Allylic Carbonium Ions. Part II.[1] Solvolysis and Cyclisation of Some Monoterpene 2,4-Dinitrophenyl Ethers

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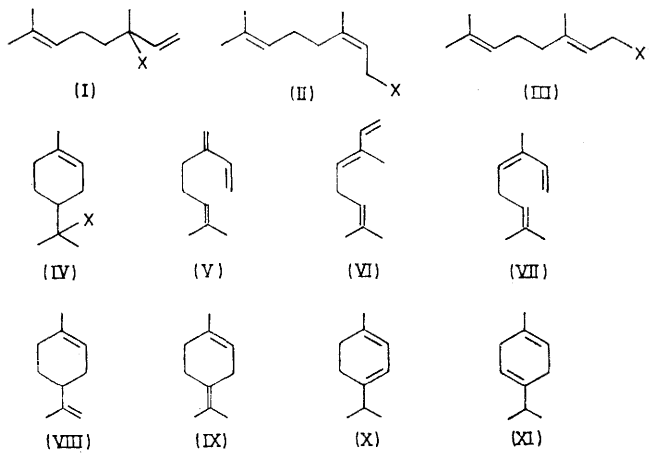
The acetolyses of the 2,4-dinitrophenolates of nerol, geraniol, linalool, and α-terpineol are examined. Rates of reaction under various conditions are reported, and products are identified and analysed. Suggestions are made for harmonising proposals made earlier for solvolyses in other solvents and involving other leaving groups. The detailed mechanism of the acetolysis process is considered in terms of the Ingold S_N1–S_N2 and the Sneen ion-pair hypotheses, and difficulties encountered by either of these schemes are discussed.

THE acid-catalysed cyclisations of linalool (Ia) [2] and of nerol (IIa) [3] to menthane derivatives are among the earliest known examples of such processes in terpene chemistry, and two attempts have been made to link them to theories of nucleophilic intramolecular participation in cationic intermediates. Winstein *et al.*[4] have studied the solvolysis of the two *p*-nitrobenzoates (Ib) and (IIb), and those of geraniol and α-terpineol (IIIb) and (IVb), in aqueous acetone, and clarified the complex kinetic behaviour of the linalool derivative. They have also analysed the products from the last ester (only). Cramer and Rittersdorf have examined [5a] the rate and products of the solvolysis of the phosphates and pyrophosphates of the same alcohols, *e.g.* (Ic)—(IVc), in strongly acid aqueous solution, and compared their behaviour with allylic analogues lacking the remote double bond.[5b] Both groups have shown that the cyclisation of the linalyl derivative (I) involves, in effect, a *syn*-S_N2' substitution by the remote double bond, giving α-terpinyl derivatives with high stereospecificity.

[1] Part I, K. B. Astin and M. C. Whiting, preceding paper.
[2] O. Zeitschel, *Ber.*, 1906, **39**, 1780.
[3] K. Stephan, *J. prakt. Chem.*, 1898, **58**, 109.
[4] S. Winstein, S. Valkanas, and C. F. Wilcox, jun., *J. Amer. Chem. Soc.*, 1972, **94**, 2286.
[5] F. Cramer and W. Rittersdorf, *Tetrahedron* (*a*) 1967, **23**, 3015; (*b*) 1968, **24**, 43.

Bunton *et al.*[6] have reported hydrogen kinetic isotope effects at various positions in the solvolysis of the two



a; X = OH
b; X = $OCOC_6H_4NO_2$
c; X = $OPO(OH)_2$
d; X = $OC_6H_3(NO_2)_2$
e; X = Cl
f; X = OAc

primary chlorides (IIe) and (IIIe) in aqueous acetone, and partial product analyses. We now describe work on the acetolysis of the four 2,4-dinitrophenyl ethers (Id)—(IVd), intended to resolve an important difference between the conclusions of the first two groups and to relate the system to extensive work on nucleophilic participation of neighbouring groups by Winstein,[7] and to theories on the competition between solvent molecules and external nucleophiles.

