The Degenerate Isomerization of Adamantane

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Summary Treatment of specifically labelled [2-^{14}C]-adamantane with aluminium bromide in CS_2 solution at 110° for 8 h leads to 78·4% of the total scrambling of carbon atoms possible on a statistical basis.

ADAMANTANE is by far the most stable $C_{10}H_{16}$ isomer.[1–3] As expected on thermodynamic grounds,[1] all tricyclodecanes investigated to date have rearranged in the presence of AlX_3 or similar Lewis-acid catalysts completely to adamantane.[1–3] No other isomer has been detected at equilibrium. This indicates that adamantane is probably at least 5—6 kcal/mol more stable than any of its isomers; a free-energy difference of this magnitude at 25° corresponds to an equilibrium containing about 0·01% of the minor component, the practical g.l.c. detectability limit. Computer conformational analysis calculations and free-energy analyses of protoadamantyl–adamantyl solvolysis product and rate data[3b] both indicate that the strain in protoadamantane exceeds that in adamantane by 10—11·5 kcal/mole.[4]

Recently, a deliberate attempt to observe rearrangement processes with the stable 1-adamantyl cation failed.[5] N.m.r. studies in SbF_5-based super acid media on the 1-adamantyl cation up to 130° gave no detectable line broadening. This shows that these conditions are unable to effect any rearrangement, either of the carbon skeleton or of the 1,2-shift variety, which would lead to the interchange of the various types of hydrogen atoms.

Summary of rearrangement experiments on [2-^{14}C]*adamantane*[a]

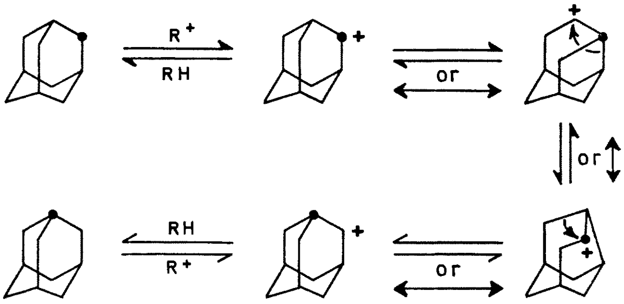
			Degradation products (nCi/mg C)			
Expt.	Rearrangement conditions	1-CH_3Ad[a] (nCi/mg C)	TlOAc	CH_3NH_2[b]	CO_2	% Net scrambling[c]
A	None, control	3·52	0·245	0·445	0·040	
B	$AlBr_3$, CS_2, 25°, 14 days	3·53	0·346	0·561	0·113	1·9
C	$AlBr_3$, CS_2, 110°, 8 h[d]	3·51	1·76	0·474	3·05	78·4

[a] Products from expt. A—C were converted into 1-methyladamantane[8] before Kuhn–Roth oxidation;[7–9] conditions: *ca.* 800 mg 1-CH_3Ad, 50 ml 2·5 M aq. CrO_3, and 12·5 ml conc H_2SO_4 were heated in heavy-walled ampoules at 150° for 16·5 h. [b] Assayed as *N*-phenyl-*N'*-methylthiourea (spec. act. CH_3NH_2 = spec. act. *N*-phenyl-*N'*-methylthiourea × 8). [c] For complete scrambling of (I) (spec. act. 3·83 nCi/mg C) the activity of *each* carbon would be, of course, 3·83 nCi/mg C. The % net scrambling is then calculated as follows: [spec. act. CO_2 (from TlOAc) — 0·04 nCi/mgC (from control)]/3·83 nCi/mg C × 100 = % net scrambling. [d] Mixture stirred in a high-pressure bottle.

The general opinion about the stability of adamantane has been summarized by Whitlock and Siefkin:[2a] "Adamantane may be conceived as a bottomless pit into which rearranging molecules may irreversibly fall." We demonstrate here that this overstates the case; the "pit" is *not* "bottomless." Adamantane can be made to undergo automerization[6] (degenerate isomerization) with scrambling of the carbon atoms if the conditions are made vigorous enough.

Specifically labelled [2-^{14}C]adamantane (spec. act. 3.83 nCi/mg C) was synthesized[7] and subjected to $AlBr_3$ rearrangement conditions. The location of the label was established by conversion of the samples, *via* 1-bromoadamantane, into 1-methyladamantane.[8] Kuhn–Roth oxidation of the latter gave acetic acid, isolated as the thallous salt, which was further degraded to CO_2 and methylamine (assayed as *N*-phenyl-*N'*-methylthiourea).[7–9]

At 25°, stirring [2-^{14}C]adamantane for 14 days (expt. B) led only to 1·9% of the total theoretical carbon scrambling, but this figure was raised to 78·4% by treatment at 110° for 8 h (expt. C). This is the first time such skeletal reorganization has been demonstrated for adamantane itself. Although only inferential mechanistic information is now available,[3,10] we believe a likely rearrangement sequence to be that illustrated.



It has been known for only a short time that the adamantane skeleton is not inviolate,[3] but the rearrangements which have been observed with adamantane and its isomer, protoadamantane, are much less extensive than required to scramble the carbon atoms of adamantane.[3b] In a companion study we have shown that the rearrangement of 2-methyladamantane to 1-methyladamantane also proceeds with a similar kind of carbon skeleton rearrangement.[10] However, this reaction is markedly facilitated by the methyl group, since it is complete in a few days at 25°. Under these conditions, adamantane gave no significant automerization, even after 14 days. The 2-methyl group evidently facilitates the formation of the necessary

2-adamantyl cation intermediate; without the 2-methyl group the 2-cation concentration is too small (relative to the 1-cation concentration) to permit ready rearrangement. This helps explain also why no rapid rearrangement is observed in SbF_5 at 130°;[5] the concentration of the 2-cation at equilibrium is too small. Basic differences in the behaviour of *hydrocarbons* with $AlBr_3$ and *cations* in SbF_5-type solutions have been noted before.[11]

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