Classical Carbonium Ions. Part VII.[1] Nucleophilic Assistance by Solvent during Acetolysis of Secondary Alkyl Derivatives

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Two different methods recently described for estimating the nucleophilic assistance by solvent in the solvolysis of (*a*) secondary alkyl bromides and (*b*) secondary alkyl arenesulphonates, have been simultaneously applied to secondary alkyl picrates, using tertiary alkyl 2,4-dinitrophenyl ethers as a point of reference. To a first approximation they give similar results and confirm earlier conclusions; their difference allows the estimation of small (*ca.* 4 kJ mol^{-1}) amounts of anchimeric assistance in 2-adamantyl and 1,2,2-trimethylpropyl systems. It is concluded that these secondary solvolyses are well described as 'S_N1 reactions,' but not as 'limiting.'

THE problem of 'borderline mechanisms' in aliphatic nucleophilic substitution has been extensively discussed.[2] Recently Schleyer and his collaborators have suggested that the acetolysis of simple secondary arenesulphonates, which has explicitly or (more often) implicitly been regarded as 'unimolecular' or 'limiting' in mechanism, actually involves substantial nucleophilic assistance from the solvent.[3] We have recently described preparative methods for secondary alkyl picrates [4] and tertiary alkyl 2,4-dinitrophenyl ethers;[5] shown that their acetolysis meets the same classical criteria [2a-c] for 'the S_N1 mechanism' as does that of secondary arenesulphonates; and emphasised the advantages that these leaving groups possess, as compared with arenesulphonate, halide, and carboxylate ions. We now report their use in a series of tests of Schleyer's hypotheses,[3] and thus of the general theory of one graded mechanism for aliphatic solvolysis.[2c]

Schleyer used two methods for estimating nucleophilic assistance,[3b,c] in each case contrasting isopropyl derivatives, the subject of enquiry, with 2-adamantyl derivatives, which were shown to behave very differently in respect of rates of reaction. His rationalisation of these differences was simply that the 2-adamantyl system is sterically hindered (as was proved by its very low reactivity toward azide ion [6]) to nucleophilic attack from the rear. We comment on this below, but first deal with Schleyer's experiments and our variations on them. [All Schleyer's reported rate-ratios, which are sensitive to temperature, have here been converted into $\delta\Delta G^{\ddagger}$ values ($\delta\Delta G^{\ddagger} = RT \ln k_1/k_2$).]

In the first method,[3b] involving bromides in 80% ethanol and acetic acid, changes in free energy of activation brought about by changing the group geminal to bromide from hydrogen to methyl (here denoted δ_{Me-H}) were considered. The difference (δ_R) between the $\delta_{Me-H}\Delta G^{\ddagger}$ values for the systems (isopropyl ⟶ t-butyl) and (2-adamantyl ⟶ 2-methyl-2-adamantyl) was taken

[1] Part VI, H. J. Storesund and M. C. Whiting, preceding paper.

[2] (*a*) C. K. Ingold, 'Structure and Mechanism in Organic Chemistry,' 2nd edn., Cornell University Press, Ithaca, New York, 1969; (*b*) E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, 1948, **70**, 846; (*c*) S. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, 1951, **73**, 2700; (*d*) M. C. Whiting, *Chem. in Brit.*, 1966, **2**, 482; (*e*) D. J. Raber, J. M. Harris, R. E. Hall, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1971, **93**, 4821; (*f*) H. C. Brown and C. J. Kim, *ibid.*, p. 5765.

[3] (*a*) J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1970, **92**, 2538; (*b*) J. L. Fry, J. M. Harris, R. C. Bingham, and P. von R. Schleyer, *ibid.*, p. 2540; (*c*) P. von R. Schleyer, J. L. Fry, L. K. M. Lam, and C. J. Lancelot, *ibid.*, p. 2542; T. W. Bentley, F. L. Schadt, and P. von R. Schleyer, (*d*) *J. Amer. Chem. Soc.*, 1972, **94**, 992; (*e*) *Tetrahedron Letters*, 1974, 2335; (*f*) D. N. Kevill, K. C. Kolwyck, D. M. Shold, and C.-B. Kim, *J. Amer. Chem. Soc.*, 1973, **95**, 6002.

[4] M. L. Sinnott and M. C. Whiting, *J. Chem. Soc.* (*B*), 1971, 965.

