# Classical Carbonium Ions. Part IV.[1] Absence of Hydride Shift in the Solvolysis of 1- and 2-Adamantyl Toluene-*p*-sulphonate

By **Michael L. Sinnott** and **Mark C. Whiting**,* Department of Organic Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS

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

In Part I[2] we showed that, contrary to earlier belief, a 2→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 $S_N1$ 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. measurements[3] indicated that the acetolysis product from 2-adamantyl toluene-*p*-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→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→2 shift in the acetolysis of the 2-toluenesulphonate. This was examined by preparing [2-$^2$H]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 $\tau$ 5.50 with that of the $^{13}$C sideband of the methyl peak, using a concentrated solution. Acetolysis gave an acetate which was isolated and examined similarly, the hydrogen at position 2 having $0.32 \pm 0.08\%$ 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→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 *exo*-norbornan-2-yl arenesulphonates, at 45 °C the proportion of 6→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-$^2$H]*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% $^2$H; 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 $C_{12}H_{18}O_2$: C, 74.25; H, 9.25%). Since our work, Stepanov and Stolyarov[7] have

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

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reported this compound, m.p. 33—34°. 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; $\nu_{CH}$ (cyclopropane) 3 035 cm$^{-1}$ in $CCl_4$] 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 mg ml$^{-1}$, for 18 h. A temperature of 100 °C was necessary except 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 ($MgSO_4$) 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 ($Me_4Si$ as internal standard). Six integrations of $\alpha$-protium ($\tau$ 5.50) and the tolyl methyl $^{13}C$ side-band ($\tau$ 7.03 at 100 MHz) were performed on [2-$^2$H]-2-adamantyl toluene-*p*-sulphonate, and four each of $\alpha$-protium ($\tau$ 5.28) and the acetyl methyl $^{13}C$ side-band ($\tau$ 7.42) on this instrument) on each of the products of two acetolyses. The natural abundance of $^{13}C$ is taken as 1.108%;[10] quoted errors are sample standard deviations.

We thank the S.R.C. for a research studentship (to M. L. S.).

[5/315 *Received*, 14*th February*, 1975]

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