Classical Carbonium Ions. Part VI.[1] Rearrangement during Acetolysis of Some 2-Adamantyl Derivatives

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Deamination of 2-aminoadamantane in acetic acid gives 2-adamantyl acetate but no detectable 1-adamantyl acetate; a 4→2 hydride shift is also undetectable. Unexpectedly the products include substantial amounts of skeletally rearranged products which are much less stable than adamantane derivatives. Acetolysis of 2-adamantyl toluene-*p*-sulphonate also gives, in smaller yield, a skeletally rearranged acetate. The significance of these highly endothermic alkyl shifts is discussed, and reasons are advanced for postulating weak σ-participation in the 2-adamantyl cation.

SOME solvolytic reactions, including deamination, generally give rise to larger yields of rearranged products than do others, such as arenesulphonate acetolysis; the term ' hot carbonium ion ' has been used to describe the intermediates present in the former group.[2] The 2-adamantyl system appeared to show resistance to rearrangement by hydride shift during arenesulphonate acetolysis,[3] and we therefore sought to apply the same tests in deamination reactions, that is, to measure 1→2 shift, as the yield of 1-adamantyl acetate formed during the deamination of 2-adamantylamine, using g.l.c., and 4→2 shift, by determining 2-adamantyl acetate having protium adjacent to oxygen formed during the deamination of [2-^{2}H]-2-adamantylamine. We assumed that the notoriously stable adamantane nucleus would resist skeletal rearrangement.[4]

2-Adamantylamine was known, and its 2-deuterio-derivative was readily prepared by reduction of adamantanone oxime with lithium aluminium deuteride. For deamination we employed the aryltriazene method of White and Sherrer:[5] crystalline 2-adamantylphenyltriazene proved unstable, but was obtained with some difficulty (whereas attempts to prepare related nitrosoamides were unsuccessful). On treatment of the triazene with acetic acid, a product was obtained which was analysed for 1-adamantyl acetate. None was found; an upper limit of 0.02% yield was established. We then prepared the phenyltriazene derived from [2-^{2}H]-2-adamantylamine. This amine was analysed for protium adjacent to nitrogen by comparing the area of the n.m.r. band at τ 5.8 with that of the ^{13}C sideband of the methyl peak of its acetyl derivative,[3b] which indicated 0.43 ± 0.04%. Acetolysis of the triazene and careful purification of the 2-adamantyl acetate gave a product which was analysed in a similar way, and found to contain 0.44 ± 0.10% α-protium, implying a negligible amount of 4→2 hydride shift. This result also eliminates a significant contribution from a reaction *via* 2-diazoadamantane.

These experiments precisely parallel those described for 2-adamantyl toluenesulphonate described in our earlier paper,[3b] and were those envisaged at the outset of our work; they prove comparably low upper limits to the hydride shifts considered. They are, however, surpassed in interest by experimental results that had

[1] Part V, J. A. Bone, J. R. Pritt, and M. C. Whiting, preceding paper.