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

[6] J. M. Harris, D. J. Raber, R. E. Hall, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1970, **92**, 5729.

as an estimate of the nucleophilic assistance to isopropyl bromide, on the assumptions that such assistance would be negligible for t-butyl bromide and 2-bromoadamantane (if not, then the true value would be higher than that calculated) and *a fortiori* for 2-bromo-2-methyladamantane. Rate ratios were quoted for reactions at 25 °C (80% ethanol; results extrapolated from 100—150 °C for 2-bromoadamantane, and from 45—75 °C for isopropyl bromide), and at 100 °C (acetic acid; results extrapolated from 150—174 °C for 2-bromoadamantane, from 17—40 °C for 2-bromo-2-methyladamantane, and from 25—50 °C, and also extrapolated to correct for buffer salt concentration, for t-butyl bromide). Derived $\delta_{Me-H}\Delta G^{\ddagger}$ values were 21 and 43.5 kJ mol^{-1} for isopropyl and 2-adamantyl bromide in 80% ethanol, and 30 and 48 kJ mol^{-1} in acetic acid; the differences, $\delta_R\delta_{Me-H}\Delta G^{\ddagger}$, 22.5 kJ mol^{-1} in 80% ethanol at 25 °C and 18 kJ mol^{-1} in acetic acid at 100 °C (both $\pm ca.$ 0.5 kJ mol^{-1}), were interpreted as largely due to nucleophilic assistance by the solvent for isopropyl bromide, a downward correction of 4 ± 4 kJ mol^{-1} being needed for *B*-strain relief during heterolysis in the 2-adamantyl system.

In Schleyer's second approach,[3c] a change of solvent from S to trifluoroacetic acid (here denoted δ_{TFA-S}) is employed to annul nucleophilic assistance in place of geminal substitution of methyl for hydrogen, with a parallel set of assumptions (no nucleophilic assistance in the 2-adamantyl system in any solvent, or in the isopropyl system in trifluoroacetic acid). For formic acid, acetic acid, aqueous 50, 60, and 80% ethanol, and pure ethanol, minimal values for the free energy increment, $\delta_R\delta\Delta_{TFA-S}G^{\ddagger}$, were 15.5, 19, 20.5, 22, 24.5, and 30 kJ mol^{-1} (all $\pm ca.$ 0.2 kJ mol^{-1}) at 25 °C, the leaving group in this series being toluene-*p*-sulphonate. Again, Arrhenius extrapolations over *ca.* 50 °C were needed, but this time the results for aqueous ethanol also required interpolation from solvolysis rates in other solvents using the Winstein–Grunwald *mY* relationship.[2b,7] The figures quoted, though assumed during our work, are now obsolete, as changes were made in more recent work by the Princeton group in rates reported for 2-adamantyl toluene-*p*-sulphonate in trifluoroacetic acid [from $(3.67 \pm 0.01) \times 10^{-3}$ to 9×10^{-4} s^{-1}], acetic acid, formic acid, 50% ethanol, and 80% ethanol,[3d] and for 2-propyl toluene-*p*-sulphonate in acetic acid.[3e] A new value for 2-adamantyl toluene-*p*-sulphonate in ethanol has also appeared.[3f] Derived values for $\delta_R\delta_{TFA-S}\Delta G^{\ddagger}$ at 25 °C are, in kJ mol^{-1}, formic acid 10, acetic acid 15, 50% ethanol 17.5, 80% ethanol 21, and ethanol 25.

We have concentrated on acetolysis, because the non-limiting character of alcoholysis reactions of secondary systems has long been recognised; moreover for one of our leaving groups, picrate, solvolysis in aqueous ethanol is now known to involve a significant contribution from a mechanistically distinct process involving Ar–O fission,[8] correction for which would involve uncertainty. We began by modifying the first method; instead of measuring large values, in the range 21—48 kJ mol^{-1}, which necessitate long extrapolations, we have compared the rates of solvolysis of secondary picrates, $>CH{\cdot}O{\cdot}C_6H_2(NO_2)_3$, with those of tertiary 2,4-dinitrophenolates, $>CMe{\cdot}O{\cdot}C_6H_3(NO_2)_2$, giving free energy of activation differences, denoted $\delta_{Me,din-H,pic}\Delta G^{\ddagger}$, which fall in the range −9 to 17 kJ mol^{-1}. These were measured directly or with slight extrapolation.

