Classical Carbonium Ions. Part V.[1] Stereochemistry of Substitution in the Solvolysis of 2-Adamantyl and 2-Methyl-2-adamantyl Derivatives

By **John A. Bone, John R. Pritt,** and **Mark C. Whiting,*** School of Chemistry, The University, Bristol BS8 1TS

Derivatives of the two 5-methyladamantan-2-ols and of the two 2,5-dimethyladamantan-2-ols have been submitted to solvolysis conditions, and the products have been analysed. The secondary alcohol derivatives show a preference for the formation of products of retained configuration; in the tertiary derivatives a similar but much weaker tendency is observed. Superimposed on these tendencies is one, similar in magnitude, favouring the formation of products of preferential nucleophilic attack from the side *syn* to the 5-methyl group. These preferences are rationalised.

We have described the preparation of stereoisomeric pairs of the 5-methyladamantan-2-ols and the 2,5-dimethyladamantan-2-ols,[2] and assigned geometrical configurations to them.[3] These were chosen as examples of secondary and tertiary alcohols having a remote substituent considered to be incapable of seriously distorting their reactivity, yet perturbing the carbon skeleton enough to allow some hope of analysing, with the accuracy and sensitivity peculiar to g.l.c., the products of the solvolyses of their derivatives. We also hoped that the unstrained nature of the adamantane system would inhibit elimination and 1→2 hydride shift without evoking σ-bond participation, and would thus allow the convenient study of the stereochemical course of substitution reaction in systems that could be regarded as typical of cyclohexanes, and so comparable with, *e.g.*, the t-butylcyclohexanes studied earlier.[4] Not all these expectations were realised, and we find ourselves forced to

[1] Part IV, M. L. Sinnott and M. C. Whiting, preceding paper.
[2] J. A. Bone, J. R. Pritt, and M. C. Whiting, *J.C.S. Perkin I*, 1972, 2644.
[3] C. Cloke, J. R. Pritt, and M. C. Whiting, *J.C.S. Perkin I*, 1972, 2648.
[4] 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.

postulate that σ-bond delocalisation is far more general than had previously been accepted.

As derivatives of the 5-methyladamantan-2-ols we employed the toluene-*p*-sulphonate, the *p*-nitrobenzenesulphonate, and the picrate.[5] We have stressed [2] the difficulty of obtaining the stereoisomers of the alcohols pure, and we therefore required a means of regenerating the incompletely separated alcohols from their derivatives for analysis. For the arenesulphonates cleavage by the sodium adduct of naphthalene in 1,2-dimethoxyethane [6] proved to be less convenient, in our hands, than reduction with lithium aluminium hydride [7] in ether at 25 °C—a reaction which in this case gave no hydrocarbon, no doubt because of the resistance of 2-adamantyl derivatives to bimolecular nucleophilic substitution.[8] The sequence alcohol ⟶ arenesulphonate ⟶ alcohol, without any attempt at purification of the intermediate ester, gave an unchanged mixture of stereoisomers (analysed as trifluoroacetates), and was judged satisfactory. The picrates were much more easily cleaved stereospecifically to the alcohols, by reaction with aqueous alcoholic ammonia, or by passing down an alumina column. For definitive experiments on product ratios, derivatives of virtually pure *cis*-alcohol and of a 19 : 81 mixture of *cis*- and *trans*-alcohol (containing small quantities of adamantan-2-ol) were used.

The formates and trifluoroacetates (as well as the acetates) of the stereoisomeric alcohols proved to be stable, within experimental error, under the conditions of toluenesulphonate solvolysis in the corresponding acid. This is not true of, *e.g.*, these derivatives of the 4-t-butylcyclohexanols.

Rates of solvolysis for the toluenesulphonates of adamantan-2-ol and the two 5-methyl derivatives in trifluoroacetic acid, and of the three *p*-nitrobenzenesulphonates in acetic acid, were determined spectrophotometrically, and are listed in Table 1. Other rates of solvolysis of secondary derivatives were estimated roughly, for the purpose of product study under conditions of minimal severity, by approximately quantitative i.r. measurements.