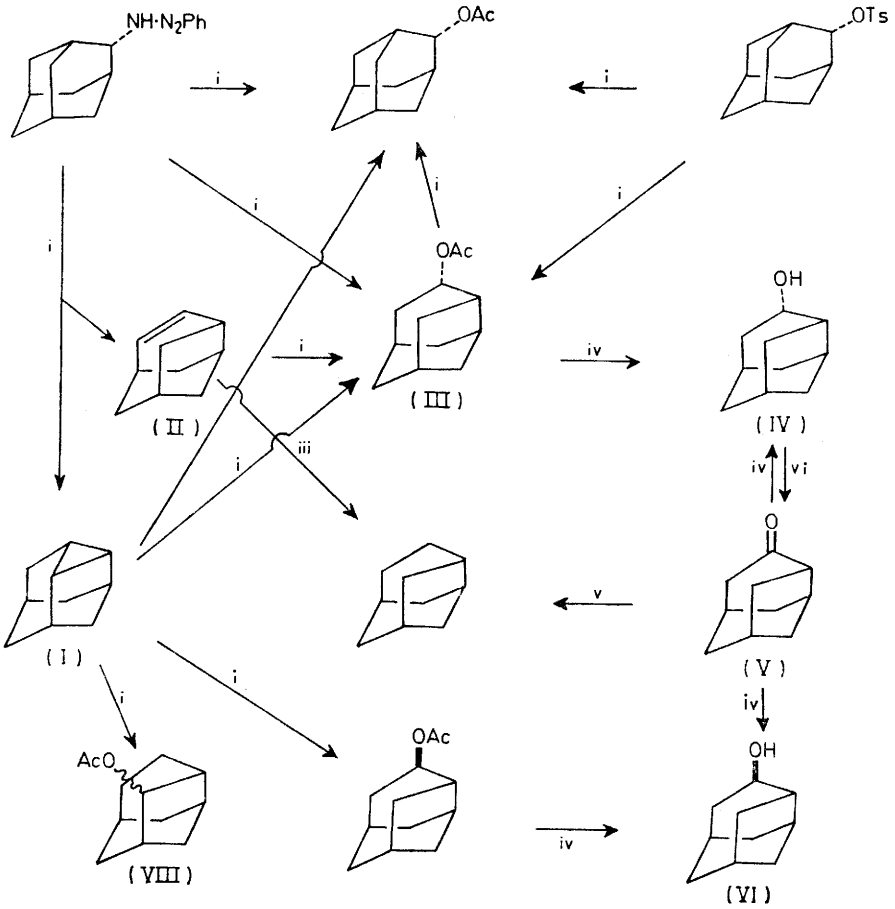
[2] (*a*) L. S. Ciereszko and J. G. Burr, *J. Amer. Chem. Soc.*, 1952, **74**, 5431; (*b*) J. D. Roberts, G. C. Lee, and W. H. Saunders, jun., *ibid.*, 1954, **76**, 4501.

[3] (*a*) P. von R. Schleyer and R. O. Nicholas, *J. Amer. Chem. Soc.*, 1961, **83**, 182; (*b*) M. L. Sinnott and M. C. Whiting, *J.C.S. Perkin II*, 1975, 1446.

[4] H. W. Whitlock and M. W. Siefken, *J. Amer. Chem. Soc.*, 1968, **90**, 4929.

[5] E. H. White and H. Sherrer, *Tetrahedron Letters*, 1961, 758.

not been predicted. As well as 2-adamantyl acetate, and a basic compound (*ca.* 30%; presumably mainly *N*-2-adamantylaniline, discussed below), g.l.c. of the triazene decomposition products revealed six additional products. Three were relatively trivial; they were adamantan-2-ol (2%), and adamantane (0.4%) and adamantanone (1.5%), evidently formed by hydride transfer from the already formed 2-acetate to the 2-cation. When the concentration of the 2-acetate was greatly increased by adding authentic material to the adamantene (II), then unreported, and the new acetate proved to be that (III) of *exo*-protoadamantan-4-ol (IV). The transformations which establish these conclusions are outlined in the Scheme and described in the Experimental section; these compounds, of some theoretical interest, have, since our work was published briefly,[6] become more readily available, and the spectra of our first samples agree with those prepared by later and better methods.[7] Although protoadamantan-4-one (V) on reduction gives *endo*- (VI) and *exo*- (IV) alcohols in



SCHEME Reagents: i, HOAc; ii, HOAc–TsOH; iii, H_2–PtO_2; iv, $LiAlH_4$; v, N_2H_4–NaOH; vi, CrO_3–H_2SO_4

reaction mixture, the yields of these products increased to 25 and 40%; the lower yield of adamantane emphasises that our recovery of such volatile products was incomplete. A fourth by-product was the known 2,4-didehydroadamantane (I) (7.8%), which under the mild deamination conditions survives. There remained two more products, one appearing in the hydrocarbon region of the chromatograph, and one in the acetate region.

The new hydrocarbon was proved to be proto-comparable (69 : 31) yields, the acetolysis product of the triazene was exclusively (>99.5%) the *exo*-isomer.

The basic product from the triazene was essentially crystalline and, no doubt, was essentially *N*-2-adamantylaniline, which structure fitted analysis and i.r. spectrum. However, one would expect that a proto-adamantyl derivative would be present, and *C*-alkylation *ortho* and *para* to the amino-group would also be possible; we did not investigate this fraction. The conclusions of Maskill, Southam, and Whiting as to the concerted mechanism of s-alkylaryltriazene acetolysis[8] are probably valid also for the 2-adamantyl case. Apart from

[6] H. Storesund and M. C. Whiting, *Chem. Comm.*, 1969, 1000.

