**131.** *Solvolysis of Some Trimethylnorbornyl Chlorides.*

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Hydrolysis and methanolysis of bornyl and isobornyl chloride, and of camphene hydrochloride, in alkaline or neutral solution, give only camphene and camphene hydrate or methyl ether, which rearrange in acid to isoborneol or its methyl ether. In alkali the product composition is independent of the substrate, but the amount of elimination increases with increasing concentration of lyate ion, with increasing temperature, and on addition of 1,2-dimethoxyethane. Lyate ions retard reaction slightly, and camphene is not formed by an $E2$ reaction.

The approximate rates of solvolysis, relative to that of bornyl chloride, are isobornyl chloride 1.5×10^5 and camphene hydrochloride 3×10^8. Water speeds reaction, and 1,2-dimethoxyethane retards it.

The bicyclic chlorides formed by reaction of hydrogen chloride with α-pinene and camphene provided the first example of the Wagner–Meerwein rearrangement. The *exo*-isomers, isobornyl chloride (I) and camphene hydrochloride [*exo*-2,2,3-trimethylnorbornyl chloride (III)], ionise much faster than the corresponding open-chain or monocyclic chlorides, but bornyl chloride (II) has a "normal" rate of ionisation.[1] [The configurations of (I)—(III) are that of (+)-camphor.[2]]
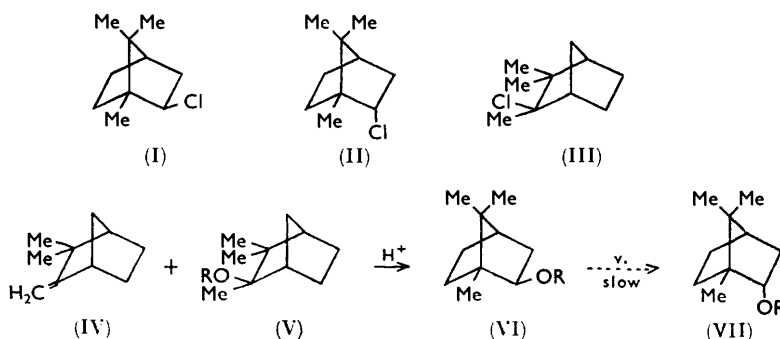
The first products of hydrolysis or alcoholysis are camphene (IV) and camphene hydrate or its ether (V; R = H or alkyl). They are unstable to acid and rearrange to isoborneol or its ether (VI; R = H or alkyl), and finally to borneol or its ether (VII); *e.g.*, in initially neutral water isobornyl chloride (I) gave a mixture of camphene and

[1] (a) Brown, Hughes, Ingold, and Smith, *Nature*, 1951, **168**, 65; (b) Ingold, "Structure and Mechanism in Organic Chemistry," Bell, London, 1953, Ch. X; (c) Winstein, Morse, Grunwald, Jones, Corse, Trifan, and Marshall, *J. Amer. Chem. Soc.*, 1952, **74**, 1127; (d) Roberts and Bennett, *ibid.*, 1954, **76**, 4623.
[2] Birch, *Ann. Reports*, 1950, **47**, 190.

isoborneol, and camphene hydrochloride (III) gave these two products and camphene hydrate, but bornyl chloride (II) in aqueous calcium hydroxide gave mainly camphene hydrate.[3a] A preliminary account has been given of the determination of the products of methanolysis.[3b]

Chloride exchange between camphene hydrochloride (III) and hydrogen chloride in aprotic solvents is faster than rearrangement to the thermodynamically more stable isobornyl chloride (I).[4]

Our study of product composition was intended to test the assumption that the products are formed from a common intermediate whose structure is similar to that of a classical camphene carbonium ion (VIII) [although (VIII) is written here as a classical structure a non-classical structure is probably a better representation [1]].
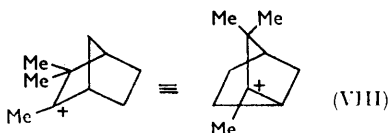

Neutral or alkaline solutions were generally used, so that the kinetically controlled products did not rearrange. Our rate measurements supplement existing results [1] and show that the chlorides are solvolysed by a unimolecular, S_N1 mechanism, even in strongly basic media.