The stereochemical consequences of solvolytic reactions were ascertained by isolating products after at least ten half-lives. The acetates, from acetic acid or (*via* unstable imino-ester cations) dimethylacetamide solvolyses, and the trifluoroacetates, were analysed directly by g.l.c. The alcohols, from aqueous acetone, were converted into trifluoroacetates; the formates were cleaved to alcohols and trifluoroacetylated. In all cases duplicate analyses on two or more mixtures of esters derived from starting materials of known composition were made, baseline separations being obtained; short extrapolation to pure *trans*-derivatives gave the stereoisomeric composition of the products to be expected; and small corrections were applied for the behaviour of the *ca.* 2% of adamantyl esters, present in the *trans*-5-methyl derivatives, which would, necessarily, give products co-chromatographing with the retention products from the latter. For this reason, and because a few small arithmetical errors are now rectified, some of the figures listed (Table 2) differ (by less than the experimental error estimates) from those listed in our 1970 communication.[7] They indicate a remarkable and unexpected tendency for substitution to proceed with predominant retention of configuration, and are further considered below.

TABLE 1

Kinetic data on the solvolyses of 5-methyl-2-adamantyl and 2-adamantyl derivatives

Substrate	X	t/°C [a]	Solvent [b]	k/s^{-1}
2-Adamantyl	OTs [c]	32.0	$CF_3 \cdot CO_2H$	$(4.36 \pm 0.09) \times 10^{-3}$
	ONs [c]	73.6	$MeCO_2H$	$(7.95 \pm 0.76) \times 10^{-5}$
trans-5-Methyl-2-adamantyl	OTs	32.0	$CF_3 \cdot CO_2H$	$(2.14 \pm 0.16) \times 10^{-3}$
	ONs	73.6	$MeCO_2H$	$(4.36 \pm 0.23) \times 10^{-5}$
cis-5-Methyl-2-adamantyl	OTs	32.0	$CF_3 \cdot CO_2H$	$(2.68 \pm 0.13) \times 10^{-3}$
	ONs	73.6	$MeCO_2H$	$(3.04 \pm 0.13) \times 10^{-5}$

[a] ±0.1 °C. [b] Containing the sodium salt (0.15M). [c] Ts = *p*-tolylsulphonyl; Ns = *p*-nitrophenylsulphonyl.

When, in 1970, we rationalised our results [7] in terms of σ-electron participation in the 2-adamantyl cation, we realised that an alternative type of explanation existed in which the adamantyl nucleus itself perturbed the substitution process in some way so as to favour retention; and that a good criterion for distinguishing such explanations from that which we favoured was a comparison between the secondary derivatives discussed above and analogous derivatives of tertiary alcohols, in this case the two 2,5-dimethyladamantan-2-ols. Our work on the preparation and solvolysis of compounds containing the hitherto little studied leaving groups, picrate [5] and 2,4-dinitrophenolate,[9] was aimed at making possible and valid just such comparisons between well-behaved tertiary systems and their often controversial secondary analogues. We therefore prepared and separated the 2,5-dimethyladamantan-2-ols,[2] converted them and 2-methyladamantan-2-ol into their 2,4-dinitrophenolates, and submitted the three compounds to

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

[6] S. Ji, L. B. Gortler, A. Waring, A. Battisti, S. Bank, and W. D. Closson, *J. Amer. Chem. Soc.*, 1967, **89**, 5311.

[7] J. A. Bone and M. C. Whiting, *Chem. Comm.*, 1970, 115.

[8] (*a*) J. M. Harris, D. J. Raber, R. E. Hall, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1970, **92**, 5729; (*b*) V. J. Shiner and R. D. Fisher, *ibid.*, 1971, **93**, 2553; (*c*) D. J. Raber, J. M. Harris, R. E. Hall, and P. von R. Schleyer, *ibid.*, p. 4821.