[7] (*a*) J. Boyd and K. H. Overton, *J.C.S. Perkin I*, 1972, 2533; (*b*) D. Lenoir and P. von R. Schleyer, *Chem. Comm.*, 1970, 941; (*c*) D. Lenoir, R. E. Hall, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1974, **96**, 2138.

[8] H. Maskill, R. Southam, and M. C. Whiting, *Chem. Comm.*, 1965, 495.

these basic compounds and also the redox products the yields of compounds produced by rearrangement are about 5.8% (protoadamantyl acetate), 3.6% (protoadamantene), and (probably from the same intermediate) 11.3% (didehydroadamantane).

As a rule, deamination reactions and arenesulphonate solvolysis give qualitatively similar results; the discovery of rearranged products in the deamination therefore prompted the reinvestigation of the acetolysis of 2-adamantyl toluene-*p*-sulphonate in the presence of a buffer salt, which had been stated by Schleyer and Nicholas [3a] to give only 2-adamantyl acetate. When g.l.c. methods known to be capable of separating the two acetates at a large weight ratio were used, *exo*-4-protoadamantyl acetate (III) was readily observed in a yield of 0.4—0.5%. Its identity with the deamination product followed not only from g.l.c. inseparability at 10 000 plates, but also from the measurement of its rate of disappearance (isomerisation to 2-adamantyl acetate) in similar solutions of toluenesulphonic acid in acetic acid. Under these conditions *endo*-4-protoadamantyl acetate was unreactive. This latter compound was absent (yield <0.001%) from the toluenesulphonate acetolysis products also. Such experiments persuaded us that the whole chemistry of the 2-adamantyl–4-protoadamantyl system could be worked out by sub-milligram g.l.c. methods; the prompt appearance of a good synthesis of protoadamantane derivatives [7b] has allowed this to be done [7c] instead by orthodox means. In the solvolysis of 2-adamantyl toluenesulphonate, the formation of 2,4-didehydroadamantane (I) could be estimated only indirectly (≯0.3%), as it is unstable under the conditions of the experiment; protoadamantene (II) could not be conclusively proved to be present, although a minute peak probably indicated a yield of 0.005%. Thus, whereas in the deamination (at 25 °C) the relative yields of protoadamantyl acetate, protoadamantene, and didehydroadamantane are about 1 : 0.6 : 2, in the arenesulphonate solvolysis (at 100 °C) they are about 1 : 0.01 : <0.7. If, in each reaction, the rearranged products come from one intermediate, the two intermediates, although related, cannot be identical, since the variation of such ratios with temperature would be expected to be, and in related cases is,[9] much less drastic than this. The direct equilibration of protoadamantyl and 2-adamantyl acetates was attempted in acetic acid containing toluenesulphonic acid at 20 °C, the experimental technique being pushed to its limits both by overloading the column and using the detector at extreme sensitivity. The measured ratio was 400 000 : 1 subject, of course, to poor signal-to-noise ratio and possible systematic errors; this corresponds to $\Delta G =$ 31 kJ (7.5 kcal) mol^{-1}, as compared with a calculated value [10] of *ca.* 47 kJ (11.3 kcal) mol^{-1}, and $\Delta\Delta G^{\ddagger}$ values of only *ca.* 3.6—5.9 (0.9—1.4) and 7.9—10.0 kJ (1.9—2.4 kcal) mol^{-1} for rearranged to unrearranged products in the deamination and arenesulphonate acetolysis (the ranges quoted allow for whether or not didehydroadamantane is formed from the toluenesulphonate, and whether or not it is attributed to the same intermediate from the aryltriazene).