RESULTS

The composition of the products is given in Table 1. In most of the experiments the hydro-chloric acid was neutralised by adding an excess of alkali or silver oxide, and the products were then kinetically controlled. When these products rearranged in acid, isoborneol or its ether (VI; R = H or Me) was always formed, not borneol or its ether (VII), although on prolonged treatment with dilute acid the products (VI) rearrange in part to borneol (VII).[3b] Solvolysis catalysed by mercuric chloride was so fast that the kinetically controlled products did not rearrange. The very reactive camphene hydrochloride (III) was studied only at low, and the unreactive bornyl chloride (II) at high temperatures (Table 1). The product composition depends only on environment, and isobornyl compounds were formed in traces ($<1\%$), if at all, in alkaline solution.

The differences between the energies of activation for elimination, E_E, and substitution, E_S, were calculated for solvolysis of isobornyl chloride, in conditions where the amounts of elimination and substitution were similar, over the temperature range 25—60°, with [OMe⁻] = 0·2M, $E_E - E_S = 5$ kcal. mole⁻¹, and with [OMe⁻] = 0·5M, $E_E - E_S = 4$ kcal. mole⁻¹ in methanol and in 90 : 10 v/v methanol–water. The differences in activation energy were not calculated for solvolyses of camphene hydrochloride or bornyl chloride, because the temperature ranges were small. Tricyclene (IX) and bornylene (X) were not formed.

The first-order rate constants, k, for solvolysis are given in Table 2. Because of the high reactivity of camphene hydrochloride, and the low reactivity of bornyl chloride, these com-pounds were studied less extensively than isobornyl chloride.
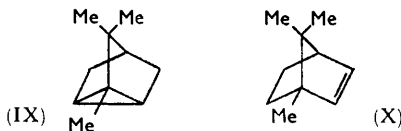
In methanol at 25·3° camphene hydrochloride (III) is 2100 times as reactive as isobornyl chloride (I), which is $1·5 \times 10^5$ times as reactive as bornyl chloride (II); in 1 : 1 v/v 1,2-dimethoxyethane–methanol, camphene hydrochloride (III) is 1800 times as reactive as iso-bornyl chloride (I). These rate differences are caused largely by differences in the activation

[3] (a) Simonsen and Owen, " The Terpenes," Vol. II, Cambridge University Press, 1949, pp. 317, 347; (b) Beltramé, Bunton, and Whittaker, *Chem. and Ind.*, 1960, 557.
[4] Nevell, de Salas, and Wilson, *J.*, 1939, 1188.

TABLE 1.

Solvolysis products.

(a) *In methanol.*

Camphene hydrochloride

	At 0°						At 25·3°		
[OMe⁻] (M)	—	—	0·1	0·2	1·5	3·0	0·2	1·5	3·0
[Camphene] (mole %)	7 *	15 †	15	20	50	82	22	55	87

Isobornyl chloride

	At 0°		At 25·3°					At 45·1°				
[OMe⁻] (M)	—	—	—	0·2	0·5	1·5	3·0	0·2	0·5	1·5	3·0	3·2
[Camphene] (mole %)	14 *	14 *	26 *	25	35	55	85	35	46	70 73	90	94

	Isobornyl chloride						Bornyl chloride		
	At 59·8°				At 100°		At 100°		
[OMe⁻] (M)	0·2	0·5	1·5	3·0	0·2	1·5	0·2	1·5	3·0
[Camphene] (mole %)	42	51	71	90	61 ‡	86 ‡	61	89	100

(b) *In 9 : 1 v/v methanol water.*

Isobornyl chloride

	At 25·3°			At 45·1°		At 59·8°
[OR⁻] (M)	—	0·2	0·5	0·2	0·5	0·2
[Camphene] (mole %)	20 §	25	41	36	47	54
[Ether]/[Alcohol]	3·9 §	3·2	6·4	3·7	7·8	5·6

(c) *In 1 : 1 v/v methanol–1,2-dimethoxyethane* ([NaOMe] = 0·2M).

	Camphene hydrochloride		Isobornyl chloride	
	At 25·3°	At 45·1°	At 45·1°	At 59·8°
[Camphene] (mole %)	52, 89 ¶	64	64	73, 74

(d) *Miscellaneous.* In initially neutral methanol, after 12 half-lives, bornyl chloride at 145°, and isobornyl chloride at 60°, gave isobornyl methyl ether, and a small amount of camphene; and camphene hydrochloride at 25° gave camphene 26%, isobornyl methyl ether 26%, camphene hydrate methyl ether 1%.

In 3 : 2 v/v dioxan–water with 0·2M-NaOH, camphene hydrochloride (at 25°) and isobornyl chloride (at 60°) gave only camphene (*ca.* 20%) and camphene hydrate.