Following Schleyer *et al.*,[3b] we equate $\delta_R\delta_{Me,din-H,pic}\Delta G^{\ddagger}$ with the nucleophilic assistance in the solvolysis of isopropyl picrate; we are freed from the assumptions made by these authors concerning linearity in their extrapolations, but we do have to make an additional assumption, that any free energy difference resulting from the relief of steric strain between the leaving group and the alkyl residue (*F*-strain) does not vary greatly as between the similar leaving groups, picrate and 2,4-dinitrophenolate, and that any such small difference there may be involves proximate hydrogen atoms, and so does not itself differ between the isopropyl and 2-adamantyl systems. The examination of molecular models, in the light of recent evidence that *F*-strain relief is important in all-*trans*-perhydrophenalen-9b-yl, but not in *trans*-9-decalyl *p*-nitrobenzoate solvolysis,[9a] confirms this; Tidwell[9b] observed little difference in toluene-*p*-sulphonate/mesitylenesulphonate acetolysis rate ratio between the isopropyl and 2-adamantyl systems. *B*-Strain relief, involving the axial methyl-hydrogen interactions in 2-methyladamantyl compounds, again has to be allowed for, and we accept the value[3b] of *ca.* 4 ± 4 kJ mol^{-1}. With this correction, nucleophilic assistance in the acetolysis of isopropyl picrate on Schleyer's assumptions is *ca.* 7 ± 4 kJ mol^{-1} (*cf.* 14 ± 4 kJ mol^{-1} for the bromide). The experimental data, interpolated or slightly extrapolated from rate measurements already described,[4,5] are summarised in Table 1; these also allow the calculation of analogous values of the differences in $\delta_{Me,din-H,pic}\Delta G^{\ddagger}$ value between the 2-adamantyl system and the s-butyl, 1,2,2-trimethylpropyl (pinacolyl), phenethyl, and *cis*- and *trans*-4-t-butylcyclohexyl systems. For the acetolysis of s-butyl picrate, this difference (with a constant correaction, the *ca.* 4 kJ term) can again be equated with nucleophilic assistance by solvent; and a similar value is obtained. In the other cases, additional free energy terms have to be considered. In the 1,2,2-trimethylpropyl system there will be more relief of *B*-strain during heterolysis in the tertiary than in the secondary ether, although this seems unlikely to equal the correction for the 2-adamantyl system. In the incipient 1-phenylethyl cation, benzylic delocalisation and stabilisation is likely to be more important than in

[7] A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, 1956, **78**, 2770.

[8] P. R. Luton and M. C. Whiting, in preparation; P. R. Luton, Ph.D. Thesis, Bristol, 1972.

[9] (*a*) J. Slutsky, R. C. Bingham, P. von R. Schleyer, W. C. Dickason, and H. C. Brown, *J. Amer. Chem. Soc.*, 1974, **96**, 1969; (*b*) T. T. Tidwell, *J. Org. Chem.*, 1974, **39**, 3533.

the incipient tertiary cation, and the difference probably contributes more than nucleophilic assistance by solvent to the large $\delta_R\delta_{Me,din-H,pic}$ value observed. In the cyclohexyl derivatives both 1,2-diequatorial and 1,3-diaxial Me,H interactions are introduced, and require correction for. Many of these terms are in principal calculable, but the method requires caution.