We now turn to the significance of the results recorded in this and the previous two papers. The non-occurrence of 1→2 hydride shift in the adamantane nucleus has been stressed by Schleyer; [11] in the light of experiments reported subsequent to our work such processes in the short-lived intermediates of solvolysis are now seen to be improbable. The observation of rearranged products, however, was unexpected, and its importance can hardly be overstated; we know of no related case in which rearrangement has occurred to a derivative of a much less stable carbon skeleton without simultaneous stabilisation at the cationic centre. Thus Streitweiser and Schaeffer write of deamination [12] ' rearrangement apparently occurs only when a more stable carbonium ion results '; but they anticipate our view by adding ' these reactions are perhaps better regarded as resulting from the tendency of the leaving nitrogen to *pull* over the *trans* group.' Reutov and Shatkina state [13] without including details of how it was identified, that cyclohexylamine gives, in unstated yield, cyclopentylmethanol along with cyclohexanol on deamination; such a process would, formally, involve a primary carbonium ion less stable than that initially formed. Unpublished work in these laboratories confirms their report. Evidently carbon–carbon σ-bond migration is a process which, when the geometrical constraints of the system impose the correct stereoelectronic arrangement, happens even when it leads, eventually in part, to a much less stable product. If we accept the view that σ-bond migration in the overall process, an observed fact, is a consequence of σ-bond electron delocalisation in the cationic intermediate, we may frame a further hypothesis; that weaker σ-delocalisation is likely to occur in the transition state leading to the cationic intermediate (with a resultant acceleration of the reaction by a factor which may be too small to be detected). The intermediate itself is of course a cyclic two-electron system analogous to cyclopropenyl cation, to which it bears the same topological relationship that the symmetrical transition state (or metastable intermediate) in the Cope rearrangement does to benzene In the further transformation of the intermediate to products, independent access of a nucleophile is possible at any site having net positive charge, and as these reactions are strongly exothermic, the selectivity is small and significant amounts of the less stable products result. Because these sites are involved in an intermediate having a delocalised 2-electron 3-centre bond, the

[9] 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.
[10] D. Lenoir, D. J. Raber, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1974, **96**, 2149.
[11] P. von R. Schleyer, *Angew. Chem. Internat. Edn.*, 1969, **8**, 529.
[12] A. Streitwieser, jun., and W. D. Schaeffer, *J. Amer. Chem. Soc.*, 1957, **79**, 2888.
[13] O. A. Reutov and T. N. Shatkina, *Tetrahedron*, 1962, **18**, 237.

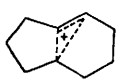
addition of a nucleophile is usually stereospecific. The same intermediate is a potential source of a cyclopropane, by proton abstraction with the concomitant conversion of C–C half-bonds to full bonds. This set of hypotheses, variously formulated, is of course the essence of ' non-classical carbonium ion theory.' Many of the phenomena which it was created in order to rationalise can be explained on the basis of pairs of rapidly interconverting carbonium ions; but we cannot see how such a hypothesis could plausibly explain the formation of rearranged products from the 2-adamantyl cation, in yields far exceeding equilibrium ratios. If we take the measured value (probably underestimated) of 2-adamantyl acetate to 4-protoadamantyl acetate as 400 000 : 1 and to apply to the hypothetical equilibrating 2-adamantyl and 4-protoadamantyl cations, as to a good approximation it should, then the observed yield ratio of about 13 : 1 requires that the former reacts with acetic acid about 30 000 times more slowly than does the latter. But even the latter cannot react at more than the diffusion-controlled limiting rate, while on the other hand the former is known to react with aniline, liberated in the immediate vicinity of the cation, faster than the latter can diffuse away (since the products include 30% of *N*-2-adamantylaniline). In the triazene deaminations of primary carbinylamines, where a long-lived reactive intermediate (alkanediazonium ion) is involved, this diffusion does occur and the yield of alkylated aniline is negligible.[8]

In the deamination of 2-adamantylamine the abundant formation of very unstable rearrangement products makes the postulated intervention of a σ-delocalised intermediate almost inescapable; what can one say of the acetolysis of the arenesulphonate, where the yield of protoadamantyl acetate is ' only ' about two thousand times the equilibrium value? We have argued above that a different but related intermediate must be involved, and have suggested [6] that this is an ion-pair of which the cation is a more perturbed form of that involved in the deamination, and that its tendency to give substitution products in which the original configuration is retained (preceding paper) is closely related to the simultaneous formation of *exo*-4-protoadamantyl acetate. Such an intermediate must differ from an ion-pair related to the potentially symmetrical 2-norbornyl cation, for example, in having the charge distributed between the original centre and that to which it is transferred by skeletal arrangement in a ratio greatly favouring the former. It is important that the acetates formed by collapse at the minor centre of charge are almost entirely one stereoisomer of 4-protoadamantyl acetate, but that collapse at the major centre to give 2-adamantyl acetate proceeds with only a *ca.* 2 : 1 advantage for the retained product. Evidently, with a so weakly developed fractional σ-bond on the side *anti* to the departing anionic group, the approach of a solvent molecule from that side is only discouraged, not forbidden. Alternatively the ill-understood phenomenon of ' leakage ' could be postulated—this would give in the 5-methyl derivative an epimeric, *i.e.* ' inverted,' 2-adamantyl acetate, but in the unsubstituted case, merely the enantiomeric protoadamantyl acetate.