The preparation and properties of the four dinitrophenyl ethers required are summarised in Table 1; the geranyl and linaloyl derivatives were crystalline. The advantages of the potassium hydride method of arylation [1] are evident. The rates of acetolysis and activation parameters are given in Table 2. In all cases good first-order behaviour was observed, as expected from the large reactivity ratio between the linaloyl ether and the others. A small amount (10%) of rearrangement accompanied the acetolysis of this compound. The main point of interest, however, is the unusually negative entropy of activation of the neryl ether (IId). In a primary derivative solvolysing in a pure solvent such behaviour invited explanation as the consequence of the localisation of a solvent molecule at the transition state, *i.e.* a bimolecular mechanism.[8] This cannot be the explanation here (a) because the products are inconsistent with such a process, and (b) because, instead of revealing an increased susceptibility to lyate ion concentration,[9] a study of the effect of salts on the rate of acetolysis (Table 3) shows the neryl derivative to be exceptionally insensitive to sodium or tetrabutylammonium acetate (but not to lithium perchlorate) concentrations. Accordingly, we propose that the difference between the geranyl and neryl dinitrophenyl ethers is due mainly to the freezing, in the process of solvolysis with cyclisation, of the two (enantiomeric) conformations allowing this process in the neryl derivative. As a first approximation we may divide the conformations (*i.e.* energy minima) of the neryl and geranyl dinitrophenyl ethers into allowed and disallowed, and assume the former to be equally populated; similarly with transition states, that for geranyl dinitrophenyl ether (IIId) being taken to involve simple heterolysis without the localisation of a solvent molecule, while that for the neryl ether (IId) requires an intramolecular S_N2 reaction. If the numbers of allowed conformations are n_n, n_g, $n_n^{\ddagger}$ and $n_g^{\ddagger}$, then the combinatorial component of the difference in $\Delta S^{\ddagger}$ between geranyl and neryl dinitrophenyl ethers should be R ln $(n_n\, n_g^{\ddagger}/n_g\, n_n^{\ddagger})$; of the approximations involved, most cancel out, leaving a predicted value of R ln $(44 \times 38/57 \times 2) = 22$ J (5.4 cal) K mol^{-1}, which, according to our assessment of molecular models, is of the right order of magnitude. The effect on observed entropies of activation of the cyclisation of a hydrocarbon chain has been discussed by Kohnstam and Penty,[10] and a general discussion of combinatorial entropies is given by Gordon and Temple.[11]

Indirect evidence against a bimolecular–unimolecular difference between the acetolysis of neryl and geranyl 2,4-dinitrophenyl ethers comes from the relationship between solvent composition and rate [12] in the aqueous ethanolysis of these compounds, and of linaloyl and t-butyl dinitrophenyl ethers (Table 4). The products

TABLE 1

2,4-Dinitrophenyl ethers synthesised

Ether	Synthesis method and yield (%)	M.p. (°C)	Found [d] (%) C	H	N	$\lambda_{max.}$/nm (iso-octane)
(IIId)	56,[a] 57 [a]	31—33	59.8	6.5	9.1	284.5
(IId)	62 [a]	Oil	60.0	6.4	9.0	284.0
(Id)	6,[c] 3,[c] 50 [b]	35—36	60.1	6.6	8.5	287.0
(IVd)	57 [b]	Oil	59.75	6.1	9.0	283.0

[a] Diazabicyclo[2.2.2]octane method.[21] [b] Potassium hydride method.[1] [c] Phenyl-lithium method.[18] [d] $C_{16}H_{20}O_5N_2$ requires C, 60.0; H, 6.25; N, 8.75%.

[6] C. A. Bunton, J. P. Leresche, and D. Hachey, *Tetrahedron Letters*, 1972, 2431.
[7] S. Winstein, *Experientia Suppl. No.* 2, 1955, 137.
[8] R. E. Robertson and J. M. W. Scott, *J. Chem. Soc.*, 1961, 1596.
[9] A. Streitwieser, jun., *Chem. Rev.*, 1956, **56**, 585.
[10] G. Kohnstam and M. Penty, 'Hydrogen Bonded Solvent Systems,' Proc. Symp. eds. A. K. Covington and P. Jones, 1968, p. 275.
[11] M. Gordon and W. B. Temple, *J. Chem. Soc.* (*A*), 1970, 729.
[12] S. Winstein and E. Grunwald, *J. Amer. Chem. Soc.*, 1948, **70**, 828.