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

TABLE 2

Stereochemistry of solvolysis of 5-methyl-2-adamantyl derivatives

		cis			*trans*		2-Adamantyl	
X	Solvent	*t*/°C	Ratio [a]	ΔΔ*G*‡/ J mol^{-1} (cal mol^{-1})	Ratio [a]	ΔΔ*G*‡/ J mol^{-1} (cal mol^{-1})	Ratio [a]	ΔΔ*G*/ J mol^{-1} (cal mol^{-1})
OTs	HOAc	100	4.26	4 500 (1 100)	0.98	−63 (−15)	2.04	2 200 (530)
OTs	HOAc *	100	4.00	4 300 (1 000)	0.83	−580 (−140)	1.82	1 900 (445)
OTs	HOAc *	130	3.35	4 050 (970)	0.94	−210 (−50)	1.77	1 900 (460)
ONs	HOAc *	52	4.55	4 100 (980)	1.02	54 (13)	2.16	2 100 (500)
ONs	HOAc *	100	4.00	4 300 (1 000)	0.94	−190 (−46)	1.94	2 100 (490)
OPic	HOAc *	100	6.69	5 900 (1 400)	0.77	−820 (−195)	2.26	2 500 (610)
OTs	$MeCO{\cdot}NMe_2$	160	0.92	−300 (−72)	0.23	−5 300 (−1 300)	0.46	−2 800 (−670)
OTs	$CF_3{\cdot}CO_2H$ *	100	3.76	4 100 (980)	0.83	−580 (−140)	1.76	1 800 (420)
OTs	HCO_2H *	100	6.69	5 900 (1 400)	2.31	2 600 (620)	3.93	4 200 (1 000)
OTs	H_2O–Me_2CO †	100	9.00	6 800 (1 600)	3.15	3 600 (850)	5.31	5 200 (1 200)

[a] Of retained to inverted products; geometric mean of *cis*- and *trans*-5-methyl derivatives for 2-adamantyl.
* Solvent contains the sodium salt (0.15M). † 1 : 1 v/v; containing 2,6-lutidine (0.15M).

TABLE 3

Kinetic data on the acetolysis of the 2,4-dinitrophenolates

Parent alcohol	*t*/°C	*k*/s^{-1}	Δ*H*‡/kJ mol^{-1} (kcal mol^{-1}) at 100 °C	Δ*S*‡/J K^{-1} mol^{-1} (cal K^{-1} mol^{-1} at 100 °C)
2-Methyladamantan-2-ol	50.00 ± 0.05	(9.59 ± 0.04) × 10^{-6}	109.6 ± 0.4	−1.7 ± 1.3
	64.85 ± 0.05	(6.02 ± 0.03) × 10^{-5}	(26.2 ± 0.1)	(−0.4 ± 0.3)
	69.50 ± 0.05	(1.04 ± 0.01) × 10^{-4}		
	72.20 ± 0.05	(1.45 ± 0.01) × 10^{-4}		
	78.40 ± 0.05	(2.82 ± 0.03) × 10^{-4}		
	100.0	(2.64 ± 0.46) × 10^{-3} [a]		
cis-2,5-Dimethyladamantan-2-ol	60.90 ± 0.05	(2.39 ± 0.02) × 10^{-5}	113.3 ± 1.5	5.1 ± 4.4
	64.05 ± 0.05	(3.73 ± 0.03) × 10^{-5}	(27.1 ± 0.4)	(1.2 ± 1.0)
	73.00 ± 0.05	(1.14 ± 0.01) × 10^{-4}		
	78.60 ± 0.05	(2.08 ± 0.02) × 10^{-4}		
	89.95 ± 0.2	(7.0 ± 0.1) × 10^{-4} [b]		
	100.0	(2.03 ± 0.69) × 10^{-3} [a]		
trans-2,5-Dimethyladamantan-2-ol	64.10 ± 0.05	(2.19 ± 0.02) × 10^{-5}	111.3 ± 1.5	−5.2 ± 4.2
	69.50 ± 0.05	(4.22 ± 0.02) × 10^{-5}	(26.6 ± 0.4)	(−1.2 ± 1.0)
	74.35 ± 0.05	(7.86 ± 0.07) × 10^{-5}		
	78.25 ± 0.05	(1.17 ± 0.01) × 10^{-4}		
	89.95 ± 0.2	(4.0 ± 0.1) × 10^{-4} [b]		
	100.0	(1.13 ± 0.40) × 10^{-3} [a]		

[a] Extrapolated using Δ*H*‡, Δ*S*‡ at 100 °C; standard errors quoted previously [9] are incorrect. [b] Mean of two ampoule kinetic runs.