Since our first proposal [6] that the 2-adamantyl cation was weakly delocalised, the work of Lenoir, Raber, and Schleyer [10] on the 1-methyl-2-adamantyl cation has provided valuable confirmation and clarification; the balancing of the increased strain energy of the protoadamantyl system (>30 kJ mol^{-1}) by the stabilisation of a carbonium ion centre by an additional alkyl substituent (*ca.* 45 kJ mol^{-1}) leads to an intermediate which is much more equally related to its two extreme forms, as shown by its reaction products, and therefore more obviously stabilised.

In a recent discussion of our work on 2-adamantyl toluenesulphonate which ignores the simultaneously reported deamination results,[6] Harris *et al.* propose [14] ' rate-limiting formation of a classical solvent-separated ion-pair which is subject to destruction by three competitive pathways: frontside collapse, backside nucleophilic displacement, and backside neighbouring group attack to give a rearranged carbocation or possibly a non-classical ion.' One difficulty of this proposal is that it uncouples the exothermic section of the process, lying between the main transition state and the ion-pair intermediate, from the highly endothermic skeletal rearrangement; it is difficult to see why this should occur at all, unless the product is not merely non-classical but is extensively stabilised by its σ-delocalisation, which is improbable. To us it seems that there is no advantage in inserting a second intermediate between the initial ion-pair (which indeed would, on time and population average, be ' solvent-separated,' and would be almost classical, in the sense that its bond-order and charge-distribution would be highly asymmetric in favour of the 2-adamantyl canonical form) and the final products.

If our views on the 2-adamantyl cation are accepted, one may ask what happens in systems which are similarly constrained to a configuration allowing participation by a C–C σ-bond, but even more unfavourable to such a process than the 2-adamantyl system. In *trans,trans*-α-decalyl toluenesulphonate, for example, rearranged products were sought but not found; [9] however, the substitution : elimination ratio is unusually high, and so is the retention : inversion ratio (0.49 : 1 as compared with 0.1 : 1 or less in typical cyclohexane systems). Here there is, of course, less steric hindrance to solvent approach *anti* to the leaving group. In *trans,trans*-bicyclo[4.3.0]nonan-1-yl toluenesulphonate the only



(VII)

indication that the potentially symmetrical cation (VII), which is considered by Foote and Woodward in

[14] J. M. Harris, A. Becker, J. F. Fagan, and F. A. Walden, *J. Amer. Chem. Soc.*, 1974, **96**, 4484.

another connection,[15] may play a part is that the substitution : elimination ratio is unusually high (retention : inversion ratio not known). Further investigation of this system could throw more light on the way in which very weak C–C participation affects products. It seems at least possible that, as σ-delocalisation increases, the effects successively observed are (i) an increase in substitution : elimination ratio; (ii) an increase in the retention : inversion ratio; (iii) formation of skeletally rearranged products; and (iv) accelerated solvolysis. However, symptom (i) may well find better explanations; and we may have to distinguish between systems where σ-participation is weak because of asymmetry in charge distribution, and those where it is weak through weak development of cationic character, in reactions involving little-hindered, reactive intimate ion-pairs. It may suffice that caution is exercised in accepting any system as free from weak σ-delocalisation if it has a C–C bond antiparallel to the leaving group.

A third method of generating the 2-adamantyl cation was briefly examined; didehydroadamantane is unstable even in buffered acetic acid. The main products proved to be 2-adamantyl and *exo*-4-protoadamantyl acetates, this time in a ratio of 54 : 1, intermediate between, and significantly different from, the ratios (*ca.* 13 : 1 and 200 : 1) observed for the deamination and arenesulphonate solvolysis products. A third compound was present in appreciable (0.4%) yield, and this behaved gas-chromatographically like *endo*-4-protoadamantyl acetate, and the derived alcohol and ketone were also inseparable from 4-protoadamantyl derivatives; however, the *endo*-acetate is stable to mild treatment with toluenesulphonic acid in acetic acid, and this compound was not [although its removal left what may have been a much smaller (0.05%) yield of the *endo*-4-acetate]. The new acetate is thus possibly a 2-protoadamantyl acetate, or its further isomerisation product.