We now turn to Schleyer's second method, and again use picrate as our leaving group and acetic acid as our solvent S; here we again can reduce extrapolation errors, by measuring all trifluoroacetolysis rates at 65 °C and using only a short extrapolation (35 °C) of acetolysis rates. The relative insensitivity of the rate of picrate solvolysis to the nature of the solvent is helpful. However, the real advantage is that we can apply *both* Schleyer's methods to the *same* leaving group (whereas this would be difficult with any one leaving group employed by Schleyer. It was not in fact attempted, and Schleyer rightly did not compare values involving different leaving groups). The trifluoroacetolysis data are listed in Table 2 (parenthetically, the trifluoroacetolysis of tertiary 2,4-dinitrophenolates appears to be an inconveniently fast reaction). The value for the isopropyl case, $\delta_R\delta_{TFA-HOAc}\Delta G^\ddagger = 14.7 \pm 0.5$ kJ, is significantly larger than the $\delta_R\delta_{Me,din-H,pic}\Delta G^\ddagger$ value of 11 kJ (which is to be reduced by 4 ± 4 kJ for strain relief); whereas for the 1,2,2-trimethylpropyl case the value of $\delta_R\delta_{TFA-HOAc}\Delta G^\ddagger$, at 9 kJ, is smaller than the $\delta_R\delta_{Me,din-H,pic}\Delta G^\ddagger$ value, at 12 kJ. At this point it must be emphasised that to a first approximation the results from the two methods are in agreement with each other and with Schleyer's numerical conclusions; these free energy differences can to a fair approximation be interpreted as estimates of the nucleophilic assistance afforded by acetic acid in the solvolysis of isopropyl and 1,2,2-trimethylbutyl picrates. Without doubt Schleyer's views [3] supersede the generally accepted picture of 'limiting' acetolysis of secondary bromide and arenesulphonates, and the treatment of its rate as 'k_c' in the dissection of solvolysis rates for compounds having various routes to their final products. The recent reassessment of the solvolysis of 2-aryl-1-methylpropyl arenesulphonate solvolysis and analogous reactions, by various authors,[2f,10] is clearly correct. These things said, some reservations must be made.

The assumption [3] that 2-adamantyl derivatives are solvolysed by a simple 'k_c' process to a classical 2-adamantyl cation (as ion-pair) conflicts with the known behaviour of that species. When the system is generated in acetic acid from the amine by deamination-type

TABLE 1

Acetolysis kinetic data at 65 °C †

2,4-Dinitrophenolates	k/s^{-1}	Picrates	k/s^{-1}	$\delta_{Me,din-H,pic}\Delta G^\ddagger$/kJ mol^{-1}
1-1-Dimethylethyl	$(5.6 \pm 0.1) \times 10^{-6}$	Isopropyl	$(6.6 \pm 0.6) \times 10^{-7}$	6.0 ± 0.4
1,1-Dimethylpropyl	$(1.37 \pm 0.01) \times 10^{-5}$	s-Butyl	$(1.8 \pm 0.3) \times 10^{-6}$	5.8 ± 0.4
1,1,2,2-Tetramethylpropyl	$(1.96 \pm 0.03) \times 10^{-5}$	1,2,2-Trimethylpropyl	$(2.8 \pm 0.4) \times 10^{-6}$	5.4 ± 0.4
1α-Methyl-4β-t-butylcyclohexyl	$(6.9 \pm 0.2) \times 10^{-6}$	*cis*-4-t-Butylcyclohexyl	$(2.9 \pm 0.3) \times 10^{-6}$ [a]	2.4 ± 0.3
1α-Methyl-4α-t-butylcyclohexyl	$(1.14 \pm 0.05) \times 10^{-5}$	*trans*-4-t-Butylcyclohexyl	$(1.2 \pm 0.1) \times 10^{-6}$ [a]	6.3 ± 0.3
1-Methyl-1-phenylethyl	$(1.55 \pm 0.01) \times 10^{-3}$	1-Phenylethyl	$(3.8 \pm 0.4) \times 10^{-2}$	-9.0 ± 0.3
2-Methyl-2-adamantyl	$(6.16 \pm 0.04) \times 10^{-5}$	2-Adamantyl	$(1.3 \pm 0.2) \times 10^{-7}$	17.3 ± 0.4

Errors quoted are standard errors.

† Interpolated or slightly extrapolated for 2,4-dinitrophenolates from data at other temperatures;[5] extrapolated for picrates from data at other temperatures.[4]

[a] Estimated from results in 0.15M-NaOAc.

TABLE 2

Trifluoroacetolysis kinetic data

Substrate	t/°C	k/s^{-1}	$\Delta H^\ddagger$/kJ mol^{-1} at 100 °C	$\Delta S^\ddagger$/J K^{-1} mol^{-1} at 100 °C
2-Adamantyl picrate	32.30 ± 0.05	$(4.80 \pm 0.03) \times 10^{-5}$	84.5 ± 0.5	-52 ± 1.5
	48.95 ± 0.05	$(2.89 \pm 0.01) \times 10^{-4}$		
	64.70 ± 0.05	$(1.17 \pm 0.01) \times 10^{-3}$		
	64.80 ± 0.05	$(1.31 \pm 0.03) \times 10^{-3}$		
1,2,2-Trimethylpropyl picrate	64.80 ± 0.05	$(1.20 \pm 0.01) \times 10^{-3}$		
Isopropyl picrate	64.20 ± 0.05	$(4.16 \pm 0.01) \times 10^{-5}$		
	64.60 ± 0.05	$(3.80 \pm 0.03) \times 10^{-5}$		