TABLE 4

Product analyses from the acetolysis of the 2,4-dinitrophenolates

Parent alcohol	*t*/°C	10^4*k*/s^{-1} [a]	Reaction time [b]	Olefin (%) [c]	Acetates (%) [c]	Ratio [f]	ΔΔ*G*‡/ J mol^{-1} (cal mol^{-1})
2-Methyladamantan-2-ol	100	26.6	1	59	41	1.24 ± 0.04	670 ± 100
	76	2.18	18	57 ± 3 [d]	43 ± 3 [d]		(160 ± 24)
cis-2,5-Dimethyladamantan-2-ol	76	1.54	2	70 ± 2	30 ± 2	2.05 ± 0.05	2 100 ± 71
	76	1.54	13	57.6 ± 0.7 [e]	42.4 ± 0.6 [e]		(500 ± 17)
trans-2,5-Dimethyladamantan-2-ol	76	0.90	2	70 ± 2	30 ± 2	0.77 ± 0.02	−760 ± 67
	76	0.90	7.5	59.5 ± 0.7 [e]	40.5 ± 0.6 [e]		(−180 ± 16)

[a] Interpolated or extrapolated from data in Table 3; errors ⩽ ±1%. [b] Half-lives. [c] Molar %. [d] Mean of 6 runs. [e] Mean of 2 runs. [f] Of retained to inverted products; geometric mean of 2,5-dimethyl derivatives for 2-methyl-2-adamantyl.

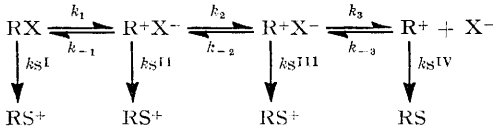
acetolysis under conditions comparable with the reaction of 2-adamantyl picrate. Reaction rates are given in Table 3, and product analyses in Table 4. Regarding rate, the puzzling [10] effect of remote methyl groups on the solvolyses of adamantane derivatives is seen again, the factor of 2.3 for the *trans*-isomer being one of the largest yet observed. We propose that in this case at least it results from a steric effect of the hydrogen atoms of the 5-methyl group on the hydrogen atoms at positions 4 and 6 which are in a diaxial relationship to the leaving

[10] (*a*) P. von R. Schleyer and C. W. Woodworth, *J. Amer. Chem. Soc.*, 1968, **90**, 6528; (*b*) V. Buss, R. Gleiter, and P. von R. Schleyer, *ibid.*, 1971, **93**, 3927; (*c*) D. Lenoir, P. Mison, E. Hyson, P. von R. Schleyer, M. Saunders, P. Vogel, and L. A. Telkowski, *ibid.*, 1974, **96**, 2157.

group, or to the 2-methyl group which can relay this effect to the leaving group. In either case, this deformation should reduce a compression which tends to promote ionisation. A similar explanation is given below for the effect of the 5-methyl group on the product mixture.

The reaction products are less straightforward to discuss than those of the secondary system, because much olefin is formed, more than at equilibrium. Furthermore, it was clear that the ratios of acetates to olefin, and of *cis*- to *trans*-acetate, were affected by reaction time, because the olefins underwent slow addition reactions in acetic acid. The rates of addition were measured approximately by g.l.c. and found to be 5.9 ± 0.2 and $3.1 \pm 0.2 \times 10^{-6}$ s^{-1} at 76 °C for 2-methyleneadamantane and for 5-methyl-2-methyleneadamantane, respectively. Although not sufficiently rapid, relative to 2,4-dinitrophenolate solvolysis under similar conditions, to require elaborate treatment of the kinetic data to arrive at the composition of the kinetically controlled product mixture, this did require the analysis of the products of incomplete reaction (1—2 half-lives). The results show (*a*) that the effect of a methyl group in facilitating attack of nucleophile from its own side of the molecule is comparable with (about 0.8 times as large in terms of $\Delta\Delta G^{\ddagger}$) the same effect in the secondary system; and (*b*) that the tendency of the tertiary 2,4-dinitrophenolates to give an excess of retained over inverted product is considerably reduced (about 0.3 times as large), relative to the secondary analogues. As expected, there were no indications of rearranged products. Thus, the system approximates reasonably well to the S_N1 paradigm, in giving 'racemisation'; but the small deviation is in the same sense as in the secondary system. As a guide to the reasons for the behaviour of the latter, the result is inconclusive.

