Classical Carbonium lons. Part IV.¹ Absence of Hydride Shift in the Solvolysis of 1- and 2-Adamantyl Toluene-p-sulphonate

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Upper limits of 0.1, 0.01, 0.15, and 0.3%, respectively, have been placed on $2 \rightarrow 1$ hydride shift in the acetolysis of 1-adamantyl toluene-p-sulphonate, $1\rightarrow 2$ and $4\rightarrow 2$ hydride shifts in the acetolysis of 2-adamantyl toluenep-sulphonate, and the formation of 2,4-didehydroadamantane in the latter reaction. These hydride shifts may well not occur at all.

IN Part I² we showed that, contrary to earlier belief, a $2 \rightarrow 1$ hydride shift is important (ca. 15%) in the solvolysis of such (mainly) equatorial arenesulphonates as that of trans-4-t-butylcyclohexanol, as in other systems examined. It was suggested that its occurrence might be necessary, prima facie, for the postulation of an $S_{\rm N}$ process. To this generalisation one system seemed likely to be an exception; that of adamantane, where 60° torsion angles and rigid geometry might well inhibit rearrangements. Indeed, i.r. measurements³ indicated that the acetolysis product from 2-adamantyl toluene- ϕ sulphonate contained little, if any, 1-acetate-no error limit was given, but 5-10% might be a reasonable estimate. We wished to consider much smaller amounts of $1 \rightarrow 2$ shift than that, and by g.l.c. were able to show that the proportion of 1-acetate was less than 0.01%. Acetolysis of the 1-toluenesulphonate gave a product containing less than 0.1% of the 2-acetate, the separation here being less favourable. It is of course probable that no hydride shift occurs in these reactions.

We also considered the possibility of a $4 \rightarrow 2$ shift in the acetolysis of the 2-toluenesulphonate. This was examined by preparing [2-2H]adamantan-2-ol, converting into the toluene-p-sulphonate, and measuring the protium content at C-2 $(0.27 \pm 0.05\%)$ † by comparing the area of the band at τ 5.50 with that of the ¹³C sideband of the methyl peak, using a concentrated solution. Acetolysis gave an acetate which was isolated and examined similarly, the hydrogen at position 2having $0.32 \pm 0.08\%$ of protium. This implies that $0.05 \pm 0.1\%$ of protium had migrated from position 4 to position 2 during the solvolysis, or that intermolecular processes had led to a similar result. It seems safe to assume that direct $4 \rightarrow 2$ rearrangement in this process probably does not occur at all, and if it does, it accounts for <0.15% of the 2-adamantyl acetate formed. In the formally related case of the acetolysis of exonorbornan-2-yl are nesulphonates, at 45 $^{\circ}\mathrm{C}$ the proportion of $6 \rightarrow 2$ hydride shift is $27\%.^5$

2,4-Didehydroadamantane is a possible product of the acetolysis of the 2-arenesulphonate; if it is formed, it would not be detectable directly, as it is unstable under the reaction conditions giving mainly 2-adamantyl acetate.⁴ Its yield cannot exceed 0.3%, on the evidence cited.

The solvolysis of 2-adamantyl toluenesulphonate is further discussed in the following paper.

EXPERIMENTAL

[2-2H]Adamantan-2-ol.—This was made by addition of adamantanone (312 mg) in dry ether (1 ml) to a suspension of lithium aluminium deuteride (0.50 mg; >99% ²H; CIBA) in the same solvent (10 ml). Destruction of the excess of deuteride with wet ether, washing of the combined ethereal solutions with aqueous 2N-sulphuric acid and then saturated aqueous hydrogen carbonate, and evaporation gave a residue which on recrystallisation from light petroleum (b.p. 60-80°) afforded the title compound, m.p. 300-304° (sealed capillary) (lit.,³ 296–298° for adamantan-2-ol).

1-Adamantyl toluene-p-sulphonate, m.p. 79-83° (decomp), has been reported.6 2-Adamantyl toluene-p-sulphonate, m.p. 83-83.5° (lit., 3 82.7-83.7) and its α-deuterio-analogue, m.p. 83.5-84.5°, were made by standard procedures.

1- and 2-Adamantyl Acetates .- The alcohol (76 mg) was heated with acetic anhydride (3 ml) for 6 h at 100 °C. The cooled solution was then poured into a mixture of water (ca. 50 ml) and pyridine (3 ml) to destroy the excess of anhydride. Extraction of the aqueous solution with light petroleum (b.p. 30-40°) free of aromatic impurities, thorough washing of the organic layer with aqueous 2n-hydrochloric acid and saturated aqueous sodium hydrogen carbonate, and evaporation yielded the products. Five-fold recrystallisation of crude 1-adamantyl acetate from light petroleum between 20 and -70 °C yielded crystals, m.p. 28-30° (Found: C, 73.8; H, 9.25. Calc. for C₁₂H₁₈O₂: C, 74.25; H, 9.25%). Since our work, Stepanov and Stolyarov 7 have

4 M. L. Sinnott, H. J. Storesund, and M. C. Whiting, Chem. Comm., 1969, 1000.

⁵ J. A. Berson, R. G. Bergman, J. H. Hammons, and A. W. McRowe, *J. Amer. Chem. Soc.*, 1967, 89, 2581.
 ⁶ M. L. Sinnott and M. C. Whiting, *J. Chem. Soc.* (B), 1971,

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⁷ F. N. Stepanov and Z. J. Stolya.ov, Zhur. Vsesoyuz. Khim. obshch. in D.I. Mendeleeva 1968, 18(b), 713 (Chem. Abs., 1969, 70, 77,422s).

