The Stereochemistry of Solvolysis for 2-Adamantyl Derivatives, and the Non-classical Carbonium Ion Question

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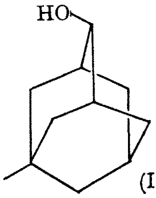
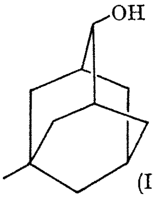
Summary When derivatives of adamantan-2-ol solvolyse they usually exhibit a preference for retention of configuration; as they also rearrange skeletally to some extent, the 2-adamantyl cation meets, in some measure, two of the familiar criteria for delocalisation of C–C σ-electrons, hence general conclusions regarding "non-classical carbonium ions" are drawn.

IN the acetolysis of arenesulphonates, $R^1{\cdot}CH_2{\cdot}CHX{\cdot}CH_2{\cdot}R^2$, unrearranged substitution products are formed with a small retention : inversion ratio, typically $\leqslant$ 0·025—0·1.[1,2] Much higher values characterise branched systems, $R^1{\cdot}CH_2{\cdot}CHX{\cdot}CHR^2R^3$ (*e.g.* 0·49 for *trans, cis*-α-decalyl toluene-*p*-sulphonate[2]), while the doubly-branched 7-norbornyl derivative gives[3] a value of 6—19, and *exo*-2-norbornyl gives[4] much larger values still. The latter have been associated with the non-classical carbonium ion question.[5] The solvolysis of derivatives of the 5-methyladamantan-2-ols, throws new light on these matters.

The oxidative rearrangement of either 2-methyladamantan-2-ol or 3-methyladamantan-1-ol,[6] or the direct oxidation of 1-methyladamantane with 96% sulphuric acid,[6] gives a mixture, separable by chromatography on alumina, of 1-methyladamantanone, m.p. 105—107°, and 5-methyladamantanone, m.p. 125—126° (*ca.* 1 : 8). Reduction of the 5-methyl derivative with conventional reagents gives the *cis* (I) and *trans* (II) alcohols in a 1 : 1 ratio. They were quite exceptionally difficult to separate, as they and all their derivatives prepared formed solid solutions, but systematic chromatography on alumina followed by fractional crystallisation of the least-adsorbed fractions gave mixtures of ratios 99·7 : 0·3, favouring (II), and 83 : 17, favouring (I), from the behaviour of which that of the pure epimers could be inferred by slight extrapolation. Configurations were assigned from the long-range shielding of the methyl group when n.m.r. spectra of the acetates were examined ($\Delta\tau = 0{\cdot}02$). Mixtures were best analysed by chromatography of the trifluoroacetates on Carbowax; arenesulphonates and picrates were analysed after regeneration of the alcohols with lithium aluminium hydride and ammonia,[7] respectively. Rates of acetolysis of the *p*-nitrobenzenesulphonates of adamantan-2-ol, (I) and (II), at 73·6° were 7·95, 3·04, and 4·36, all $\times 10^{-5}$; for trifluoroacetolysis of the toluene-*p*-sulphonates at 32° the values were 4·36, 2·68, and 2·14, all $\times 10^{-3}$ (sec.$^{-1}$). Thus the influence of the methyl group hardly discriminates between the isomers, and is comparable with that in the alcoholysis of 1-bromo-3-methyladamantane.[8] However, product-analyses are more important.



(I)



(II)

TABLE 1

Stereochemistry of acetolysis of (I) *and* (II); *X varies*

X	T	*trans* Ratio†	*trans* $\Delta\Delta G^{\ddagger}$ (cal./mole)	*cis* Ratio†	*cis* $\Delta\Delta G^{\dagger}$ (cal./mole)	2-Adamantyl Ratio†	2-Adamantyl $\Delta\Delta G^{\ddagger}$ (cal./mole)
OTs*	100°	4·26	1070	1·00	0		
OTs	100	4·00	1020	0·85	−120	1·84	450
OTs	130	3·35	965	0·96	−30	1·79	465
ONs	52	4·55	975	1·04	25	2·18	500
ONs	100	4·00	1020	0·96	−30	1·96	495
OPic	100	6·69	1400	0·79	−180	2·29	610

* No NaOAc present; all other runs contain 0·15 M-NaOAc; † retention : inversion.

