed with water and dried over $MgSO_4$. Distillation gave 2.98 g (57%) of pure $\Delta^{7,8}$-hydrindene (**11**), b.p. 166°. – IR. (CCl_4): 3040, 860 (=C—H), 1675 (C=C), 2920, 2860 (C—H), 1450 (C—C). – NMR. (CCl_4): 0.8–2.4 (13H, *m*) CH_2, CH; 5.30 (1H, *s*) =CH.

C_9H_{14} (122.21) Calc. C 88.45 H 11.77% Found C 88.26 H 11.68%

$\Delta^{1,8}$-Hydrindene (bicyclo[4.3.0]nonene-1(9)) (**12**). 3.06 g (14 mmol) 2-(3-bromopropyl)cyclohexanone (**16**) [5] and 3.66 g (14 mmol) triphenylphosphine were dissolved in 20 ml dry ether and heated to 100° for 15 h in a sealed tube. The strongly hygroscopic, crystalline precipitate was filtered, washed with dry ether and dried at 0.01 Torr to give 1.87 g (28%) phosphonium bromide **17** which was used without purification. This (3.83 mmol) was reacted with dimethylsulfoxide anion in dimethylsulfoxide as described above. Distillation gave 274 mg (59%) of pure $\Delta^{1,8}$-hydrindene (**12**), b.p. 137–138°. – IR. (CCl_4): 3035, 905 (=C—H), 1675 (C=C), 2920, 2860 (C—H), 1440 (C—C). – NMR. (CCl_4): 5.17 (1H, *s*) =CH; 0.8–2.7 (13H, *m*) CH_2, CH.

cis-*8-Hydrindanol* (**7**) was prepared by catalytic hydrogenation of the epoxide **18** (from pure $\Delta^{8,9}$-hydrindene (**10**) and peracetic acid) over *Raney* nickel at 100 atm in methyl formiate. Colourless crystals from pentane, m.p. 63–64° (Lit. [6]: m.p. 49°).

trans-*8-Hydrindanol* (**7**) was prepared by reduction of epoxide **18** with lithium aluminium hydride in tetrahydrofuran [6].

cis-*8-Ethoxyhydrindane* (**9**) was prepared from the lithium salt of *cis*-8-hydrindanol (7) and ethyl iodide in hexamethylphosphortriamide as described for *cis*-1-ethoxy-1,2-dimethylcyclohexane in Part 1 [1]. – IR. (CCl_4): 1386 (C—C), 1072 (C—O). – NMR. (CCl_4): 1.10 (3H, *t*) CH_3; 3.29 (2H, *q*) OCH_2; 0.8–2.1 (15H, *m*) CH_2, CH.

trans-*8-Ethoxyhydrindane* (**9**) was prepared likewise from *trans*-8-hydrindanol (**7**). – IR. (CCl_4): 1385 (C—C), 1052 (C—O), 960, 862. – NMR. (CCl_4): 1.10 (3H, *t*) CH_3; 3.22 (2H, *q*) OCH_2; 0.8–2.2 (15H, *m*) CH_2, CH.

*3-(Cyclohexen-1-yl)propyl-*p*-toluenesulfonate* (**6**). 1.75 g (9.2 mmol) *p*-toluenesulfonyl chloride in 5 ml pyridine were added to 1.0 g (7.2 mmol) 3-(cyclohexen-1-yl)propanol (**19**) [7] in 5 ml pyridine at 0° over 10 min. After standing at 2° over night the excess *p*-toluenesulfonyl chloride was hydrolysed with water. The solution was treated with 30 ml 2N hydrochloric acid and extracted with ether. The extracts were washed with saturated aqueous $NaHCO_3$ and water, dried over $MgSO_4$ and evaporated. The crude product was dissolved in pentane, cooled to –35°, when 1.82 g (87%) tosylate **6** separated as an oil. – IR. (CCl_4): 3030 (ArH), 1370, 1178 (OSO_2). – NMR. (CCl_4): 1.2–2.2 (12H, *m*) CH_2; 2.47 (3H, *s*) CH_3; 3.96 (2H, *t*) OCH_2; 5.30 (1H, broad *s*) =CH; 7.35 and 7.75 (2H each, *d*) ArH.