* Ag₂O. † Solid NaHCO₃. ‡ Calc. from other temp. § 0·5M-HgCl₂. ¶ 1 : 4 v/v Methanol–1,2-dimethoxyethane.

energies, and the Arrhenius parameters are: camphene hydrochloride in methanol, $A = 4\cdot2 \times 10^{12}$ sec.⁻¹, $E = 20\cdot2$ cal. mole⁻¹; isobornyl chloride in methanol, $A = 1\cdot3 \times 10^{12}$ sec.⁻¹, $E = 24\cdot8$ kcal. mole⁻¹; and in 1 : 1 v/v 1,2-dimethoxyethane–methanol, $A = 8\cdot5 \times 10^{11}$ sec.⁻¹, $E = 24\cdot6$ kcal. mole⁻¹; bornyl chloride in methanol (0·2M-NaOMe), $A = 1\cdot9 \times 10^{10}$ sec.⁻¹, $E = 28\cdot2$ kcal. mole⁻¹.

Addition of 10% of water to methanol increases reaction rate 3—4-fold; addition of 50% of 1,2-dimethoxyethane decreases it 10—13-fold, and of 80% 1,2-dimethoxyethane 160-fold. These values depend slightly on the substrate and temperature (Table 2).

DISCUSSION

Products.—Because these three chlorides give the same mixtures of products in alkaline and neutral solution they must generate a common carbonium ion, whose structure must be similar to (VIII). This ion eliminates a proton only from the methyl group adjacent to the positive charge, located largely on the tertiary carbon atom. Tricyclene (IX) is not formed in appreciable quantity, but camphene formed by the thermal rearrangement of α-pinene sometimes contains large amounts of tricyclene, and it is formed during deaminations of bornylamines.[5] Solvolysis and deamination therefore give different carbonium-ion intermediates.

[5] Morris, unpublished results; cf. Skell and Starer, *J. Amer. Chem. Soc.*, 1960, **82**, 2871; Silver, *ibid.*, p. 2871.

TABLE 2.

First-order rate constants of solvolysis.

Camphene hydrochloride.

Solvent	MeOH				1 : 1 (CH₂·OMe)₂–MeOH	4 : 1 (CH₂·OMe)₂–MeOH
Temp.	0°	0°	21·6°	25·3°	25·3°	25·3°
[OR⁻] (M)	—	0·20	—	—	—	—
10^4k (sec.⁻¹)	6·60	4·90	115	170 *	13·3	1·06

Isobornyl chloride.

Solvent	MeOH								
Temp.	0°	25·3°	35·1°	45·0°				59·8°	
[OR⁻] (M)	—	—	—	—	0·20	0·80	1·50	—	0·20
10^6k (sec.⁻¹)	0·187	8·16	31·6 *	117	92·3	66·2	45·6	453	370

Solvent	9 : 1 MeOH–H₂O		1 : 1 (CH₂·OMe)₂–MeOH			
Temp.	35·1°		25·3°	35·1°	45·1°	59·3°
[OR⁻] (M)	—	0·06	—	—	—	—
10^6k (sec.⁻¹)	141	141	0·755 *	3·14	10·5	52·7

Bornyl chloride

Solvent	MeOH			9 : 1 MeOH–H₂O	
Temp.	81·0°	100·0°	126·1°	126·1°	
[Lyate ion]	0·20	0·20	0·20	0·015	0·06
10^7k (sec.⁻¹)	1·00	7·64	90 *	275	281

* Calc. from other temperatures.

Addition of a lyate ion (usually methoxide ion) increases the proportion of elimination, and reaction can be changed from predominant substitution in very dilute alkali to almost complete elimination in concentrated alkali (Table 1). Camphene is not formed by a bimolecular *E*2 reaction between lyate ion and alkyl chloride because (*a*) the overall rate of reaction is not increased by addition of lyate ion (Table 2), and (*b*) elimination from compounds (I), (II), and (III) gives camphene. Although bornylene (X) was not formed during our experiments, even with high concentrations of methoxide ion, it can be prepared from bornyl halides and strong bases at high temperatures in solvents of low dielectric constant.[6] This illustrates the importance of the *trans-anti*-configuration of the C–H and C–Cl bonds in the transition state,[7] and bornylene may be formed only by an *E*1*cb* mechanism.[8] Although the C–H and C–Cl bonds are eclipsed, bimolecular elimination is very slow (cf. ref. 9).

