Lewis Acid-catalysed Conversion of Homoadamantene into 2-Methyladamantane

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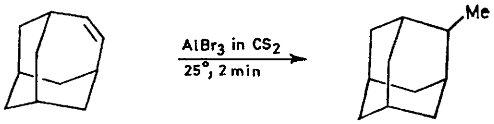
Summary Aluminium tribromide-catalysed disproportionation of homoadamantene yielded 2-methyladamantane and almost no 1-methyladamantane; this reaction and the $AlBr_3$-catalysed rearrangement of homoadamantane to 2-methyladamantane appear to involve the same intermediate(s).



(1) (2)

Lewis acid-catalysed rearrangements of saturated hydrocarbons are well known[1a] and occasionally useful in syntheses (*e.g.*, preparation of adamantane, alkyladamantanes, noradamantane, and diamantane[1a]). Olefins under these conditions usually polymerize[2] or disproportionate to give mixtures of hydrocarbons in low yields.[3]

We report the $AlBr_3$-catalysed disproportionation of homoadamantene (**1**)† in CS_2 at 25°. G.l.c. of the product

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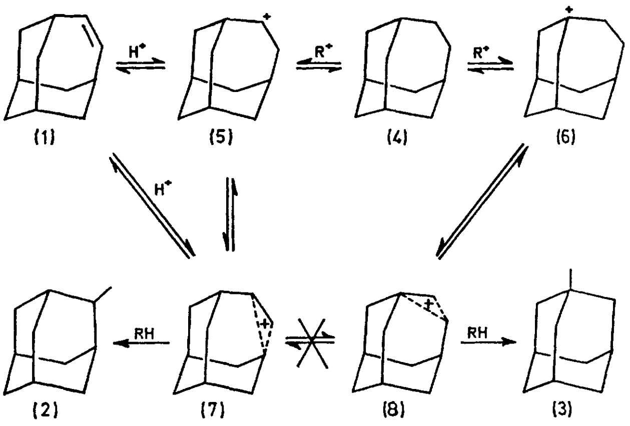
† Homoadamantene ($\geqslant$ 98% pure by g.l.c.) was prepared in 58—65% yield by the reaction of 4-homoadamantyl tosylhydrazone[4] with Bu^nLi in dry ether.

after reaction for 2 min indicated a single major component (76—84%) which was shown by i.r., ^{1}H n.m.r., and mass spectra, and g.l.c. comparison with an authentic sample to be 2-methyladamantane (**2**). After 2 min no homoadamantane (**1**) was left and less than 0·5% of 1-methyladamantane (**3**) (identified by g.l.c.) had been formed.‡ After 60 min, >90% of (**2**) had rearranged to (**3**), so the small amount of (**3**) in the product mixture after 2 min was probably formed by rearrangement of (**2**)[5] rather than by the disproportionation of (**1**).

A likely mechanism for the AlBr$_3$-catalysed conversion of (**1**) into (**2**) is shown on the left side of the Scheme. The initial step almost certainly involves addition of a proton[2] (AlBr$_3$,HBr) to (**1**) producing the 4-homoadamantyl cation (**5**) (or a π-complex) which probably collapses through the nonclassical cation (**7**) to (**2**). Cation (**7**), however, might be formed directly from (**1**).§ Although polymers were also formed, the yield of (**2**) was fairly high for such a reaction, possibly owing to retardation of the competing polymerization process owing to steric hindrance in (**1**).

Schleyer and Bingham suggested[1b] a similar mechanism for the AlBr$_3$-catalysed rearrangement of homoadamantane (**4**) to 2-methyladamantane (**2**) and 1-methyladamantane (**3**)[6] (see Scheme). In our hands the ratio of (**2**) to (**3**) at the start of the reaction was *ca.* 2:1. The product-controlling step should thus be ring contraction rather than hydride abstraction from (**4**). Since no (**3**) was found in the disproportionation of (**1**) the possible equilibrium between the nonclassical cations (**7**) and (**8**) must be too slow compared with hydride abstractions and formation of (**2**) and (**3**).



Scheme

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‡ The major sublimable impurity (10—12%) had considerably longer retention time than (**2**) and the highest mass spectral peak was at *m/e* 164. A substantial amount of polymer was also formed. Both the amount of polymer and the product composition varied considerably with the quality of AlBr$_3$. In all experiments anhydrous AlBr$_3$ from freshly opened ampoules was used.

§ An alternative mechanism *via* the primary 2-adamantylcarbinyl cation is very improbable owing to the high instability of primary cations.

[1] R. C. Bingham and P. v. R. Schleyer, *Fort. Chem. Forsch.* (Topics in Current Chemistry), Band 18, 'Chemistry of Adamantanes,' New York 1971: (a) p. 4 and refs. therein; (b) p. 17.

[2] A. G. Evans and M. Polanyi, *J. Chem. Soc.*, 1947, 252; J. E. Germain, 'Catalytic Conversion of Hydrocarbons,' Mir, Moskva, 1972, p. 47 and refs. therein.

[3] P. v. R. Schleyer, personal communication.

[4] Z. Majerski, S. H. Liggero, and P. v. R. Schleyer, *Chem. Comm.*, 1970, 949.

[5] Z. Majerski, P. v. R. Schleyer, and A. P. Wolf, *J. Amer. Chem. Soc.*, 1970, **92**, 5731 and refs. therein.

[6] K. R. Blanchard, Ph.D. Thesis, Princeton University, 1966.