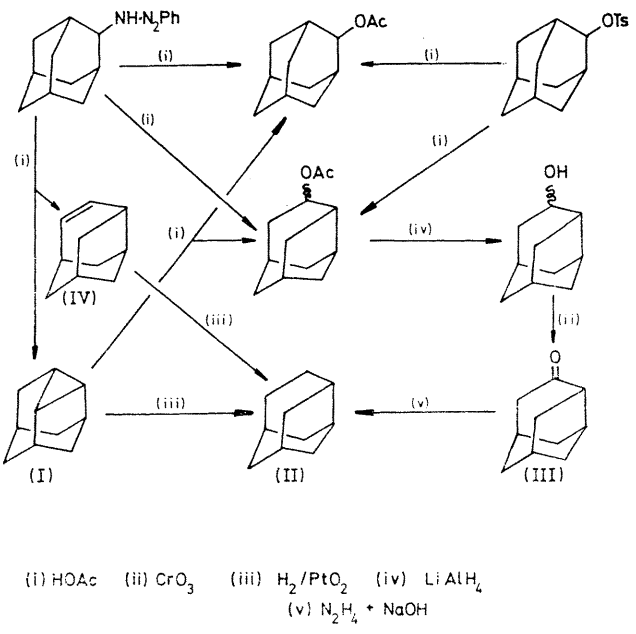
Rearrangements in the Adamantane Nucleus

By M. L. SINNOTT, H. J. STORESUND, and M. C. WHITING*
(*Department of Organic Chemistry, University of Bristol, Bristol* BS8 1TS)

Summary Processes (arenesulphonate solvolysis and deamination *via* the arylalkyltriazene) involving a 2-adamantyl cation as intermediate lead to products free from 1-substituted adamantanes but containing tricyclo-[4,3,1,$0^{3,8}$]decane derivatives.

THE adamantane skeleton is uniquely suited to the testing of stereoelectronic relationships because of its rigidity, high symmetry, and stability. It has been vividly described[1] as "a bottomless pit into which rearranging molecules may irreversibly fall." Nevertheless, acetolysis of 2-adamantyl toluene-*p*-sulphonate gives, in addition to 2-adamantyl acetate,[2] 0·4—0·5% of another acetate with a retention time (Carbowax 1540) identical to one formed in much larger yield (*ca.* 7·5% of total acetates) in the deamination of 2-aminoadamantane by the phenyltriazene method.[3] This was converted *via* the alcohol into a ketone, ν_{max} (CCl_4) 1729 and 1719 cm.$^{-1}$ (*cf.* adamantanone, ν_{max} 1739 and 1729 cm.$^{-1}$), which on Wolff–Kishner reduction gave a hydrocarbon, $C_{10}H_{16}$, chromatographically inseparable on three gas–chromatographic columns at *ca.* 10,000 plates from the minor (*ca.* 20%) product of the catalytic hydrogenation of dehydroadamantane (I), and assumed to be protoadamantane (II). The ketone was assigned structure (III) because the carbonyl stretching band, though complicated by splitting (Fermi resonance?), was generally at lower frequency than that of adamantanone, and therefore incompatible with location in a five-membered ring. The



(i) HOAc (ii) CrO_3 (iii) H_2/PtO_2 (iv) $LiAlH_4$
(v) N_2H_4 + NaOH

deamination also gave dehydroadamantane, protoadamantene (IV), and alkylated anilines.[3b,c]

Scarcely less interesting is the absence of hydride shift in

this system, no doubt because of the impossibility of the correct stereoelectronic relationship between C–H and leaving group. Neither acetate fraction from the 2-toluenesulphonate and the 2-phenyltriazene contained any 1-acetate (detection limit *ca.* 0·02%). The reason must be kinetic, not thermodynamic; contrary to an earlier report[2] 1-adamantyl toluene-*p*-sulphonate can be prepared from the acid chloride and pyridine and purified, m.p. 79—83°. It undergoes acetolysis with $k = 4{\cdot}36 \pm 0{\cdot}08 \times 10^{-4}$ sec.$^{-1}$ at 25°, $\Delta H^{\ddagger} = 20{\cdot}6 \pm 0{\cdot}3$ kcal./mole, $\Delta S^{\ddagger} = -5 \pm 1$ cal.(degree mole)$^{-1}$, to a product which contains no 2-adamantyl acetate (limit 0·1%). (The rate constant differs from an estimate[2] based on acetolysis of a 40% concentrate).

In the solvolysis of the 2-arenesulphonate a 1,3-hydride shift cannot be detected directly; we therefore prepared and acetolysed the toluenesulphonate of [2-^{2}H]adamantan-2-ol. This and the acetate formed were analysed (n.m.r., 100 MHz.) for protium at C-2, and the percentage was found to increase only from 1·08 ± 0·18 to 1·28 ± 0·28, giving an estimate of 0·2 ± 0·4% of (4 → 2) hydride shift. Dehydroadamantane is unstable to buffered acetic acid under the conditions of solvolysis, and so cannot be proved absent from the initial products, but this result limits the yield to < 1·2%, barring large isotope effects on ring-opening. Its reaction with acetic acid gives 2-adamantyl and protoadamantyl acetates (55 : 1).

In short, the tendency to preserve intact the adamantane nucleus is less remarkable than the absence of the hydride shifts that are ubiquitous[4] in other systems.

(*Received, July 14th*, 1969; *Com.* 1048.)

[1] H. W. Whitlock and M. W. Siefken, *J. Amer. Chem. Soc.*, 1968, **90**, 4929.
[2] P. von R. Schleyer and R. D. Nicholas, *J. Amer. Chem. Soc.*, 1961, **83**, 182, 2700.
[3] E. H. White and H. Scherrer, *Tetrahedron Letters*, 1961, 758; H. Maskill, R. M. Southam, and M. C. Whiting, *Chem. Comm.*, 1965 496; E. H. White, H. Maskill, D. J. Woodcock, and M. A. Schroeder, *Tetrahedron Letters*, 1969, 1713.
[4] N. C. G. Campbell, D. M. Muir, R. R. Hill, H. Parish, R. M. Southam, and M. C. Whiting, *J. Chem. Soc.* (*B*), 1968, 355.