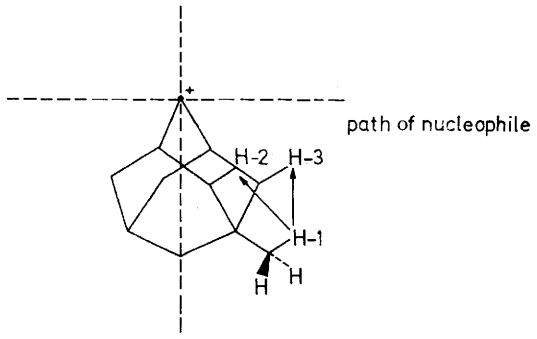
It is becoming popular to discuss solvolysis in terms of four increasingly electrophilic entities [11] (see Scheme). A



SCHEME

description in which the relative probability of different fates for R^+ varied continuously with the R–X distance could account for the same phenomena. Thus, one could postulate three qualitatively distinct intermediates, and make the stereochemical outcome of substitution by solvent a criterion of which was assumed, with the intimate ion-pair giving only inverted product, the solvent-separated ion-pair only (or, alternatively, mainly) the retained product, and the dissociated ion, by definition, equal amounts of both. Instead, one could say simply that after heterolysis, the stereochemical outcome of a substitution process with a solvent molecule would be affected by the ability of the anion X^- to perturb the environment of the cation R^+, so that attack from the hemisphere containing X^- was less probable (because the bulk of the X^- group hindered the approach of S) or more probable (because the anionic charge rendered the nearby solvent molecules more nucleophilic), these two effects varying in relative magnitude from case to case. Either description is a mere restatement of the facts until phenomena other than the product analysis can be brought in, or the behaviour of one carbon skeleton related to that of others. Two aspects of the present work encourage such explanations in the case of the secondary derivatives; the fact that 2-adamantyl derivatives are known to be resistant to bimolecular attack,[8] and the fact that the only aprotic solvent investigated did give small excess of inversion—this would fit the weaker attachment of such solvent molecules to an anionic leaving group than of molecules of a protic solvent, and consequently weaker enhancement of nucleophilicity of the counter-ion. However, the variation with solvent nucleophilicity and polarity of the inversion: retention ratio does not otherwise accord well with this simple picture; and the discovery that rearranged products are formed in the acetolysis of 2-adamantyl toluenesulphonate allows the formulation of a less simplistic treatment, which we defer to the following paper. Here we note that if a larger yield of rearranged product is formed in the trifluoroacetolysis reaction, the retention: inversion ratio measured would be affected by the probable further reaction of the methylprotoadamantyl trifluoroacetates. For the 2-methyl-2-adamantyl derivatives, an explanation along the above lines for the small preference for retention appears adequate.

The tendency of both the 2,5-dimethyl-2-adamantyl and 5-methyl-2-adamantyl cations/ion-pairs to react with acetic acid with a preference (*ca.* 2 : 1) for nucleophile on the side *syn* to the bridgehead methyl group can best be understood by reference to the Figure. The methyl group is too far from the line drawn perpendicular to the three bonds formed at the cationic centre to repel a nucleophile moving along it; indeed, at this range (*ca.*



270 pm) some attractive van der Waals force is possible. It will, however, tend to distort the two hydrogen atoms in an axial 1,3-relationship, moving them further from

[11] (*a*) S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck, and G. C. Robinson, *J. Amer. Chem. Soc.*, 1956, **78**, 328; (*b*) R. A. Sneen, *Accounts Chem. Res.*, 1973, **6**, 40.

the path of the nucleophile, and thus assisting the latter's approach.

EXPERIMENTAL

The preparation of partially separated mixtures of the 5-methyladamantan-2-ols has been described;[2] we had, in quantities of *ca.* 1 g, mixtures containing 99.7% of the *cis*-isomer, and 81% of the *trans*- isomer. Although we did not know it at the time of much of the work described here, the former also contained about 3% of an alcohol having a secondary methyl group, while the latter contained 2% of adamantan-2-ol; the secondary methyl compound gave derivatives (acetates *etc.*) with much longer g.l.c. retention times, which were not measured and caused no analytical problems, while the 2-adamantyl derivatives co-chromatographed with corresponding *trans*-5-methyl-2-adamantyl, increasing the apparent proportion of retained products; all product analyses reported have been corrected for this.