Analysis of acetolysis products from 1-(2-adamantyl)-3-phenyltriazene

Run *	2-Ada-OAc	2-Ada-OH	Adamantane	Adamantanone	Amines	(III)	(II)	(I)
1	49.5	0.8	0.4	0.9	26.5	3.7	2.3	7.2
2	49.7	0.9	0.3	0.9		3.8	2.5	7.5
3	49.2	0.8	0.3	0.8	27.1	3.6	2.2	6.9
(4)	54.0	0.9	0.4	1.0	29.4	4.0	2.5	7.8
(5)	79.0					5.9	3.7	11.4

* 1,2,3, Experimental runs; (4), average of 1—3 normalised to 100% from average total yield of 91.5%; (5), yields normalised to Σ(significant products) = 100.

EXPERIMENTAL

[2-^{2}H]-2-*Adamantylamine*.—Adamantanone oxime (11.0 g) was dissolved in dry ether (50 ml) and added slowly to a stirred suspension of lithium aluminium deuteride (1.0 g; isotopic purity >99.5%) in dry ether (30 ml). After 1 h the excess of deuteride was destroyed by addition of a few drops of concentrated aqueous sodium sulphate. The inorganic salts were filtered off and the solution was dried and evaporated. The amine was immediately dissolved in methanol (50 ml) to which had been added concentrated hydrochloric acid (1 ml). After 15 min the solution was diluted with water (50 ml) and evaporated to *ca.* 20 ml. The amine hydrochloride precipitated upon cooling. It was twice recrystallised from dilute hydrochloric acid giving [2-^{2}H]-2-adamantylamine hydrochloride (2.5 g, 20%), m.p. 300—312° (decomp.).

1-(2-*Adamantyl*)-3-*phenyltriazene and* 1-([2-^{2}H]-2-*Adamantyl*)-3-*phenyltriazene*.—2-Adamantylamine hydrochloride (3.0 g) and anhydrous sodium carbonate (11.5 g) were stirred under nitrogen at 20 °C for 2 h in tetrahydrofuran (60 ml; redistilled from potassium hydroxide pellets). The mixture was then cooled to −5 to −10 °C and, over 15 min, a pre-cooled (−15 °C) slurry of benzenediazonium tetrafluoroborate (3.02 g) in tetrahydrofuran (100 ml) was added. Stirring at −5 °C was continued for *ca.* 1½ h until diazonium ions were no longer detected (test with alkaline 2-naphthol). The solution was then filtered and the clear red filtrate was distilled under reduced pressure at 0 °C. The dark red residue was extracted four times with pre-cooled (−5 °C) light petroleum (b.p. 30—40°) to give an orange-yellow solution (60 ml). After filtration this solution was evaporated *in vacuo* to *ca.* 20 ml and quickly cooled to −70°, whereupon a semi-solid precipitate was formed. When the temperature was allowed to rise to 0 °C, the precipitate did not dissolve completely. The insoluble side products were filtered off. This purification was performed five times until the precipitate formed at −70 °C went completely into solution at 0 °C. The mixture was then placed in a refrigerator (−30°) whereupon large, brick-red crystals were formed. The mother-liquor was removed with a pipette at −30 °C and the crystals were washed twice at −70 °C with light petroleum (b.p. 30—40°), and finally dried at 0.5 mmHg and −15° giving 1-(2-*adamantyl*)-3-*phenyltriazene* (820 mg, 20%), m.p. 74.5—75.5°, $\lambda_{max.}$ (iso-octane) 273 (ε 13 400) and 298sh nm (Found: C, 74.8; H, 8.2; N, 16.3. $C_{16}H_{21}N_3$ requires C, 75.2; H, 8.3; N, 16.4%). An exactly analogous procedure with [2-^{2}H]-2-adamantylamine hydrochloride (1.7 g) gave (1-[2-^{2}H]-2-adamantyl)-3-phenyltriazene (302 mg, 13%) whose semi-solid nature indicated some impurities. (It was solvolysed directly.)