TABLE 2

Acetolysis rates for dinitrophenyl ethers

Compound	t/°C	k/s^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1} (kcal mol^{-1}) at 100°	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1} (cal K^{-1} mol^{-1}) at 100°
(IVd)	61.7 ± 0.1	(1.45 ± 0.06) × 10^{-5}	114.7 ± 1.7	−1.7 ± 4.6
	61.7 ± 0.1	(1.42 ± 0.02) × 10^{-5}	(27.3 ± 0.4)	(−0.4 ± 1.1)
	73.55 ± 0.1	(5.62 ± 0.10) × 10^{-5}		
	73.55 ± 0.1	(6.09 ± 0.16) × 10^{-5}		
	73.55 ± 0.1	(5.91 ± 0.16) × 10^{-5}		
	82.25 ± 0.1	(2.21 ± 0.04) × 10^{-4}		
	82.25 ± 0.1	(2.36 ± 0.06) × 10^{-4}		
	100.0	(6.70 ± 0.24) × 10^{-4} [a]		
(IId)	61.2 ± 0.1	(2.62 ± 0.08) × 10^{-5}	98.7 ± 1.8	−42.0 ± 5.3
	61.2 ± 0.1	(2.61 ± 0.10) × 10^{-5}	(23.6 ± 0.4)	(−10.0 ± 1.3)
	61.2 ± 0.1	(2.73 ± 0.09) × 10^{-5}		
	61.2 ± 0.1	(2.89 ± 0.09) × 10^{-5}		
	73.0 ± 0.1	(8.57 ± 0.18) × 10^{-5}		
	73.0 ± 0.1	(8.44 ± 0.17) × 10^{-5}		
	73.0 ± 0.1	(9.01 ± 0.20) × 10^{-5}		
	86.6 ± 0.1	(3.64 ± 0.14) × 10^{-4}		
	86.6 ± 0.1	(3.79 ± 0.05) × 10^{-4}		
	86.6 ± 0.1	(2.96 ± 0.12) × 10^{-4}		
	86.6 ± 0.1	(3.44 ± 0.05) × 10^{-4}		
	100.0	(7.46 ± 0.34) × 10^{-4} [a]		
(IIId)	63.0 ± 0.1	(1.05 ± 0.02) × 10^{-5}	114.1 ± 2.1	−5.8 ± 6.1
	63.0 ± 0.1	(1.04 ± 0.03) × 10^{-5}	(27.3 ± 0.5)	(−1.4 ± 1.5)
	63.0 ± 0.1	(1.03 ± 0.03) × 10^{-5}		
	73.0 ± 0.1	(3.89 ± 0.20) × 10^{-5}		
	73.0 ± 0.1	(3.29 ± 0.20) × 10^{-5}		
	73.0 ± 0.1	(3.25 ± 0.15) × 10^{-5}		
	86.6 ± 0.1	(1.60 ± 0.04) × 10^{-4}		
	86.6 ± 0.1	(1.51 ± 0.02) × 10^{-4}		
	86.6 ± 0.1	(1.79 ± 0.08) × 10^{-4}		
	86.6 ± 0.1	(1.61 ± 0.03) × 10^{-4}		
	100.0	(4.16 ± 0.22) × 10^{-4} [a]		
(Id)	34.1 ± 0.05	(4.17 ± 0.05) × 10^{-5}	97.8 ± 3.2	−10.8 ± 9.9
	41.3 ± 0.05	(9.47 ± 0.04) × 10^{-5}	(23.4 ± 0.8)	(−2.6 ± 2.4)
	51.1 ± 0.05	(3.09 ± 0.04) × 10^{-4}		
	60.2 ± 0.05	(7.89 ± 0.05) × 10^{-4}		
	100.0	(4.32 ± 0.75) × 10^{-2} [a]		

[a] Extrapolated from $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values at 100°.