$C_{16}H_{22}O_3S$	Calc.	C 65.29	H 7.53 S 10.89%
(294.41)	Found	,, 65.59	,, 7.50 ,, 10.61%

*3-Cyclohexylpropyl-*p*-toluenesulfonate* (**20**) was made from 2.0 g (14 mmol) 3-cyclohexylpropanol and 3.4 g (18 mmol) *p*-toluenesulfonyl chloride as above. Yield 3.51 g (84%) oil. – IR. (CCl_4): 3030 (ArH), 1370, 1178 (OSO_2). – NMR. (CCl_4): 0.8–1.9 (15H, *m*) CH_2, CH; 2.47 (3H, *s*) CH_3; 3.96 (2H, *t*) OCH_2; 7.30 and 7.75 (2H each, *d*) ArH.

$C_{16}H_{24}O_3S$	Calc.	C 64.84	H 8.16 S 10.81%
(296.43)	Found	,, 64.70	,, 8.24 ,, 10.59%

Diethyl 2-(cyclopenten-1-yl)ethylmalonate (**23**). 2-(Cyclopenten-1-yl)ethyl *p*-toluenesulfonate (**22**) was prepared from 30 g (0.27 mol) 2-(cyclopenten-1-yl)ethanol (**21**) [8] and 60 g (0.315 mol) *p*-toluenesulfonyl chloride in pyridine as above (yield 60.2 g, 85%) and used without purification. 5.7 g (0.248 mol) sodium were dissolved in 250 ml abs. ethanol, then 43 g (0.268 mol) diethyl malonate and 60 g (0.226 mol) of the above tosylate added. The reaction mixture was refluxed for 4 h, ethanol distilled off and the residue treated with 600 ml water. The aqueous layer was extracted with ether. The organic layer and the extracts were washed with 5% aqueous K_2CO_3 and water

and dried over $MgSO_4$. Distillation gave 40.3 g (70%) **23** as a colourless oil, b.p. 98–105°/0.05 Torr. – IR. (CCl_4): 3040 (=C—H), 1750, 1735 (C=O), 1370. – NMR. (CCl_4): 1.34 (6H, *t*) CH_3; 1.6–2.5 (10H, *m*) CH_2; 3.20 (1H, *m*) CH; 4.17 (4H, *q*) OCH_2; 5.37 (1H, broad *s*) =CH.

$C_{14}H_{22}O_4$ (254.33) Calc. C 66.11 H 8.72% Found C 66.29 H 8.53%

2-(Cyclopenten-1-yl)ethylmalonic acid. 37 g (0.146 mol) diethyl 2-(cyclopenten-1-yl)ethylmalonate (**23**) were refluxed for $2^1/_2$ h with 26 g (0.32 mol) KOH in 320 ml methanol. 250 ml water were added, methanol was distilled off and the remaining solution acidified with 2N sulfuric acid. The aqueous layer was extracted with ether. The organic layer and the extracts were washed with water, dried over $MgSO_4$ and evaporated to give 27.5 g (96%) 2-(cyclopenten-1-yl)ethylmalonic acid. From ether/petrol ether colourless crystals, m.p. 124–126°. – IR. ($CHCl_3$): 3000 (broad, COOH), 1720 (C=O), 1048. – NMR. ($CDCl_3$): 1.6–2.7 (10H, *m*) CH_2; 3.5 (1H, *m*) CH; 5.43 (1H, broad *s*) =CH; 9.4 (2H, *s*) COOH.

$C_{10}H_{14}O_4$ (198.22) Calc. C 60.59 H 7.12% Found C 60.31 H 7.05%

4-(Cyclopenten-1-yl)butanoic acid (**24**). 21.6 g (0.108 mol) 2-(cyclopenten-1-yl)ethylmalonic acid were heated to 180° for 1 h. Distillation gave 15.2 g (91%) of **24** as an oil, b.p. 92–99°/0.07 Torr. – IR. (CCl_4): 3000 (broad, COOH), 1710 (C=O). – NMR. (CCl_4): 1.4–2.6 (12H, *m*) CH_2; 5.35 (1H broad *s*) =CH; 11.4 (1H, *s*) COOH.

p-*Bromophenacyl ester.* From methanol colourless crystals, m.p. 68–70°.