Solvolysis Procedure.—Acetic acid was distilled from tetra-acetyl diborate and typically contained 0.08% of water. To it (100 ml) were added *trans*-decalin (3.00 g) and anhydrous potassium acetate (1.47 g); this solution (2 ml) was added at 20 °C to the triazene (60 mg). After 1 h light petroleum (b.p. 30—40°; 3 ml) was added, the mixture was cooled in ice, and a solution (14 g) of di-

[15] C. S. Foote and R. B. Woodward, *Tetrahedron*, 1964, **20**, 687.

potassium hydrogen phosphate (200 g) and potassium hydroxide (67 g) in water (200 ml) was added. After shaking, the petroleum phase was washed with water, dilute aqueous tetrafluoroboric acid, which removed complex amines without giving precipitates, and water. G.l.c. on Carbowax 1540 at 130 °C gave three poorly separated hydrocarbon peaks, then peaks at the following retention times (min), with relative peak areas in parentheses: 42(1), identified by co-injection as adamantanone; 49(51), identified by co-injection as 2-adamantyl acetate; 56(4), protoadamantyl acetate, referred to below; and 62(1), identified as adamantan-2-ol. Similar results were obtained on Apiezon and MBM columns, the known compounds again being identified by co-injection. When the MBM column was used at 100 °C, the early peaks were at 16 min (*trans*-decalin); 22(3), identified as adamantane; 25(8), identified as protoadamantene; and 30(24), identified as didehydroadamantane (see below). When the 130 °C chromatogram was examined, at 39 min the signal was flat, where calculation showed that a 0.02% yield of 1-adamantyl acetate would have been detected.

From the tetrafluoroboric acid washings, crude *N*-2-adamantylaniline (20 mg from 150 mg of triazene) could be isolated; m.p. 150—153° (Found: C, 85.1; H, 9.5; N, 6.0. Calc. for $C_{16}H_{21}N$: C, 84.6; H, 9.2; N, 6.0%), $\lambda_{max.}$ (iso-octane) 296 nm (ε 1 600).

Interconversions.—Neutral acetolysis products (120 mg) from triazene (*ca.* 250 mg) in acetic acid–potassium acetate were chromatographed on alumina (50 g) giving hydrocarbons (*ca.* 20 mg) and acetates (93 mg). The latter fraction was reduced with lithium aluminium hydride (20 mg) to alcohols [68 mg; retention times at 130 °C on diethylene glycol succinate (DEGS) 18(50), augmented by adamantan-2-ol, and 19.5(4)]. Oxidation with chromic acid in acetone gave ketones (50 mg), with retention times on Carbowax 1540 at 130 °C of 35(50) (adamantanone) and 47(4). Such material (120 mg) was carefully chromatographed on alumina (50 g; Woelm neutral; deactivated to grade I) with 25% ether–light petroleum (b.p. 30—40°) giving early fractions containing adamantanone, $\nu_{max.}$ (CCl_4) 1 733 and 1 724 cm^{-1}, and later fractions containing the other ketone and adamantanone (3 : 1 by g.l.c.), $\nu_{max.}$ 1 722 and 1 713 cm^{-1}, M^+ (g.l.c.–mass spectrometry) 150.

The original ketone mixture (50 mg) was added to triethylene glycol (5 ml), and hydrazine hydrate (0.3 ml) was added. The mixture was heated to *ca.* 85 °C for 30 h, and cooled; dry, powdered potassium hydroxide (60 mg) was added and the mixture heated to 200 °C for 6 h. The apparatus, containing sublimed material, was washed with pentane and water; the water and glycol were extracted with pentane and the extracts were washed with sodium chloride solution and distilled at 0 °C to give a hydrocarbon mixture (27 mg) showing no carbonyl absorption. On g.l.c. on Apiezon at 121 °C two peaks were observed; 14(25), augmented by adamantane, and 15.5(2); the latter showed *m/e* 136 (isomeric with adamantane) and was recognised as protoadamantane.

2,4-Didehydroadamantane (I) [16] (100 mg) in ether (50 ml) was hydrogenated at 200 atm and 20 °C in the presence of platinic oxide. Analysis of the product indicated two hydrocarbons (ratio 4 : 1) inseparable from the above two.

The hydrocarbon mixture from the acetolysis of the triazene (*ca.* 4 mg) was treated with acetic acid (0.5 ml) at 100 °C. Analysis on MBM at 100 °C as described above showed the absence of the 30 min peak ascribed to 2,4-didehydroadamantane; the others remained. Alumina chromatography removed acetates and hydrogenation gave the same mixture of saturated hydrocarbons, protoadamantane being the main component. When a similar mixture (2 mg) of hydrocarbons from a deamination was treated with a slight excess of potassium permanganate in acetone (2 ml) at 20 °C for 2 h, the 25 min peak vanished; chromatography then gave 2,4-didehydroadamantane, identified by its characteristic 3 035 cm^{-1} i.r. band (cyclopropane C–H str.) and inseparable from authentic material on three different columns.