The variation of the ratio of elimination to substitution with lyate ion concentration (Table 1) suggests that the carbonium ion (VIII) is sufficiently stable in hydroxylic solvents to discriminate between the abundant solvent molecules, which preferentially add to the tertiary carbonium-ion centre, and the lyate ions which preferentially abstract a proton. We know of no other definitive evidence that the partitioning of a carbonium ion between elimination and substitution is affected in this way by added lyate ion. Some inconclusive evidence is provided by analysis of the concurrent elimination and substitution reactions of αα-dimethylbenzyl chloride in methanol.[10a] The amount of elimination, calculated on the assumption that partitioning of the carbonium ion is unaffected by lyate ion, is less than that found: however, similar studies of the concurrent elimination from and substitution of several alkyl halides suggested that lyate ions did

[6] Meerwein and Joussen, *Ber.*, 1922, **55**, 2529.
[7] Ref. 1*b*, p. 467.
[8] Bunnett, *Ang. Chem., Internat. Edn.*, 1962, **1**, 228.
[9] De Puy, Thurn, and Morris, *J. Amer. Chem. Soc.*, 1962, **84**, 1314.
[10] (*a*) Bunnett, Davis, and Tanida, *J. Amer. Chem. Soc.*, 1962, **84**, 1606; (*b*) ref. 1*b*, Ch. VII, section **32**.

not affect the fate of the carbonium ion.[10b]   These systems differed from ours in that the concentration of lyate ion was less, and the classical carbonium ions were probably less stable than (VIII).   We do not know how many solvent molecules are involved in addition, or whether the lyate ion removes the proton directly or through a Grotthius chain mechanism involving several solvent molecules.   The conclusion that substitution involves interaction between a carbonium ion and solvent molecules, rather than reaction with a lyate ion, accords with evidence from reactions of arylalkyl cations with hydroxylic solvents.[11]   The increase of the ratio of elimination to substitution with increasing concentration of lyate ion suggests that loss of the proton requires assistance from a base. Therefore, the step should be activated, and the ratio of elimination to substitution increases with increasing temperature.   The difference in the activation energies of elimination and substitution is *ca.* 4 kcal. mole^{-1}.

The activation energies for the S_N1 and $E1$ reactions of t-butyl halides differ similarly,[12] suggesting that the nature of the tertiary carbonium ion is unimportant in this respect. Kinetic hydrogen isotope effects provide further evidence that proton loss from a carbonium ion is an activated process, because there is a primary isotope effect increasing with increasing stability of the carbonium ion, although it is always less than the value corresponding to complete loss of the zero-point energy.[13]   There is some elimination even when the bulk lyate-ion concentration is very low, as in methanol containing sodium hydrogen carbonate, silver oxide, or mercuric chloride (Table 1).   Therefore the lyate ion is not essential for proton loss from the carbonium ion.

Addition to the methanol of either a more polar, reactive solvent, such as water, or a non-polar unreactive solvent, such as 1,2-dimethoxyethane, changes the product composition (Table 1).   Water can compete with methanol for the carbonium ion to form camphene hydrate, but for a given temperature and alkali concentration the overall ratio of elimination to substitution is almost unaffected by the addition of 10 volume % of water (Table 1).   Moreover, the ratio of alcohol to ether in substitution products of these bicyclic chlorides in aqueous methanol is very similar to that in solvolysis of t-butyl chloride;[12] *e.g.*, for isobornyl chloride (Table 1) ether/alcohol $\approx$ 3·6, in 9 : 1 v/v methanol–water and for t-butyl chloride[14] ether/alcohol = 3·5.   These ratios are very similar to the molar ratios of the solvents, *i.e.*, MeOH/H$_2$O $\approx$ 5.

Considering first only the substitution, we can suppose that reaction between a hydroxylic solvent and a tertiary aliphatic carbonium ion requires little or no activation energy, but merely the collapse of a solvation shell upon the carbonium ion centre.[11] Thus the chance of capture by a water rather than by a methanol molecule depends upon the nature of the solvation shell rather than upon the carbonium ion, and with comparatively small amounts of water it seems that the composition of the solvation shell of the carbonium ion is similar to that of the solvent.

As might be expected, the relative reactivities of water and methanol towards the carbonium ion (VIII) do not depend markedly on temperature (Table 1), although our analyses would not detect small changes.   But an increase in the lyate ion concentration decreases the ratio of alcohol to ether in the solvolysis of isobornyl chloride (I) in 9 : 1 v/v methanol–water at 25°; *e.g.*, with [OR$^-$] = 0·2M, ether/alcohol $\approx$ 3, and with [OR$^-$] = 0·5M, ether/alcohol $\approx$ 6.   If the lyate ions, and their counter-ions, are solvated more by water than by methanol they will reduce the number of water molecules in the solvation shell of the carbonium ion relative to the number of methanol molecules.   The chance of the carbonium ion's reacting with methanol rather than water will then be increased.