$C_{17}H_{19}BrO_3$ (351.25) Calc. C 58.13 H 5.45% Found C 58.10 H 5.44%

4-(Cyclopenten-1-yl)butanol (**25**). 13.6 g (0.088 mol) 4-(cyclopenten-1-yl)butanoic acid (**24**) in 50 ml ether were added over 30 min to 5.0 g (0.132 mol) $LiAlH_4$ in 200 ml ether. The mixture was refluxed for 5 h, then hydrolysed carefully with 500 ml 15% sulfuric acid. The aqueous layer was extracted with ether. The etheral solutions were washed with 2N NaOH and water, dried over $MgSO_4$ and evaporated. Distillation gave 9.0 g (73%) 4-(cyclopenten-1-yl)butanol (**25**), b.p. 64–66°/0.3 Torr. – IR. (CCl_4): 3630, 3300 (broad, OH), 3040 (=CH), 1650 (C=C), 1055, 1035 (C—O). – NMR. (CCl_4): 1.3–2.6 (12H, *m*) CH_2; 2.95 (1H, *s*) OH; 3.55 (2H, *t*) OCH_2; 5.3 (1H, broad *s*) =CH.

3,5-Dinitrobenzoate. From methanol colourless crystals, m.p. 58–59°.

$C_{16}H_{18}N_2O_6$ (334.33) Calc. C 57.48 H 5.43 N 8.38%
Found ,, 57.60 ,, 5.60 ,, 8.29%

4-(Cyclopenten-1-yl) butyl-p-toluenesulfonate (**5**) was prepared from 2.0 g (14 mmol) 4-(cyclopenten-1-yl)butanol (**25**) and 3.5 g (18 mmol) *p*-toluenesulfonyl chloride in pyridine. The oily tosylate (3.52 g, 84%) was purified by repeated freezing out from pentane at –35°. – IR. (CCl_4): 3030 (ArH), 1650 (C=C), 1370, 1178 (OSO_2). – NMR (CCl_4): 1.3–2.4 (12H, *m*) CH_2; 2.47 (3H, *s*) CH_3; 3.98 (2H, *t*) OCH_2; 5.25 (1H, broad *s*) =CH; 7.35 and 7.75 (2H each, *d*) ArH.

$C_{16}H_{22}O_3S$ (294.41) Calc. C 65.29 H 7.53 S 10.89%
Found ,, 65.06 ,, 7.49 ,, 10.76%

4-Cyclopentylbutanol (**26**) was prepared by hydrogenation of 4-(cyclopenten-1-yl)butanol (**25**) (2.0 g, 14 mmol) over 230 mg 5% Pd/C in 50 ml ethanol. Distillation gave 1.90 g (95%) saturated alcohol **26**, b.p. 54–55°/0.02 Torr, n_D^{20} 1.4532 (Lit. [20]: b.p. 87–92°/2 Torr, n_D^{20} 1.4160).

4-Cyclopentylbutyl p-*toluenesulfonate* (**27**) was made from 500 mg (3.5 mmol) 4-cyclopentylbutanol (**26**) and 870 mg (4.6 mmol) *p*-toluenesulfonyl chloride in pyridine. Freezing out from pentane at –35° gave 960 mg (92%) oily tosylate **27**. – IR. (CCl_4): 3030 (ArH), 1370, 1178 (OSO_2). – NMR. (CCl_4): 0.8–2.0 (15H, *m*) CH_2, CH; 2.47 (3H, *s*) CH_3; 3.98 (2H, *t*) OCH_2; 7.32 and 7.76 (2H each, *d*) ArH.

$C_{16}H_{24}O_3S$ (296.43) Calc. C 64.84 H 8.16 S 10.81%
Found ,, 64.71 ,, 8.24 ,, 10.71%

Preparative Solvolyses. – cis- *and* trans-*8-Chlorohydrindanes* (**3**). 0.004M solutions of 12 mg chloride mixtures rich in *cis*-chloride or *trans*-chloride and 10 mg (1.2 equiv.) triethylamine in 20 ml 80 vol. % ethanol or 68.6 vol. % dioxane were stirred at 40° for 3 h. The solutions were diluted with water and extracted continuously with pentane in a *Kutscher-Steudel* extractor. The extracts were analyzed by GLC. (10% Carbowax 20M, 100° and 2.5% SE 52, 70°). All products were identified by comparison with authentic samples. The percent composition was correct-

ed for olefins present in the initial chloride mixtures and extrapolated to pure *cis*- and *trans*-chloride. Experiments were carried out with different chloride mixtures and repeated at least twice; reproducebility was within ±2%. Solvolyses products were not stable under acid conditions. If triethylamine was omitted, less *trans*-8-hydrindanol (**7**) and $\Delta^{1,8}$-hydrindene (**12**), but more $\Delta^{8,9}$-hydrindene (**10**) was obtained.