Acetolysis of 2-Adamantyl Toluene-p-*sulphonate.*—The arenesulphonate (50 mg) was heated in buffered acetic acid (2 ml) at 100 °C for 17 h; isolation of the products with light petroleum and g.l.c. on Carbowax 1540 gave adamantyl acetate, 49(200), and *exo*-4-protoadamantyl acetate, 56(1). Cleavage ($LiAlH_4$) of the acetate mixture and analysis on DEGS gave adamantan-2-ol, 18(200), and *exo*-protoadamantan-4-ol, 19.5(1); the yield of *endo*-protoadamantanol, 23.5, was less than 0.01%. In three runs, the yields of *exo*-4-protoadamantyl acetate were 0.45, 0.5, and 0.4%.

In a similar solvolysis in unbuffered acetic acid, only 2-adamantyl acetate was observed. Protoadamantene is stable under these conditions, and a yield of 0.005% *may* have been observed; in this case the yield of *endo*-protoadamantyl acetate, 57, could be placed below the limit of 0.005%.

Acetolysis of 2,4-Didehydroadamantane.—The hydrocarbon (20 mg) was heated in buffered acetic acid (1 ml) for 17 h; isolation of the products with light petroleum gave 2-adamantyl acetate, 49(100), and (mainly) *exo*-4-protoadamantyl acetate, 56(2). The corresponding alcohols, analysed on DEGS, comprised adamantan-2-ol, 18(500), *exo*-protoadamantan-4-ol, 19.5(10), and a compound with the same retention time as *endo*-protoadamantan-4-ol, 23.5(3). The corresponding ketone fraction gave two peaks only, ratio 50 : 1, on three different columns, retention times agreeing with adamantanone and protoadamantanone; similarly, Wolff–Kishner reduction of the ketonic fraction gave two peaks, ratio 50 : 1, again agreeing with adamantane and protoadamantane, on three columns. Identification of the 23.5 min peak as *endo*-protoadamantan-4-ol would be unsafe, because treatment of the original acetate mixture with toluenesulphonic acid (0.15M in acetic acid for 10 h at 50 °C) gave a product giving only two peaks, 49(2 000) (2-adamantyl acetate) and 57(1) (*endo*-4-protoadamantyl acetate?). Under these conditions the *exo*-4-protoadamantyl acetate isomerised to adamantyl acetate, as expected, so that the greater part of the 23.5 min alcohol may have been another compound [protoadamantan-2-ol (VIII)?] which co-chromatographed with the *endo*-4-isomer.

Rate of Disappearance of exo-4-*Protoadamantyl Acetate* (III) *in Acetic Acid–Toluene*-p-*sulphonic Acid.*—The two mixed acetate products from the acetolysis of 2-adamantyl tosylate and the acetic acid deamination of 1-(2-adamantyl)-3-phenyltriazene were each weighed into a 10 ml flask and equilibrated at 51 ± 0.2 °C. Acetic acid 0.15M in toluene-*p*-sulphonic acid monohydrate (5 ml) was equilibrated at the same temperature and quickly poured into the flasks containing the acetate. Samples (0.5 ml) were taken at regular intervals and analysed by the usual solvolysis procedure, $\ln(x/y)$ being plotted against time (where x and

[16] A. C. Udding, J. Strating, H. Wynberg, and J. L. M. A. Schlatmann, *Chem. Comm.*, 1966, 657.

y are the concentrations, determined by g.l.c., of protoadamantyl and adamantyl acetates, respectively, at time t): first-order rate-constants of 1.86×10^{-4} and 1.82×10^{-4} s^{-1} for the products of tosylate solvolysis and triazene deamination, respectively, were obtained.

Equilibration of Protoadamantyl and 2-*Adamantyl Acetates in Acetic Acid containing Toluene*-p-*sulphonic Acid.*—2-Adamantyl tosylate (30 mg) was heated in unbuffered, dry acetic acid (2.0 ml) at 100 °C for 15 h. After the solvolysis products had been equilibrated at 20 °C and worked up by the usual procedure, g.l.c. analysis indicated that the ratio of 2-adamantyl acetate to *endo*- and *exo*-4-protoadamantyl acetate was about (probably more than) $4 \times 10^5 : 1$.

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