TABLE 3

Salt effects in acetic acid

	NaOAc		$(Bu^n)_4NOAc$–HOAc		$LiClO_4$	
Compound	b [c]	t/°C [a]	b	t/°C [a]	b	t/°C [a]
Linaloyl 2,4-dinitrophenyl ether	1.8 ± 0.1	58.8	3.3 ± 0.2	48.5	6.4 ± 0.5	59.0
Neryl 2,4-dinitrophenyl ether	0.6 ± 0.3	85.0	2.9 ± 0.4	85.0	10.2 ± 0.8	95.9
Geranyl 2,4-dinitrophenyl ether	3.0 ± 0.2	101.5	6.5 ± 0.3	85.0	8.2 ± 0.4	100.2
t-Butyl 2,4-dinitrophenyl ether	4.0 ± 0.3 [b]	108.8	8.6 ± 0.7	91.5	17.3 ± 1.5	103.2

[a] ±0.1°. [b] Page *et al.*[18] report a b value of 4 ± 1. [c] Standard deviations shown.

from these solvolyses and the temperature dependence of rates have not, however, been examined, and it is possible that under these conditions little cyclisation occurs and there is little difference in entropy of activation.

In the acetolysis of linaloyl 2,4-dinitrophenyl ether (Id), *ca.* 10% of the product proved to be a mixture of geranyl, neryl, and α-terpinyl dinitrophenyl ethers (46.5 : 24.5 : 29); these were analysed by u.v. spectrophotometry, followed by cleavage with piperidine and g.l.c. The first two products are, presumably, formed *via* a Braude–Jones intermediate [14] as discussed in Part I; [1] the last *via* a cyclised ion-pair, not necessarily with the same conformational preference as that giving rise to α-terpinyl acetate.

[13] P. R. Luton, Ph.D. Thesis, University of Bristol, 1972.
[14] E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 1944, 436.

The acetate and olefin acetolysis products are listed in Table 5. No rigorous attempt was made to obtain kinetically controlled mixtures, as this would be difficult because of the high solvolytic reactivity of linaloyl

TABLE 4

m Values

Compound	t/°C [a]	m Value [12]	kROH/kHOAc [c]
t-Butyl 2,4-dinitrophenyl ether	74.20	0.48 [b]	0.6 [b]
Linaloyl 2,4-dinitrophenyl ether	42.25	0.45 ± 0.01	0.28
Neryl 2,4-dinitrophenyl ether	73.70	0.41 ± 0.01	0.37
Geranyl 2,4-dinitrophenyl ether	73.70	0.42 ± 0.015	0.94

[a] ±0.1°. [b] Ref. 13. [c] kROH is the rate of solvolysis in ethanol–water of the y value [12] equal to that of acetic acid.

acetate, which resembles that of αα-dimethylallyl esters.[1] Instead, products at *ca.* 10% reaction are tabulated. Clearly, geranyl dinitrophenyl ether gives a mixture of geranyl and linaloyl acetates, but little neryl acetate or cyclic products, in the initial phase of the reaction, while neryl dinitrophenyl ether gives little geranyl acetate. When an attempt was made to correct for the products expected from the subsequent acetolysis of the linaloyl acetate initially formed, however, the small yields that were obtained of neryl acetate and of cyclic products from geranyl dinitrophenyl ether, and of geranyl acetate from neryl dinitrophenyl ether, were not at all completely accounted for. We therefore conclude that some linaloyl dinitrophenyl ether is formed from the primary isomers by ion-pair return (as, of course, the law of microscopic reversibility requires) and subsequently rapidly solvolysed. The same thing may well have happened also in the case of the *p*-nitrobenzoate in aqueous acetone,[4] but probably not in that of the phosphates in water.[5] Thus, we may still assume that allylic carbonium ions maintain their geometrical integrity in these solvolyses, as in the other systems studied.[4,5] The C_{10} compounds show lower substitution : elimination ratios than do their C_5 analogues in similar conditions;[1] this reflects the greater stability of the more substituted olefins they give rise to. The substitution : elimination ratio is much lower than in the more polar solvents investigated earlier, again a difference with well known precedents.[15] The residual rotation remaining after the almost complete acetolysis of (−)-(*R*)-linaloyl dinitrophenyl ether implies that the main optically active compound formed, α-terpinyl acetate, has predominantly the (+)-(*R*)-configuration, as in other systems studied earlier.[4,5b] The similar proportion of the three cyclic products obtained from the three dinitrophenyl ethers (Id), (IId), and (IVd) indicate that the ion-pairs involved differ little in (average) geometry; apart from the expected tendency to a lower substitution : elimination ratio at higher temperature, some minor differences in product ratio are to be expected from memory effects.[16]