The experiments were repeated with 16 mg (1.2 equiv.) silver nitrate dissolved in 18 ml 80% ethanol at 40°. 13 mg (1.5 equiv.) triethylamine in 2 ml 80% ethanol were added dropwise with stirring, followed by 12 mg *cis*- or *trans*-**3**. The suspension was stirred 2 h at 40°, then worked up and analyzed as above.

4-(Cyclopenten-1-yl)butyl tosylate (**5**) *and 3-(cyclohexen-1-yl)propyl tosylate* (**6**). 200 mg (0.68 mmol) tosylate **5** or **6** and 100 mg (1.5 equiv.) triethylamine in 15 ml 50 vol.% acetone or 80 vol.% ethanol were heated 15 h at 95° in a sealed tube. The solutions were diluted with water and extracted with pentane in a *Kutscher-Steudel* extractor. Acetolyses were carried out with 200 mg tosylate and 110 mg sodium acetate (2 equiv.) in 15 ml glacial acetic acid 15 h at 100°. The solutions were made alkaline with aqueous KOH before extraction and GLC. analysis carried out on 10% SE 30, 70–100°.

Kinetic Measurements. – 80 vol.% ethanol and 50 vol.% acetone were prepared as described in [1]. 68.6 vol.% dioxane resulted when 720.3 g dioxane (puriss.) and 317.7 g bidistilled water were mixed, d_{20}^{20} 1.042.

cis- *and* trans-*8-Chlorohydrindanes* (**3**). Reaction rates were measured by conductometric methods described earlier [21]. The conductivity cell was filled with 20 ml of 10^{-3} M solution in 80 vol.% ethanol or 68.6 vol.% dioxane containing 1.2 equiv. triethylamine, and immersed in a water thermostat, temperature deviation ±0.05°. The reaction of chloride mixtures rich in *cis*-chloride **3** was followed after one halflife, *i.e.* when less than 0.5% *trans*-**3** was left. The solvolysis rate of *trans*-chloride **3** was determined as follows: The conductivity cell containing solvent and triethylamine was brought to the reaction temperature. A chloride mixture rich in *trans*-**3** was added and conductivity measured for three half lives. From the percent composition of the chloride mixture at time zero (by GLC.) and the known solvolysis rate of *cis*-**3**, the conductivity change due to *cis*-**3** was calculated and substracted from the total conductivity change. Calculations were done with the aid of a computer program [1]. Measurements were carried out with different chloride mixtures and repeated at least twice. Reaction rate constants were reproducible within ±2%.

Tosylates **5**, **6**, **20** *and* **27**. Reaction rates in 50 vol.% acetone and 80 vol.% ethanol were measured conductometrically in a pressure cell (Firma *W. Schmid*, Basel) immersed in an oil thermostat with temperature deviation ±0.05°. Solutions were 10^{-3} M in tosylate and contained 1.5 equiv. triethylamine. Acetolysis rates were determined titrimetrically. Solutions were 10^{-2} M in tosylate and contained 2.00 equiv. of sodium acetate. Aliquots were titrated with 10^{-2} M perchloric acid in glacial acetic acid with bromophenolblue as indicator. All measurements were repeated at least twice and were reproducible within ±2%.

Equilibrations. – These were carried out with 20% zinc chloride in conc. hydrochloric acid, zinc chloride in carbon tetrachloride saturated with HCl, boron trifluoride diethyl etherate in ethyl ether saturated with HCl and 95% aqueous ethanol saturated with HCl as described in Part 1 [1]. The 8-chlorohydrindanes gave more unknown impurities and olefins under these conditions than the 1-chloro-1,2-dimethylcyclohexanes [1]. After ten days in 95% ethanol saturated with HCl, 27% hydrindenes and 4% other side products were formed.

Equilibration of 8-chlorohydrindanes was also observed in ethyl ether saturated with HCl after 20 days.

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

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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**.