[†] In our preliminary communication,⁴ an error of a factor of 4 unfortunately increased the protium contents reported; our con-clusions are now unchanged, but our upper limits are reduced by this factor.

¹ Part III, I. D. Page, J. R. Pritt, and M. C. Whiting, J.C.S. Perkin II, 1972, 906. ² N. C. G. Campbell, D. M. Muir, R. R. Hill, J. H. Parish, N. C. G. Campbell, D. M. Muir, R. R. Hill, J. H. Parish, 1968

R. M. S. Southam, and M. C. Whiting, J. Chem. Soc. (B), 1968,

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&</sup>lt;sup>3</sup> P. von R. Schleyer and R. D. Nicholas, J. Amer. Chem. Soc., 1961, 83, 182

reported this compound, m.p. $33-34^{\circ}$. 2-Adamantyl acetate is reported as a liquid.⁸

Adamantanone Phenylsulphonylhydrazone.—Adamantanone (150 mg) and benzenesulphonohydrazide (180 mg) were dissolved in ethanol (0.5 ml) and heated for 30 min at 100 °C. Cooling gave the *product* (277 mg, 92%), m.p. 162—163° (from ethanol) (Found: C, 62.8; H, 6.7. $C_{16}H_{20}N_2O_2S$ requires C, 63.15; H, 6.7%).

Crude 2,4-Didehydroadamantane and its Acetolysis Product. -A crude product [25 mg; v_{CH} (cyclopropane) 3 035 cm⁻¹ in CCl₄] was obtained from adamantanone phenylsulphonylhydrazone (152 mg) by pyrolysis of its lithium salt (procedure of Udding et al.,9 who, however, used the p-tolylsulphonylhydrazone). G.l.c. analysis (on 4 m Geo-100 at 130 °C) indicated four components with the relative retention times given (approximate relative areas in parentheses): 1(1): 1.5(10): 3.5(trace): 12(10). The first component was adamantane (retention time identical with that of a genuine sample. In the acetolysis product the second component had completely (>99.7%) disappeared and had been replaced by one with relative retention time 13.8(10), identical with that of 2-adamantyl acetate. The other constituents of the crude 2,4-didehydroadamantane preparation remained unchanged and were not identified.

Acetolysis Procedures.—Acetolyses were carried out in dry acetic acid containing potassium acetate (0.15M) in sealed glass ampoules, at substrate concentrations of $8-20 \text{ mg ml}^{-1}$, for 18 h. A temperature of 100 °C was necessary except

⁸ A. C. Udding, J. Strating, and H. Wynberg, *Tetrahedron Letters*, 1968, 1345.

A. C. Udding, J. Strating, H. Wynberg, and J. L. M. A. Schlatman, Chem. Comm., 1966, 657.

for the reactive 1-adamantyl toluene-*p*-sulphonate (25 °C). Reactions were quenched by pouring into chilled 1:1 mixtures of organic solvent and a solution of dipotassium hydrogen phosphate (30 g) and potassium hydroxide (9.3 g) in water (30 ml). For g.l.c. analysis this solvent was light petroleum, (b.p. 30-40°) free of aromatic impurities: for n.m.r. analysis it was spectroscopic grade carbon tetrachloride. The solution for n.m.r. was subsequently dried (MgSO₄) and evaporated to *ca.* 0.5 ml at atmospheric pressure through a Vigreux column.

G.l.c. analyses were performed on a 4 m Geo-100 column at 130 °C, the solution in light petroleum being injected directly. The relative retention times of 1- and 2-adamantyl acetate were 1: 1.2. Duplicate g.l.c. analyses of the products of duplicate solvolyses were performed.

N.m.r. analyses were performed with a Varian HA-100 instrument (Me₄Si as internal standard). Six integrations of α -protium (τ 5.50) and the tolyl methyl ¹³C side-band (τ 7.03 at 100 MHz) were performed on [2-²H]-2-adamantyl toluene-*p*-sulphonate, and four each of α -protium (τ 5.28) and the acetyl methyl ¹³C side-band (τ 7.42) on this instrument) on each of the products of two acetolyses. The natural abundance of ¹³C is taken as 1.108%;¹⁰ quoted errors are sample standard deviations.

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¹⁰ T. G. Pople, W. G. Schneider, and H. J. Bernstein, 'High Resolution Nuclear Magnetic Resonance,' McGraw-Hill, New York, 1959, p. 480.