[11] Bateman, Church, Hughes, Ingold, and Taher, *J.*, 1940, 979.
[12] Ref. 1*b*, p. 463.
[13] Shiner, *J. Amer. Chem. Soc.*, 1953, **75**, 2925; Boozer and Lewis, *ibid.*, 1954, **76**, 794; Silver, *ibid.*, 1961, **83**, 3482.
[14] Olson and Halford, *J. Amer. Chem. Soc.*, 1937, **59**, 2644; Bateman, Hughes, and Ingold, *J.*, 1938, 881.

Mercuric chloride also increases the ether/alcohol ratio, presumably because like the lyate ion it is solvated more by water than by methanol.

The constancy of the ratio of elimination to substitution with the addition of small amounts of water to methanol is readily understandable. Methanol is a stronger acid than water,[15] and therefore methoxide ion will still be the predominant lyate ion in 9 : 1 v/v methanol–water. Thus the reagent responsible for elimination will be the methoxide ion in both solvents, and, because water and methanol have similar reactivities towards the carbonium ion, the relative rates of elimination and substitution should be unaffected by addition of small amounts of water to methanol. If this explanation is correct, water–ethanol mixtures should behave differently, because ethanol is a weaker acid than water.[15]

Addition of 1,2-dimethoxyethane sharply increases the amount of elimination; *e.g.*, at 25° with [OMe⁻] = 0·2M, elimination/substitution = 0·28 in methanol, and 8·1 in 1 : 4 v/v methanol–1,2-dimethoxyethane. Addition of the ether could affect the ratio of elimination to substitution in two ways: (i) The ether could accept a hydrogen bond from the methanol, and therefore reduce the amount of hydrogen bonding between it and the methoxide ion; it would then increase the reactivity of the latter[16] and therefore the relative amount of elimination (we assume that addition of 1,2-dimethoxyethane to methanol will not reduce the dielectric constant so much that ion-pairing between methoxide ion and its counter-ion deactivates the methoxide ion). (ii) The ether could solvate the carbonium ion,[17] and so shield it from addition of a methanol molecule, without hindering elimination of a proton from it. Shielding by an ether molecule should be particularly effective upon a bicyclic carbonium ion which can be attacked readily from one direction only.

Rates.—The relative reactivities which we observe (p. 661) are similar to those found for solvolyses in ethanol or aqueous ethanol,[1a] and the relative reactivities of bicyclic and open-chain chlorides differ similarly; *e.g.*, in ethanol at 0° camphene hydrochloride (III) is *ca.* 6000 times more reactive than t-butyl chloride,[1a] and *ca.* 20,000 times more reactive at 25° in methanol (Table 2 and ref. 14).

It is necessary to consider the kinetic effects of changes in (i) environment and (ii) structure.

(i) The kinetic solvent effects are those predicted for an S_N1 solvolysis of an alkyl halide; *e.g.*, addition of 10 vol. % of water to methanol increases the rate of solvolysis of isobornyl chloride (I) at 35·1° 4·5-fold, and of bornyl chloride (II) at 126° 3-fold; the corresponding value is 7-fold at 25° for t-butyl chloride.[14] Methanolysis of camphene hydrochloride (III) is *ca.* 15 times as fast as ethanolysis (Table 2 and ref. 1a).

The solvolyses are retarded by added lyate ion (Table 2). This behaviour is general for S_N1 reactions of unchanged substrates in hydroxylic solvents (usually aqueous dioxan); it has been observed in hydrolyses of t-butyl nitrate,[18] alkyl halides and sulphonic esters,[19] and triphenylmethyl acetate.[20] In our experiments it was observed for solvolysis in pure methanol as well as in mixed solvents, and it has also been observed in solvolyses of camphene hydrochloride and isobornyl chloride in ethanol and aqueous ethanol.[21]

Lucas and Hammett originally suggested that hydroxide ions might attract water molecules about them, and so " dry " the solvent; other ions could have similar, but usually smaller, effects,[18] which should in general be much smaller than the accelerating,