The olefinic reaction products were studied less thoroughly than the acetates, considering the potential complexity of the mixture; three acyclic olefins (V)—(VII) and four cyclic compounds (VIII)—(XI) were deemed possible products. Our identification of the peaks observed is based on the retention times tabulated by Cramer and Rittersdorf.[5a] Although we used a 50 ft support-coated open-tubular column working at *ca.* 10 000 plates, we observed no others. We did not prepare α- and γ-terpinenes (X) and (XI) to prove them absent; we would, however, have expected at least a partial resolution of these hydrocarbons from limonene (VIII) and terpinolene (IX), respectively. Our results agree as well as could be expected, given the considerable difference in solvolysis solvent, with those of the German workers. These and ours, however, disagree sharply with those published by Winstein *et al.*,[4] who report the absence of *cis*-ocimene (VII), and do not even discuss the possible presence of *trans*-ocimene (VI), in the solvolysis products from linaloyl *p*-nitrobenzoate in 70% aqueous acetone. These acyclic compounds are absent from the product mixture from the α-terpinyl derivatives, but are major components of the elimination products from the linaloyl derivatives, in both Cramer and Rittersdorf's work in water and ours in acetic acid. They are formed, as would be expected, in higher yield from geranyl than from neryl derivatives, again in both Cramer and Rittersdorf's work[5] and ours. On the other hand, Winstein *et al.*[4] report γ-terpinene (XI) as a major product; the German workers observed only a minute yield of α- + γ-terpinenes (*ca.* 0.05%) in water, and we did not detect any (yield <2%) in acetic acid. The retention indices of the olefins on the nitropimelonitrile column used by Winstein *et al.* are not published, but were they to resemble those on polyethylene glycol,[5a] *trans*-ocimene (VI) might have been mis-identified as γ-terpinene (XI), and *cis*-

TABLE 5

Products (%) of solvolysis reactions of monoterpene derivatives

	Substrate										
Product	(Ic)	(Ib)	(Id)	(IIc)	(IIe)	(IId)	(IIIc)	(IIIe)	(IIId)	(IVc)	(IVd)
(I)	63.4	18.9	8.7	26.6	17	5.4	76.3	70	16.5		
(II)	3.8	2.4	4.1	6.0	3	10.1	0.3		0.5		
(III)	11.6	6.1	11.3	0.5		0.9	18.5	16	43.0		
(IV)	17.7	7.2	12.6	61.5	78	25.7	1.5	6	1.1	80.7	39.5
(V)	0.65	12.5	22.0	0.45		4.7	1.25		18.9		
(VI)	1.0	*	11.8	0.25	1	1.2	1.1	3	9.9		
(VII)	0.5	*	7.9	0.1		0.8	0.7		6.9		
(VIII)	0.6	1.2 *	8.6	2.2	1	38.9	0.2	4	2.4	10.3	42.8
(IX)	0.5	8.5 *	2.9	1.7		12.3	0.07		0.7	7.7	17.7
(X) + (XI)	0.03	4.8 *								0.4	
(IIb, d)		11.0	2.6								
(IIIb, d)		22.0	4.6								
(IVb, d)		4.9	2.9								
Elimination (%)	3.3	27.0	53.2	4.7	2	57.9	3.3	7	38.9	18.4	60.5
Cyclisation (%)	18.8	26.6	27.0	65.4	79	76.9	1.8	10	4.2		

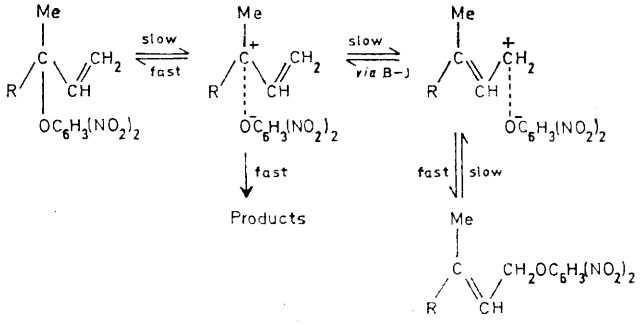
* See text.