[10] (*a*) C. J. Lancelot and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1969, **91**, 4291, 4296; (*b*) C. J. Lancelot, J. J. Harper, and P. von R. Schleyer, *ibid.*, p. 4294; (*c*) P. von R. Schleyer and C. J. Lancelot, *ibid.*, p. 4297; (*d*) A. F. Diaz and S. Winstein, *ibid.*, p. 4300; (*e*) J. M. Harris, F. L. Schadt, P. von R. Schleyer, and C. J. Lancelot, *ibid.*, p. 7508; (*f*) D. J. Raber, J. M. Harris, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1971, **93**, 4829.

reactions, or from the toluene-*p*-sulphonate, rearranged products are formed.[11] The stereochemistry of the substitution process has been shown, *inter alia* in acetic acid for the toluenesulphonate and picrate, to proceed with predominant retention of configuration.[12] Taken together these two pieces of evidence strongly suggest weak σ-bond delocalisation in the 2-adamantyl cation, for which we and Schleyer have suggested that evidence from detectably enhanced rates of reaction would not be expected.[1,11,13] However, the use in combination of the two methods of Schleyer, if both can be applied to compounds with the same type of leaving group, might allow the small degrees of anchimeric assistance which might be anticipated in such a case to be estimated. In the first method, anchimeric assistance in the 2-adamantyl system will surely be reduced to negligible proportions in the 2-methyl-2-adamantyl case, along with nucleophilic assistance from solvent; in the second, however, a change from acetic acid to trifluoroacetic acid would, at the same time as it cuts out solvent participation, *enhance* the role of anchimeric assistance from σ-delocalisation, in the 2-adamantyl cation and also in the cation, R^+, with which this is being compared. We would accordingly expect that in the isopropyl system the first free energy difference, $\delta_R\delta_{Me,din-H,pic}\Delta G^{\ddagger}$, corrected for strain relief, would be less than the second, $\delta_R\delta_{TFA-HOAc}\Delta G^{\ddagger}$, by the amount of anchimeric assistance to the ionisation of 2-adamantyl picrate in trifluoroacetic acid. This comes to *ca.* 3.5—11.5 kJ mol^{-1}, corresponding to a rate-enhancement factor of *ca.* 4—99 at 25 °C; if the 2-adamantyl system resembles others,[14] about one half of this, say 4 ± 2 kJ mol^{-1}, might be available in acetic acid, *i.e.* a factor of 2—10. A small rate increase such as this would not easily be detectable by other means;[15] Schleyer has recently proposed [13] that any anchimeric assistance would amount to less than a factor of 10 at 25 °C, *i.e.* 5.7 kJ mol^{-1}.

Turning to the 1,2,2-trimethylpropyl system, the situation changes in that we must now consider anchimeric assistance in this cation as well as in the 2-adamantyl cation; furthermore the magnitude and even the sign of the correction for the diminution of ground-state non-bonded interaction during partial rehybridisation in the two systems become uncertain. However, it does seem probable that after this correction the value of $\delta_R\delta_{TFA-HOAc}\Delta G^{\ddagger}$ (9 ± 0.6 kJ mol^{-1}) will be less than, or about equal to, the value (12 kJ mol^{-1}) for $\delta_R\delta_{Me,din-H,pic}\Delta G^{\ddagger}$. This means that the trifluoroacetolysis of 1,2,2-trimethylpropyl picrate should involve slight anchimeric assistance, comparable with that experienced by 2-adamantyl picrate. There is no discrepancy between this result and recent evidence [16] that CD_3/CH_3 isotope effects in the solvolysis of 1,2,2-trimethylpropyl *p*-bromobenzenesulphonate (in various solvents, including trifluoroacetic acid–water, molar ratio 3 : 1, but not trifluoroacetic acid itself) are indistinguishable from unity; such quantities of assistance correspond to a small movement only along the strongly exothermal rearrangement profile toward the 1,1,2-trimethylpropyl cation.