[15] Bender and Glasson, *J. Amer. Chem. Soc.*, 1959, **81**, 1590; Burns and England, *Tetrahedron Letters*, 1960, No. 24, 1; and references there cited.
[16] Parker, *Quart. Rev.*, 1962, **16**, 163.
[17] Streitweiser and Schaeffer, *J. Amer. Chem. Soc.*, 1957, **79**, 2888, 6233; Streitweiser and Andreades, *ibid.*, 1958, **80**, 6553; Smith and Rao, *J. Org. Chem.*, 1961, **26**, 254.
[18] Lucas and Hammett, *J. Amer. Chem. Soc.*, 1942, **64**, 1928.
[19] (a) Benfey, Hughes, and Ingold, *J.*, 1952, 2488; (b) Duynstee, Grunwald, and Kaplan, *J. Amer. Chem. Soc.*, 1960, **82**, 5654.
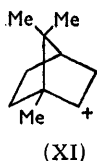[20] Bunton and Konasiewicz, *J.*, 1955, 1354; Swain, Knee, and MacLachan, *J. Amer. Chem. Soc.*, 1960, **82**, 6107.
[21] Smith, Thesis, London, 1952.

ionic-strength effect.[11,22] Benfey, Hughes, and Ingold [19a] considered this retarding effect to be specific to the lyate ion, which destabilises the carbonium ion. The polar transition state and the electrolyte will compete for the solvent molecules; *e.g.*, the rate retardation in either a mixed or pure hydroxylic solvent could arise simply because the hydrogen atoms of the hydroxyl group orient themselves around the lyate ion rather than around the incipient anion in the transition state.

(ii) Rates of overall solvolysis are often less than those of carbonium-ion formation, because the partners may recombine,[11,23] but for bornyl and isobornyl chloride they must be the rates of formation of the carbonium ion because its recapture by a chloride ion should give the highly reactive camphene hydrochloride [4] and therefore be unobservable, as should return from an ion-pair.

Both electronic and steric factors contribute to the high reactivity of isobornyl chloride, but the former are the more important. The polar transition state for the solvolysis of isobornyl chloride can be stabilised by an interaction between the σ-electrons of the 1,6-bond and the cationic centre in the transition state, which will transfer part of the charge to the tertiary carbon atom. Thus we could regard the carbonium ion as a resonance hybrid in which the canonical forms are the classical ions (VIII) and (XI), and because the tertiary ion (VIII) should be the more stable it will contribute more to the structure of a non-classical carbonium ion. This stabilisation of a carbonium ion, or the transition state which precedes it, by interaction with the σ-electrons of an adjacent carbon atom has been called " synartesis ";[1a,b] alternatively it can be regarded as an example of " anchimerism " [24] (stabilisation of a carbonium ion by a neighbouring group). Such interaction of the σ-electrons with the forming carbonium ion can occur without major distortion of the bicyclic system. The transition state for the solvolysis of bornyl chloride cannot be stabilised in this way, because the σ-electrons cannot interact with the carbonium-ion centre until the carbon–chlorine bond is broken. (Interaction between the carbonium-ion centre and the σ-electrons of the 1,7-bond is improbable because it would require formation of a strained four-membered ring and addition of hydrogen chloride to α-pinene gives bornyl chloride, by a rearrangement in which a four-membered expands to a five-membered ring.[3a])

Steric factors may affect the relative stabilities of the initial and the transition state. There is probably a small steric acceleration of the solvolysis of isobornyl relative to bornyl chloride,[25] because the equilibrium mixture in chlorobenzene contains an excess of bornyl chloride.[26] Repulsion between one of the *gem*-dimethyl groups and the chlorine atom in the *exo*-position destabilises isobornyl chloride. Consideration of the rates of solvolysis of *endo*- and *exo*-norbornyl chloride excludes steric acceleration in this reaction;[1c,d] the more stable *exo*-chloride is the more reactive, *i.e.*, it is the less reactive *endo*-chloride whose solvolysis is sterically accelerated.

There remains the possibility that the lower reactivity of bornyl than of isobornyl chloride is caused by steric destabilisation of its transition state, *e.g.*, repulsion of the displaced chloride ion by 5,6-*endo*-hydrogen atoms could hinder ionisation of bornyl and *endo*-norbornyl chloride,[27] *e.g.*, as in (XII).