[15] S. Winstein and M. Cocivera, *J. Amer. Chem. Soc.*, 1963, **85**, 1702.

[16] J. A. Berson and J. J. Gajewski, *J. Amer. Chem. Soc.*, 1964, **86**, 5020.

ocimene could have co-chromatographed with it or with limonene. In this case the results in 70% acetone would have agreed broadly with those in water and in acetic acid, the need to postulate extensive hydride shift in the newly formed α-terpinyl cation [4] would vanish, and the estimate for the degree of cyclisation in aqueous acetone would fall by 6—12%. We suggest that this emendation of the work of Winstein *et al.*[4] be considered as possibly correct.

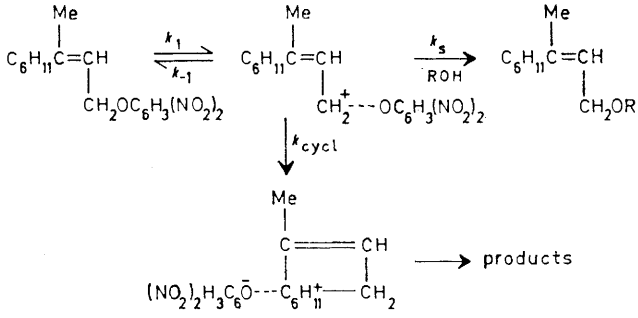
The detailed mechanism of these solvolyses presents points of general interest. Sneen *et al.*[17] have discussed allylic solvolyses in terms of 'intimate ion-pairs' in



SCHEME 1 B–J = Braude–Jones intermediate

which the counterion remains associated with the carbon atom to which it was originally attached, and a solvent-separated ion-pair in which this association is lost. The Braude–Jones intermediate is replaced by a transition state between the two intimate ion-pairs. In the present example, the Braude–Jones intermediate cannot be involved in the main linaloyl$^+$ ⟶ α-terpinyl$^+$ process, since in all three solvent systems this process occurs [5b] with preferred *syn*-stereochemistry, as expected for S_N2' substitution. A comparison of the rate data for linaloyl and 1,1-dimethylallyl dinitrophenyl ethers reveals no significant difference, apart from an advantage (factor 1.3—1.5 at 50°) for the former, smaller than that for t-pentyl over t-butyl dinitrophenyl ether [18] (*ca.* 2.5 at 75°) and attributable to a steric effect. Indeed, the steric acceleration may be larger than 1.3—1.5, but reduced to this factor by the electronic retardation caused by the remote olefinic linkage.[5] Thus, Scheme 1 is an acceptable description of the behaviour of the linaloyl and 1,1-dimethylallyl dinitrophenyl ethers. Presumably the reactions of the C_{10} tertiary intimate ion-pair are: return to starting material without racemisation; three elimination processes, giving olefins (V)—(VII); substitution with inversion, giving linaloyl acetate; rearrangement to the two primary intimate ion-pairs *via* transition-states corresponding to the Braude–Jones intermediate; dissociation to a solvent-separated delocalised ion-pair; and, in a conformer of low combinatorial probability and high enthalpy, and therefore present in very low concentration, rapid substitution by the isobutenyl carbon atom at the primary allylic centre, simulating the classical S_N2' process and giving a classical α-terpinyl cation as an ion-pair of some sort. This last process corresponds to the reaction, 3-chlorobut-1-ene ⟶ 1-phenoxybut-2-ene, proved by Sneen and Carter [17c] to be bimolecular, but when it is partly complete the entering and leaving groups will in this case have opposite partial charges, which should favour *syn*-geometry.[19] The delocalised, solvent-separated ion-pair would give rise to neryl and geranyl acetates and linaloyl acetate of retained configuration (and olefins?) but as a higher energy intermediate it is unlikely to give much cyclic product, which demands a low probability conformation; if it did, it would probably cyclise with an opposite steric preference to the intimate ion-pair. In our work stereochemical results were not measured, but in aqueous acetone [4] the specificity of the cyclisation was 50—90%, and the linalool recovered showed a 60 : 40 preference for retained configuration. In water, the specificity of the cyclisation process was 70% while the recovered linalool was racemic.[5b]