If anchimeric assistance, arbitrarily assumed to be half as important in acetic as in trifluoroacetic acid, is allowed for, values for nucleophilic assistance in acetic acid are, roughly, 11 kJ mol^{-1} for isopropyl picrate, and, however the corrections are modified, a similar amount for 1,2,2-trimethylpropyl picrate. Correspondingly, the enthalpies of activation are similar, at 127 and 122 kJ mol^{-1}.[4] In the analogous primary picrates, ethyl and neopentyl, the $\delta_R\Delta G^{\ddagger}_{ii}$ value for acetolysis at the same temperature (65 °C) is *ca.* 9 ± 1 kJ mol^{-1} before correction for any anchimeric assistance in the neopentyl case, a correction which if needed [17] would increase the value. However, here two very different processes, having $\Delta S^{\ddagger}$ values of -70 and $+6$ J K^{-1} mol^{-1}, are being compared, so that $\delta_R\Delta G^{\ddagger}$ varies sharply with temperature. The corresponding $\delta_R\Delta H^{\ddagger}$ value, of 34 ± 4 kJ mol^{-1} for the picrates,[4] or 27 kJ mol^{-1} for the toluene-*p*-sulphonates,[18] is a better guide to the situation, essentially that β-methylation is important in the primary system but much less so in the secondary system. When, however, a second t-butyl group interferes with access, in the 1-t-butyl-2,2-dimethylpropyl system, nucleophilic participation is much reduced,[19] as it is in the 2-adamantyl system.

There are several important distinctions between typical secondary and primary solvolyses. The latter, but not the former, show rate enhancement by lyate ion and a strongly negative entropy of activation;[20] neopentyl compounds are a notable exception. The former, but not the latter, show hydride shifts,[21] sensitivity to electron donation as measured by $\Sigma\sigma^*$ [22] or by σ [2f,10a,23] in neighbouring β-aryl in non-rearranging cations, and α- and β-deuterium isotope effects.[22a] We can now add

[11] M. L. Sinnott, H. J. Storesund, and M. C. Whiting, *Chem. Comm.*, 1969, 1000.
[12] J. A. Bone and M. C. Whiting, *Chem. Comm.*, 1970, 115; J. A. Bone, J. R. Pratt, and M. C. Whiting, *J.C.S. Perkin II*, 1975, 1447.
[13] D. Lenoir, D. J. Raber, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1974, **96**, 2149.
[14] P. E. Peterson, R. J. Bopp, D. M. Chevli, E. L. Curran, D. E. Dillard, and R. J. Kamat, *J. Amer. Chem. Soc.*, 1967, **89**, 5902.
[15] (*a*) C. S. Foote, *J. Amer. Chem. Soc.*, 1964, **86**, 1853; (*b*) P. von R. Schleyer, *ibid.*, pp. 1854, 1856.
[16] W. M. Schubert and P. H. Levre, *J. Amer. Chem. Soc.*, 1969, **91**, 7746.
[17] J. E. Nordlander, S. P. Jindal, P. von R. Schleyer, R. C. Fort, J. J. Harper, and R. D. Nicholas, *J. Amer. Chem. Soc.*, 1966, **88**, 4475.
[18] (*a*) S. Winstein and H. Marshall, *J. Amer. Chem. Soc.*, 1952, **74**, 1120; (*b*) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *ibid.*, p. 1115.
[19] S. H. Liggero, J. J. Harper, P. von R. Schleyer, A. P. Krapcho, and D. E. Horn, *J. Amer. Chem. Soc.*, 1970, **92**, 3789.
[20] W. Pritzkow and K. H. Schöppler, *Chem. Ber.*, 1962, **95**, 834.
[21] N. C. G. Campbell, D. M. Muir, R. R. Hill, J. H. Parish, R. M. Southam, and M. C. Whiting, *J. Chem. Soc.* (*B*), 1968, 355.
[22] (*a*) A. Streitwieser, 'Solvolytic Displacement Reactions,' McGraw-Hill, New York, 1962; (*b*) T. W. Bentley, S. H. Liggero, M. A. Imhoff, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1974, **96**, 1970.
[23] C. J. Kim and H. C. Brown, *J. Amer. Chem. Soc.*, 1969, **91**, 4286, 4287.