Evidence for this explanation is that nucleophilic attack upon a norbornanone occurs preferentially from the less hindered *exo*-direction (XIII),[28] and analogy between structures

[22] Ref. 1*b*, p. 360.
[23] Winstein, Smith, and Fainberg, *J. Amer. Chem. Soc.*, 1961, **83**, 618.
[24] Winstein, Lindegren, Marshall, and Ingraham, *J. Amer. Chem. Soc.*, 1953, **75**, 147.
[25] Bunton and Whittaker, *Chem. and Ind.*, 1960, 235.
[26] Meerwein and van Emster, *Ber.*, 1922, **55**, 2506.
[27] Brown, in " The Transition State," *Chem. Soc. Special Publn.*, No. 16, 1962, p. 140, and references cited there.
[28] Berson, Walia, Remanick, Suzuki, Reynolds-Warnhoff, and Willner, *J. Amer. Chem. Soc.*, 1961, **83**, 3986.

of carbonyl compounds and classical carbonium ions suggests that the latter should be attacked from the same direction. Therefore, by the principle of microscopic reversibility, separation of a carbonium and a chloride ion should occur most easily from the *exo*-position. This explanation is untenable when applied to bornyl and isobornyl chloride. Addition to camphor occurs preferentially from the *endo*-direction (XIV), because the

(XII)   (XIII)   (XIV)
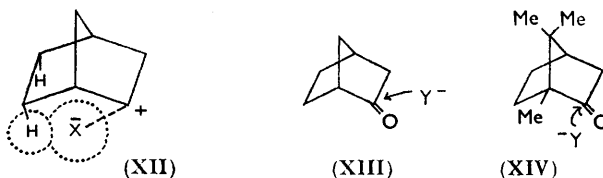
gem-dimethyl groups hinder attack from the *exo*-direction.[28] Therefore if the transition states for ionisation of bornyl and isobornyl chloride were markedly affected by steric factors it is that for isobornyl chloride which would be destabilised most. We conclude that steric factors play a minor role, and that electronic factors are the more important.

Although the rates of ionisation of the *endo*-isomers, bornyl and *endo*-norbornyl chloride, are very similar, isobornyl is much more reactive than *exo*-norbornyl chloride; *e.g.*, $k_{exo}/k_{endo} \approx 10^5$ for isobornyl and bornyl chloride, and 10^2—10^3 for the norbornyl chlorides or sulphonic esters.[1] Both steric factors and non-classical interactions contribute to these rate differences, because interference between the *gem*-dimethyl groups and the displaced group should speed ionisation of isobornyl chloride (I),[25] and delocalisation of the positive charge transfers it in part to a tertiary carbon atom, whereas in the *exo*-norbornyl system it is delocalised over two secondary carbon atoms.[1]

These conclusions about the structures of the transition states for solvolysis are strengthened by consideration of the products. The first-formed substitution product is always camphene hydrate or its derivative (Table 1), which rearranges in acid to an isobornyl, not a bornyl compound, and nucleophilic attack upon the norbornyl carbonium ion always gives an *exo*-product; [1c,d] *i.e.*, attack is always from the *exo*-direction irrespective of substituents which may sterically hinder attack. Therefore, non-classical interactions must control both the preferred direction of nucleophilic attack upon the carbonium ion, and the accelerated ionisation of the *exo*-chlorides.

Our results, by themselves, do not differentiate between a single non-classical structure for the carbonium ion and rapidly equilibriating classical carbonium ions, because the products are determined by the transition states for carbonium-ion capture rather than by the structure of the carbonium ion. Differentiation between these possibilities can be made only by physical measurements (cf. ref. 29), but unfortunately these can only be made upon the more stable carbonium ions which are inevitably of the least interest to the kineticist. However, whatever picture of the carbonium-ion structure is correct, the positive charge is located largely upon the most alkylated carbon atom, nucleophilic attack is preferentially upon this atom,[30] and the rates of reaction are controlled by electronic rather than steric factors.

EXPERIMENTAL

Materials.—Camphene and α-pinene were commercial samples. Commercial camphene usually contains tricyclene; we selected samples which were comparatively free from this material, or prepared pure camphene by dehydration of purified isoborneol with zinc chloride. Purity was tested by gas–liquid chromatography, and infrared spectra were compared with those of samples which themselves had been purified by gas–liquid chromatography. Camphene was converted into camphene hydrochloride by passing dry hydrogen chloride into a dry ethereal solution at 0°. Camphene hydrochloride is so unstable that we did not attempt

[29] von Schleyer, Kleinfelter, and Richey, *J. Amer. Chem. Soc.*, 1963, **85**, 479.
[30] Berson, *Tetrahedron Letters*, 1960, No. 16, p. 17.

to purify it, but used it immediately, or stored it for short times at $-80°$. Isobornyl chloride was prepared by rearrangement of camphene hydrochloride in dry, refluxing methylene chloride, or more conveniently in liquid sulphur dioxide. It could also be prepared by passing dry hydrogen chloride into a solution of camphene in liquid sulphur dioxide. It was recrystallised from pentan-1-ol and methylene chloride.