Turning to the acetolysis of neryl dinitrophenyl ether, the main feature to require explanation is the significant driving force associated with cyclisation. Although the conformer needed for this process has two *gauche*-butane interactions, and some other distortions, which must place it at least 6 kJ mol^{-1} above the extended conformer, the observed enthalpy of activation is lower by 21 and 15 kJ mol^{-1} than those of 3,3-dimethylallyl and geranyl 2,4-dinitrophenyl ethers. This difference must be associated with partial bonding in the incipiently cyclic transition state; on Sneen's hypotheses,[17a] it must imply the suppression of the process of ion-pair collapse from the localised neryl ion-pair back to covalent substrate, by rapid intramolecular substitution, an equivalent of external attack by azide ion. That is, using



SCHEME 2

Sneen's mechanism and replacing his term for bimolecular attack by azide on an ion-pair, $k_N[N]$ by the unimolecular term k_{cycl} (Scheme 2) we can explain the accelerated reaction rate of the neryl derivative only if Sneen's term $x(=k_{-1}/k_s)$ is large. This hypothesis explains Bunton's kinetic isotope effects [6] and the

[17] (*a*) R. A. Sneen and W. A. Bradley, *J. Amer. Chem. Soc.*, 1972, **94**, 6975; (*b*) R. A. Sneen and P. S. Kay, *ibid.*, p. 6983; (*c*) R. A. Sneen and J. V. Carter, *ibid.*, p. 6990.

[18] I. D. Page, J. R. Pritt, and M. C. Whiting, *J.C.S. Perkin II*, 1972, 906.

[19] I. Bell, R. Madroñero, and M. C. Whiting, *J. Chem. Soc.*, 1958, 3195.

difference in entropy of activation between the neryl and geranyl systems, but it also poses problems. One might expect the usual concommitants of a bimolecular solvolysis mechanism, as observed in simple primary aliphatic systems, *e.g.* a large negative entropy of activation, sensitivity to lyate ion concentration, *etc.*, and in the geranyl and 3,3-dimethylallyl dinitrophenyl ether acetolyses one does not find them. However, there are perhaps even worse problems if we abandon Sneen's mechanisms in favour of simultaneous classical S_N1 and S_N2 processes. Above all, why should the ratio of cyclic products (S_N2 by the remote group) to acyclic products (S_N1 process) occur in a ratio varying only from 1.9 in water to 3.3 in acetic acid? As Sneen says, ' The competitive formation of diverse products under varying conditions should be recognised generally as good suggestive evidence for the intervention of high energy unselective intermediates in the reaction pathway '. Steady-state treatment of the above scheme allows an estimate of x. If the rate of the unassisted process is taken to be that of the geranyl ether (*cf.* Sneen's ' no salt rate ' [17]), then $x = 1.7$; if, more realistically, we assume the geranyl ether reacts more rapidly than the hypothetical unassisted neryl ether, and use the factor of 1.45 observed by Cramer and Rittersdorf [5b] for the 6,7-dihydroneryl phosphate rate ratio, one deduces an x value of 5.0 (both x values obtained from product data at 95°). Clearly the examination of such cyclising solvolyses should in principle permit a test of Sneen's mechanism, or other similar schemes, in solvents in which convenient external reagents like N_3^- or CNS^- are unavailable. The problem of estimating what the rate of solvolysis would be if cyclisation did not occur may hinder a fully quantitative treatment, but if a set of compounds $NCH_2CH_2CMe{=}CH{\cdot}CH_2X$ were available, where the nucleophilicity of N varied, the variation in rate and in degree of cyclisation should lead to a set of consistent values for k_1/k_{-1} if the Sneen mechanism applies. We suspect, however, that wider generalisation of the theoretical depiction of ' borderline ' solvolysis–substitution is now called for, the Ingold and Sneen descriptions probably emerging as special cases.

