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PREPARATION OF ADAMANTANE-d_{16}[1]

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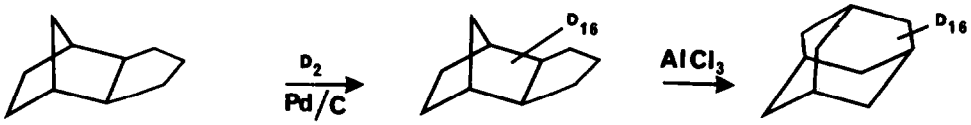
Since the discovery by Schleyer[2] of the facile preparation of adamantane by acid-catalyzed isomerization of isomeric hydrocarbons, the chemistry of this fascinating system has been the subject of continuous and vigorous investigation.[3] In view of this and because of our own interest in deuterated hydrocarbons[4] we wish to report the first successful synthesis of fully deuterated adamantane, 3.



1 2 3

Direct, metal-catalyzed exchange of adamantane with deuterium gas was found to be impractical.[5] Other unsuccessful synthetic approaches included base catalyzed exchange of cyclopentadiene[6] which, in our hands, gave low yields, and dehydrochlorination of hexachlorocyclopentadiene[7] which gave none of the desired compound.

The use of n-dodecane-d_{26}[4] as a solvent and deuterium source for the metal catalyzed exchange of adamantane was moderately successful but not as useful as the route finally chosen. Similarly, endo-tricyclo(5.2.1.$0^{2,6}$)decane exchanged readily with D_2 gas over Pd/C but the material was difficult to handle.

Exo-tricyclo(5.2.1.$0^{2,6}$)decane(1), a liquid prepared in 90% yield from the solid endo isomer by the method of Schleyer and Donaldson[8] underwent rapid exchange with deuterium over Pd/C under liquid phase exchange conditions[4] but losses due to volatilization were high. However, gas phase exchange gave excellent

results. Thus passage of deuterium gas and 102 g. 1 (vapour) through a vertical bed of 6% Pd/C heated to 250°C gave an 85% yield of 2 (99.3 atom % D) after 168 hours of exchange.

The results of isomerization experiments with Lewis acid catalysts, which had the aim of determining the optimum route to adamantane, are shown in Table I. $AlCl_3$ gave the highest yields and was investigated in most detail. Its use gave an overall yield of 26% for the three-step synthesis of adamantane-d_{16}.

Table I

Isomerization of exo-tricyclo(5.2.1.$0^{2,6}$)decane to Adamantane

Substrate	Catalyst	Conditions	Adamantane yield[a]
2 (5g.)	FSO_3H-SbF_5[9] (5 g.)	25°C, 90 min.	traces[b]
1 (25 g.)	$AlCl_3$ (25 g.)	75°C, 190 min.	32.3%
2 (25 g.)	$AlCl_3$ (25 g.)	75°C, 96 min.	24% (98.9 atom % D)[c]
2 (25 g.)	$AlCl_3$ (25 g.)	65°C, 19 hrs.	35.1%
2 (25 g.)	$AlCl_3$ (37 g.)[d]	75°C, 5 hrs.[e]	29.7% (98.9 atom % D)
1 (25 g.)	$AlBr_3$ (25 g.)	105°C, 18 hrs.	23.3%
1 (20 g.)	BBr_3 (10 g.)	80°C, 23 hrs.	none

[a] Reported as mole percent recovery of sublimed material. Isotopic analysis was by mass spec. and n.m.r.

[b] The material was 70%D and contained all possible isotopic species. Loss of isotope was probably due to abstraction of hydride from the pentane used to regenerate adamantane from its cation[9] and the known tendency[10] of certain deuterated hydrocarbons to undergo H-D exchange in magic acid.

[c] 0.16% d_{13}; 1.73% d_{14}; 15.28% d_{15}; 82.85% d_{16}.

[d] Added in two portions.

[e] Reaction killed with H_2O.

The $AlCl_3$ and $AlBr_3$ catalyzed reactions were worked up in a conventional manner.[8] Heavy runs were killed with D_2O but this was later found to be unnecessary as the product from one run quenched with H_2O was of undiminished isotopic purity. Final purification was by filtration and sublimation which yielded adamantane-d_{16}, m.p. 265-267°C. Product analysis by v.p.c. (SE-30) showed the only impurity to be 0.3% unreacted 2.

Isomerization of an equimolar mixture of 1 and 2 gave adamantane containing only 43% D, not 50% D as would have been theoretically expected. Since the isomerization reaction does not go to completion this result is probably due to an isotope effect in the hydride abstracting steps favouring the formation of adamantane containing hydrogen and leading to an enrichment in deuterium of unreacted starting material. The isotope distribution in the product and its good agreement with values calculated for random dauterium distribution is shown in Table II.

Table II

Deuterium Distribution in Adamantane (43%D)

Isotopic Species	Observed	Calculated[a]
d_0	0.06	0.01
d_1	0.25	0.15
d_2	0.94	0.85
d_3	3.01	2.99
d_4	7.15	7.32
d_5	12.7	13.2
d_6	17.5	18.3
d_7	19.7	19.8
d_8	16.9	16.8
d_9	11.7	11.2
d_{10}	6.36	5.95
d_{11}	2.64	2.45
d_{12}	0.82	0.77
d_{13}	0.20	0.18
d_{14}	0.01	0.03
	100.00	100.00

[a] Assuming random distribution for $C_{10}H_{16}$ with 6.88 deuterium atoms

Presumably, this extensive isotope redistribution occurs during rather than after isomerization to adamantane since the latter, once formed, should undergo scrambling only at bridgehead positions.[11]

The synthetic approach outlined here should be applicable to other systems. For example, the route to diamantane discovered by Schleyer and his coworkers[12] may be modified--deuterium exchange of the 'Binor-S' hydrogenation product--to yield diamantane-d_{20}.

Adamantane-d_{16} reacts cleanly under standard conditions to give derivatives containing the perdeuterated adamantane nucleus. The derivatives prepared include 1-bromoadamantane-d_{15}, 1-aminoadamantane-d_{15}, adamantane-d_{15} carboxylic acid and its methyl ester, and 1-adamantanol-d_{15}.

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