In acetolysis (Table 1) our results indicate a preference for retention of configuration, complicated by a tendency for substitution to occur from the side not encumbered by a methyl group. Temperature variation suggests that in the *trans*-case, substitution with inversion (from the more hindered side) has the higher enthalpy of activation, but in the *cis*-case imprecision due to extrapolation prevents significant conclusions, except that for both isomers the difference in entropy of activation (inversion *versus* retention) is less than 3 cal. (degrees mole)$^{-1}$ On the basis that the effects of the methyl group in favouring inversion or retention are reciprocal in the *cis*- and *trans*-isomers, estimates (as arithmetical means of $\Delta\Delta G^{\ddagger}$ values) are given for the probable behaviour of the 2-adamantyl system itself. Addition of sodium acetate or sodium toluene-*p*-sulphonate to the acetolysis medium had no effect on the retention/inversion ratio, and changes in the leaving group did not affect it dramatically, but variation of the solvent did affect the course of substitution (Table 2; remarkably, products were stable to solvolysis conditions even in formic and trifluoroacetic acids). Dimethylacetamide, giving acetates *via* imino-ether cations, alone shows a mild preference for inversion; in the three acids and in aqueous acetone a definite preference for retention is observed, the solvents of higher dielectric constant, formic acid and aqueous acetone, showing a marked excess of retention even for the *cis*-isomer. Minor products (*ca.* 3%) including 0·5% of the corresponding protoadamantanol derivatives,[9] were also obtained in these solvolyses.

TABLE 2

Stereochemistry of solvolysis of (I *and* II, $X = OTs$)

Solvent	T	*trans* Ratio*	*trans* $\Delta\Delta G^{\ddagger}$ (cal/mole)	*cis* Ratio*	*cis* $\Delta\Delta G^{\ddagger}$ (cal./mole)	2-Adamantyl Ratio*	2-Adamantyl $\Delta\Delta G^{\ddagger}$ (cal./mole)
MeCO·NMe$_2$	160	0·92	−70	0·25	−1190	0·48	−630
CF$_3$CO$_2$H†	100	3·76	980	0·85	−120	1·79	430
AcOH†	100	4·00	1020	0·85	−120	1·84	450
HCO$_2$H†	100	6·69	1400	2·33	620	3·95	1010
H$_2$O–Me$_2$CO§	100	9·00	1620	3·17	850	5·34	1235

* Retention : inversion
† Containing 0·15M of the sodium salt.
§ 1 : 1, v/v; containing 0·15M-2,6-lutidine.

Models imply a geometrical similarity between the 7-norbornyl[3] and the 2-adamantyl systems, and these are alike in giving small amounts of rearranged products[3,9] and in showing a definite preference for substitution with retention of configuration. They differ in that 2-adamantyl derivatives show essentially normal reactivity. Recent kinetic work[10] indicates that most unbranched secondary arenesulphonates solvolyse with significant "solvent participation" but that 2-adamantyl derivatives, like typical tertiary derivatives, do not, for steric reasons. Such "solvent participation" is linked to a tendency to give inverted substitution products, and is evidently reduced by branching of the skeleton. The interpretation of rates of reaction in such systems has proved controversial, with the direct steric effects[11] proving hard to disentangle from the large changes in reactivity related to intervalency angle,[12] from the anchimeric assistance provided by hydrogen participation and often leading to hydride shift in the products,[13] from contributions to reactivity made by small populations of highly reactive minor conformers,[2,13,14] and from the postulated participation by C–C σ-bonds.[15] We now suggest that in branched systems when C–H participation is stereoelectronically frustated such C–C participation occurs instead quite generally, but that it may involve little change in internuclear distances and little transfer of electronic charge. (Probably it involves little driving force also, but that cannot be proved by a comparison between the rates of reaction of one compound and another, since there may be no such thing as a "normal" compound capable of ionisation without anchimeric assistance). Such C–C delocalisation, negligible in unbranched systems not only because solvent participation is easy, but also because it would tend to transfer charge to a primary centre, increases in importance along the series *trans*, *cis*-α-decalyl, 2-adamantyl, 7-norbornyl, to 2-norbornyl; the first symptom is a change in retention : inversion ratio and the second, when delocalisation becomes more extensive, is the observation of rearranged products (*ca.* 0%,[2] 0·4%,[15] 3%,[3] *ca.* 49·9%[15] respectively). Only at a third stage, when the tendency to delocalise C–C makes itself felt even in the transition state preceding the ionic or ion-pair intermediate, does an indisputable increase in reaction-rate confirm the presence of a "non-classical carbonium ion"; but we see no evidence of a discontinuity along this sequence. In contrast to derivatives of 2-arylethyl and similar alcohols, where substantial agreement now exists[16] that rates can profitably be analysed in terms of competing k_s and k_Δ processes, these cyclic aliphatic systems are less clear-cut, and it remains to be decided whether weak C–C participation may be compatible with attack of a nucleophile from the same side of the ionising –CHX– residue, giving "inverted" product (in competition with the more favoured "retained" product formed by attack at the other side), *via* a triangular transition state[17] in which two nucleophilic centres interact with the same lobe of a developing *p*-orbital. This may become less probable, relative to displacement of the counterion and substitution with retention, as the degree of σ-participation increases. This set of hypotheses has advantages in simplicity and consistency over some earlier discussions,[5] and harmonises well with very recent work by Schleyer *et al.*[10,18]

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