EXPERIMENTAL

Solvents.—Tetrahydrofuran was dried by distillation from lithium aluminium hydride, diethyl ether by shaking vigorously overnight with freshly prepared sodium wire, acetic acid by distillation of commercial glacial acetic acid from freshly prepared tetra-acetyl diborate, and ethanol by distillation from magnesium ethoxide.[20] The alcohols used, and linaloyl and α-terpinyl acetates, were commercially available.

Primary 2,4-dinitrophenyl ethers were prepared by the reaction of the alcohol with 1-fluoro-2,4-dinitrobenzene and 1,4-diazabicyclo[2.2.2]octane.[21] Tertiary 2,4-dinitrophenyl ethers were prepared in variable yield by the reaction of the lithium alkoxide at −78° with 1-fluoro-2,4-dinitrobenzene,[18] and in better yields by the generation of the alkoxide using potassium hydride.[1] Product data and yields are given in Table 1. Neryl and geranyl acetates were prepared by reaction of the alcohol with acetic anhydride in dry pyridine for 1 h at room temperature affording neryl acetate (53%), b.p. 136—140° at 45 mmHg (lit.,[22] 93—94° at 3 mmHg), and geranyl acetate (40%), b.p. 115—120° at 50 mmHg (lit.,[23] 108—113° at 11 mmHg). I.r. and n.m.r. spectra were consistent with expectations.

Product Analyses.—The 2,4-dinitrophenyl ethers were acetolysed for short reaction times involving 5—10% reaction, and quenched with alkaline phosphate solution. The organic material was extracted into ether and dried ($MgSO_4$). The ether solution was concentrated and analysed by g.l.c. (50 ft SCOT Carbowax 20M; 135°).

Determination of Rearranged 2,4-Dinitrophenyl Ethers in the Acetolysis Products of Linaloyl 2,4-Dinitrophenyl Ether.—Linaloyl 2,4-dinitrophenyl ether was acetolysed at 60° for *ca.* 8 half-lives. The mixture was quenched and worked up in analogous fashion to that for 1,1-dimethylallyl 2,4-dinitrophenyl ether.[7] Assay by u.v. indicated a yield of *ca.* 10% of rearranged ethers (based on $\varepsilon_{max.}$ 1.42×10^4, the value for geranyl 2,4-dinitrophenyl ether). Acetolysis of the rearranged ethers at 93° afforded an approximate first-order rate constant of 4.1×10^{-4} s^{-1} (consistent with the formation of three ethers solvolysing at similar rates, Table 2) whose composition was determined as below.

Linaloyl 2,4-dinitrophenyl ether (*ca.* 25 mg) was acetolysed at 60° for *ca.* 3 half-lives, and the reaction was quenched in alkaline phosphate solution.[24] The organic material was extracted into ether and dried ($MgSO_4$). The ether was removed under vacuum and the residue was treated with dry piperidine at 100° for 15 min. This reaction was quenched with water and the organic material extracted into ether, washed with water, 2N-hydrochloric acid, and water, and dried ($MgSO_4$). G.l.c. analysis of the solution (50 ft SCOT Carbowax 20M; 135°) yielded the composition of the rearranged ethers, determined as the corresponding alcohols. A control experiment involving the reaction of piperidine under the above conditions with α-terpinyl, geranyl, and neryl acetates indicated <1% of alcohol formation.

Kinetics.—All acetolyses (excepting the K_α determination) were followed spectrophotometrically at 350 nm, in the manner described in Part I.[1] The aqueous ethanolyses were followed spectrophotometrically at 400 nm on a Unicam SP 1700 spectrophotometer in the presence of 0.05M-sodium acetate to ensure complete ionisation of liberated 2,4-dinitrophenol; with pure ethanolyses 2,6-lutidine (1mM) was added.

The polarimetric acetolysis rate of (−)-linaloyl 2,4-dinitrophenyl ether was determined in a jacketted cell in a Perkin-Elmer 114 photoelectric polarimeter at 546 nm.

Activation parameters were determined as in Part I [1] from a computerised least-squares plot of log (rate constant) *versus* $1/T$.

One of us (K. B. A.) thanks the S.R.C. for a Research Studentship.

[5/2122 *Received*, 30*th October*, 1975]

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