that although the secondary systems do indeed experience nucleophilic assistance from solvent, it is moderate in amount, and it is less susceptible to extinction by steric *hindrance*. These differences are well expressed by the classical distinction between S_N1 and S_N2 processes in solvolysis reactions;[2a] secondary alkyl solvolyses, including acetolyses, can no longer be correctly described as 'limiting,'[2c] but they can still often be profitably described as 'unimolecular,'[2a] when a nearly zero entropy of activation attests the non-involvement of surrounding solvent molecules, and thermoneutral hydride shift confirms the cationic character of the alkyl residue. Evidently there is a form of interaction effective at longer distances between a solvent molecule and a compound undergoing solvolysis, which leaves the former with most of its normal freedom of location, yet which may well involve an attenuated covalent component sufficient to predispose the nascent cation to substitute from that side. We have suggested that such an interaction between an amine, RNH_2, and a 1-propylpentyl cation, formed simultaneously a considerable distance apart from a protonated aryl-1-propylpentyltriazene, controls the amount of hydride shift in the 'octyl' acetates ultimately formed.[2d,24] Such attenuated covalent participation, insufficient to deprive the nucleophile of its entropy of translation, could be considered as excluded from the usual definition of covalency change.[2a]

There remains the relationship of our numerical result, *ca.* 11 kJ mol^{-1} of assistance for isopropyl picrate in acetic acid, with Schleyer's values of 18 kJ mol^{-1} for the bromide and 15 kJ mol^{-1} for the toluene-*p*-sulphonate (assuming now similar small corrections for anchimeric assistance to the ionisation of 2-adamantyl bromide and toluene-*p*-sulphonate, as well as the *B*-strain-relief correction in the opposite sense). We have considered three ways of reconciling these. The differential steric effects of picrate and 2,4-dinitrophenolate during ionisation in the unhindered isopropyl and the more encumbered 2-adamantyl system seem unlikely [25] to contribute even 1 kJ mol^{-1}. Analysis of the effects of various temperature errors in the Princeton work which might be thought plausible shows the final free energy differences to be less sensitive than might have been expected—even an assumed error of 1 °C in the 174 °C acetolysis of 2-bromoadamantane would affect $\delta_R\delta_{Me-H}\Delta G^{\ddagger}$ by only 1.7 kJ mol^{-1}. Finally, errors associated with long extrapolations *via* the Arrhenius equation, which is equivalent to assuming the specific heat of activation to be *R* when a more plausible value is *ca.* −125 J mol^{-1},[26] also do not greatly affect the final free energy differences. One has to conclude that the amount of nucleophilic assistance afforded to isopropyl derivatives during acetolysis actually is somewhat greater for the bromide and the toluene-*p*-sulphonate than it is for the picrate, a fact which we do not seek to explain.

[24] H. Maskill, R. M. Southam, and M. C. Whiting, *Chem. Comm.*, 1965, 496.
[25] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, 'Conformational Analysis,' Interscience, New York, 1965, p. 45.

EXPERIMENTAL

Solvents.—Acetic acid was dried by refluxing with, and distilling from, tetra-acetyl diborate.[5] Trifluoroacetic acid was dried by heating for 1 h under reflux with, and distilling from, phosphorus pentoxide.

The preparation of all picrates and 2,4-dinitrophenolates used has been described elsewhere.[4,5]

Kinetics.—The methods used to follow acetolyses have been described previously.[4,5] Trifluoroacetolyses were followed as for acetolyses, using a Cary 14 spectrophotometer.

The low solubility of picrates and 2,4-dinitrophenolates in trifluoroacetic acid caused homogeneity problems for fast reactions. These were overcome by injecting a dry solution of the ether in tetramethylene sulphone into the trifluoroacetic acid; 10 μl for picrates, or 20 μl for 2,4-dinitrophenolates, of a 0.2M-solution of the ether in dry warm tetramethylene sulphone was injected through the septum cap of a specially adapted 10 mm u.v. cell [27] into 3 ml of trifluoroacetic acid, for a full-scale optical density increase during solvolysis. The rate of trifluoroacetolysis of 2-adamantyl picrate at 64.2 °C without the sulphone was $(1.19 \pm 0.02) \times 10^{-3}$ s^{-1}, and $(1.17 \pm 0.01) \times 10^{-3}$ s^{-1} with the sulphone.

Slow trifluoroacetolyses at 65 °C often involved problems due to attack of the acid on the silicone rubber seal of the screw-top cell. Analysis of the optical density output showed the first-order rate constant to decrease with time, and data from such runs were discarded.

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