Derivatives.—The *cis*-toluene-*p*-sulphonate was prepared from 99.7% *cis*-alcohol (50 mg) and the sulphonyl chloride (58 mg) in pyridine (0.1 ml) at 25 °C for 3 days. Isolation and chromatography on alumina (8 g) gave unchanged alcohol (8 mg) and the *toluenesulphonate* (80 mg), which after recrystallisation at −78 °C formed needles, m.p. 97—98° (63 mg) (Found: C, 67.2; H, 7.75. $C_{18}H_{24}O_3S$ requires C, 67.5; H, 7.5%). Similarly prepared, the p-*nitrobenzenesulphonate* had m.p. 149.5—151° (Found: C, 58.2; H, 6.45. $C_{17}H_{21}NO_5S$ requires C, 57.95; H, 6.25%). The picrate was obtained from the alcohol (30 mg), picryl fluoride (47 mg), methylene chloride (1.5 ml), and 1,4-diazabicyclo-[2.2.2]octane (20 mg); after 10 min at 25 °C the initially deep-red solution became yellow, and isolation gave the *picrate* (33 mg) as cream plates, m.p. 145—147° (from methanol) (Found: C, 53.9; H, 5.25. $C_{17}H_{19}N_3O_7$ requires C, 54.1; H, 5.05%).

Similar derivatives were prepared from the crude *trans*-alcohol, but no attempt to purify them proved successful, and they were therefore used directly for solvolysis, the same specimen being analysed. For picrates this merely involved treatment with ammonium hydroxide (*d* 0.88) (in excess) and methanol for 16 h; arenesulphonates were best cleaved by addition of arenesulphonate (6 mg) to a suspension of lithium aluminium hydride (10 mg) in dry ether (1 ml). After 90 min at 25 °C, a deoxygenated, saturated aqueous solution of tartaric acid (1 ml) was added; isolation of the neutral fraction gave the alcohol mixture, analysed as trifluoroacetates.[1]

2-*Adamantyl* p-*nitrobenzenesulphonate*, prepared in the same way as its homologue, had m.p. 144—145° (Found: C, 57.1; H, 5.85. $C_{16}H_{19}NO_5S$ requires C, 56.8; H, 5.9%).

2-*Methyl*-2-*adamantyl* 2,4-*dinitrophenolate*. The phenyllithium method[9] was used, giving, in 50% yield, the *ether*, m.p. 135—136° (Found: C, 61.6; H, 5.8. $C_{17}H_{20}N_2O_5$ requires C, 61.5; H. 6.0%), $\lambda_{max.}$ (iso-octane) 290 nm. Similarly, *trans*-2,5-dimethyladamantan-2-ol gave in 50% yield the corresponding *ether*, m.p. 115—117.5° (Found: C, 62.6; H, 6.45. $C_{18}H_{22}N_2O_5$ requires C, 62.4; H, 6.35%), $\lambda_{max.}$ (iso-octane) 289 nm. The corresponding derivative of *cis*-2,5-dimethyladamantan-2-ol was an oil which had $\lambda_{max.}$ (iso-octane) 288 nm and the expected i.r. and n.m.r. spectra.

2-Methyl-2-adamantyl acetate was prepared by the method of De Puy and King;[12] the corresponding alcohol (2.32 g), dimethylaniline (18 ml), and acetyl chloride (3.3 ml) were mixed at 0 °C. The mixture was kept overnight at 25 °C, heated to 100 °C for 1 h, and then added to water. The product was isolated with petroleum and distilled, giving the *acetate*, b.p. 157—159°, $\nu_{max.}$ (CCl_4) 1725 cm^{-1} (Found: C, 75.4; H, 9.15. $C_{13}H_{20}O_2$ requires C, 75.0; H, 9.6%). The acetates of the two 2,5-dimethyladamantan-2-ols were prepared similarly.

Kinetic Measurements.—These were spectrophotometric, a Cary 14 spectrophotometer being employed for runs below 80 °C; the cell compartment was held at the quoted temperatures with an estimated precision of ±0.1 (secondary derivatives) or ±0.02 °C (tertiary ethers). Optical densities (10—20 per run) were measured at 300 nm (*p*-nitrobenzenesulphonates; *ca.* 10^{-3}M), 273.3 nm (toluene-*p*-sulphonates; *ca.* 10^{-3}M), or 350 nm (2,4-dinitrophenolates; *ca.* 10^{-4}M) and rates were calculated by the method of Guggenheim.[13] Typically, runs (concordant duplicates) were taken to 6 half-lives. Correlation coefficients were 0.999 or better for the tertiary ethers. The rate constants for *trans*-5-methyl-2-adamantyl derivatives were obtained by correcting each optical density measurement for the behaviour of the small amount of *cis*-derivative known to be present, after its rate of reaction had been determined. Runs above 80 °C were carried out in ampoules (3 ml) placed in a constant temperature bath (±0.2 °C); the first ampoule was withdrawn after 5 min, and others successively (9—12 per run), and spectra were obtained with a Unicam SP 800 spectrophotometer; infinity values (≮3 per run, concordant, for absorbance at the chosen wavelength) were determined experimentally. The least-squares slopes of normal first-order plots were calculated; correlation coefficients were