Bornyl chloride was prepared from hydrogen chloride and α-pinene. The crude bornyl chloride was recrystallised from pentan-1-ol and methylene chloride. Occasionally recrystallisation gave sticky crystals; we then distilled the bornyl chloride under reduced pressure before recrystallisation. Methanol was dried over magnesium by Bjerrum's method,[31] or by passing it through a column of molecular sieve 4A. 1,2-Dimethoxyethane was dried over sodium wire and distilled. Dioxan was purified by standard methods.[31] Silver oxide was prepared by treating silver nitrate with lithium or sodium methoxide in methanol.

Determination of Products.—Kinetically controlled conditions were used, with ∼0·1M-alkyl chloride. After reaction, water was added, the excess of acid, if any, was neutralised, and the organic products were extracted in a small continuous-extractor with redistilled pentane. Control experiments were made to determine the conditions necessary for complete reaction; *e.g.*, solvolysis of isobornyl chloride in 9 : 1 v/v methanol–water containing mercuric chloride was complete in 10 min. at 25°, and solvolyses with added silver oxide were complete in 1 day.

Camphene hydrochloride is always contaminated by camphene and isobornyl chloride. We treated camphene with hydrogen chloride for a time sufficient for nearly all of it to be converted into its hydrochloride, but inevitably this meant that appreciable amounts of isobornyl chloride ($<10\%$) were formed by rearrangement, but $<1\%$ of camphene was present. Camphene is the more objectionable impurity, because it complicates determination of the product composition. Isobornyl chloride does not react in the time required for solvolysis of camphene hydrochloride, but it is hydrolysed by water during the continuous extraction. Hydrolysis gives mainly camphene hydrate which does not interfere with determination of the products of methanolysis. The purity of the camphene hydrochloride was tested by titration,[26] and by infrared spectroscopy; these precautions were not taken in our preliminary experiments.[3b] The experiments in aqueous dioxan are unreliable for this reason, and because the solubility of the chloride is very low in this solvent.

The products were separated by gas–liquid chromatography on a 6-ft. Tween–Celite column at 120°, with nitrogen as carrier gas. (Silicone oil was the stationary phase in the early experiments;[3b] separation was then sometimes unsatisfactory because rearrangements occurred on the column.) Our present experiments, with a Tween–Celite column, show that $<1\%$ of isobornyl methyl ether is formed during solvolysis in alkali. The katharometer detector was calibrated by means of known samples. In some experiments the individual samples were trapped and identified by their infrared spectra. The products were stable under the reaction conditions in the presence of silver oxide or mercuric chloride.

Kinetics.—Reaction was carried out in stoppered flasks at low temperatures, and in sealed glass or silver tubes at high temperatures. Silver tubes were used for strongly alkaline solutions. Reaction was followed by acid–base titration, or by potentiometric titration of chloride ion with silver nitrate.

In the first method a tube was opened under acetone, or the contents of a pipette were added to acetone, to stop the reaction. The acetone was cooled to $-80°$ for the experiments with isobornyl chloride. The acid produced from isobornyl chloride was titrated with sodium ethoxide in ethanol, with lacmoid as indicator. For some of the camphene hydrochloride runs samples were withdrawn directly from the reaction vessel at 0°, into a jacketed pipette, which delivered a given volume into acetone at $-80°$. These samples were titrated with sodium methoxide in 50% dioxan–methanol. For other of the camphene hydrochloride runs a standard solution of sodium methoxide in dry methanol was added directly to the reacting solution, again with lacmoid as indicator. Provided that there is little dilution of the reaction solution by the titrant this procedure does not destroy the kinetic form of the run; we therefore used dilute solutions of camphene hydrochloride (0·05M), and more concentrated solutions of sodium methoxide. Water was excluded by the use of drying tubes in all these experiments with camphene hydrochloride.

For runs in dilute alkali the excess of alkali was titrated against acid, or samples were added

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[31] Vogel, " Practical Organic Chemistry," Longmans, Green, London, 1948, Ch. II.

to an excess of acid and this excess was back-titrated with alkali. Freshly prepared solutions of hydrogen chloride in methanol were used for the reactive chlorides.

Acid–base titration cannot be used with a large excess of alkali. Potentiometric titration of chloride ions with silver nitrate was therefore used. Unchanged isobornyl chloride was extracted before addition of silver nitrate. Portions of the reaction mixture were added to pentane, and the inorganic chloride was then extracted with water; the aqueous-alcoholic layer was acidified with dilute nitric acid and the chloride titrated against silver nitrate. This procedure could not be used with the very reactive camphene hydrochloride.

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