TABLE 5

Product analyses from 5-methyl-2-adamantyl derivatives

t/°C	X	Solvent	% *cis* (starting)	% *cis* (product)	Mean
100	OTs	HOAc	99.7	80.7, 80.7	80.7
100	OTs	HOAc	19	55.2, 55.6	55.4
100	OTs	HOAc *	99.7	80.1, 79.7, 79.8, 79.7	79.8
100	OTs	HOAc *	95.5	79.3, 78.7, 78.9, 79.2	79.1
100	OTs	HOAc *	27	62.4, 61.9, 61.7, 61.5	61.9
100	OTs	HOAc *	19	56.9, 57.3, 57.2, 57.5	57.2
100	OTs	HOAc *	99.7	80.3, 79.7	80.0
100	OTs	HOAc *	27	59.4, 59.8	59.6
130	OTs	HOAc *	99.7	76.9, 77.0	77.0
130	OTs	HOAc *	19	55.9, 56.1	56.0
52	ONs	HOAc *	99.6	81.5, 81.9	81.7
52	ONs	HOAc *	42.4	65.0, 64.6, 65.5, 65.1	65.0
52	ONs	HOAc *	19	54.9, 54.5, 53.4, 53.8	54.1
100	ONs	HOAc *	99.6	79.2, 79.2, 79.0	79.1
100	ONs	HOAc *	42.4	64.0, 63.7, 63.1, 63.8	63.7
100	ONs	HOAc *	19	55.4, 56.5, 55.4, 56.3	55.9
100	OPic	HOAc *	99.0	87.2, 86.9	87.1
100	OPic	HOAc *	27.0	64.4, 64.4, 63.9, 63.7	64.1
100	OTs	HCO_2H *	99.7	87.4, 87.3, 86.5	87.1
100	OTs	HCO_2H *	27	44.7, 43.8	44.2
100	OTs	HCO_2H *	19	40.1, 40.9, 42.3, 42.7	41.5
100	OTs	$CF_3{\cdot}CO_2H$ *	99.7	78.8, 78.0, 78.3, 77.4	78.1
100	OTs	$CF_3{\cdot}CO_2H$ *	19	59.2, 58.3	58.9
100	OTs	aq. Me_2CO †	99.7	88.9, 88.7	88.8
100	OTs	aq. Me_2CO †	27	40.9, 40.4	40.7
160	OTs	$Me_2N{\cdot}COMe$	99.7	47.4, 48.7	48.1
160	OTs	$Me_2N{\cdot}COMe$	27	70.8, 71.3	71.1

* Containing the sodium salt (0.15M). † 1 : 1 v/v; containing 2,6-lutidine (0.15M).

[12] C. H. DePuy and R. W. King, *J. Amer. Chem. Soc.*, 1961, **83**, 2743.

[13] E. A. Guggenheim, *Phil. Mag.*, 1926, **7**(2), 538.

0.995—0.999. No corrections were applied for the small quantities of 2-adamantyl derivatives present in the crude *trans*-5-methyl-2-adamantyl arenesulphonates.

Product Analyses.—Solvolyses were effected with the derivative (4 mg) in solvent (2 ml) in ampoules immersed in a constant-temperature bath for *ca.* 10 half-lives (except for 2,5-dimethyl- and 2-methyl-2-adamantyl 2,4-dinitrophenolates, where 1 half-life was used; here the product-analysis was unaffected by added ether). Analytical methods involved g.l.c. of secondary acetates (50 ft SCOT columns of Apiezon L, at 130 °C, working at *ca.* 10 000 plates); or trifluoroacetates, which gave a rather better separation, at 120 °C with the same column. For the tertiary acetates, squalane was used at 120 °C. The secondary formates could not be separated directly, and formolysis products were cleaved to alcohols; these, obtained thus or directly by solvolysis in aqueous acetone, were analysed as trifluoroacetates. In all cases, isomers were assumed to have the same molar response factor. Additional small peaks were found in acetolysis product derived from 5-methyl-2-adamantyl derivatives, which disappeared on treatment with acetic acid containing toluene-*p*-sulphonic acid, and were assumed to be methyl-protoadamantyl acetates (see following paper).

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