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A SIMPLE EFFECTIVE CATALYST FOR THE PREPARATION OF ALKYL DERIVATIVES OF ADAMANTANE

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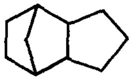
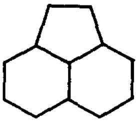
The discovery that tricyclic saturated hydrocarbons containing ten or more carbon atoms may be rearranged by the action of aluminium halides to adamantane and its bridgehead alkyl derivatives has made the latter comparatively readily available (1-3). The very effective complexes of aluminium bromide developed by Schneider and his co-workers (3), however, apparently require manipulation in a dry box and the use of carefully purified solvents and substrates. The hydrocarbons used to prepare the complexes are a mixture of dimethylcyclohexanes and are cracked by aluminium bromide and hydrogen bromide at 50° in a reaction which is not very precisely defined but which may well involve t-butyl or similar cations as intermediates. We have found that an effective catalyst is formed t-butyl bromide is added to a stirred suspension of aluminium bromide in the hydrocarbon to be rearranged. This catalyst has been used successfully for rearrangements of very varied facility with only the time of reaction being adjusted (Table). The completion of rearrangements may be determined very simply from IR spectra run on either neat liquid samples (0.1 mm path length) or on concentrated solutions after washing a small sample of the hydrocarbon layer with dilute hydrochloric acid. When intermediate products are required, e.g., 1-ethyladamantane instead of 1,3-dimethyladamantane IV from perhydro-acenaphthene III other analytical methods may be preferable (3).

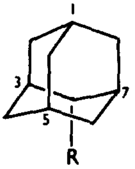
Although the yields are not always the highest obtainable, e.g., aluminium chloride is superior for the rearrangement of dihydrocedrene VII (4), fair to good yields may be obtained from new rearrangements without preliminary experimentation.

If the rearrangement is very slow the catalyst becomes deactivated and may need to be replaced, while in other instances the catalyst may be used a second time if a longer reaction time is used (Table). In the examples given the substrates were either commercially available (V, Koch-Light) or were the crude products from catalytic hydrogenation of unsaturated or aromatic hydrocarbons. After the initial exothermic reaction the reaction mixtures were stirred magnetically in a thermostated oil bath.

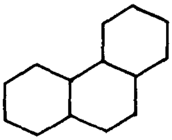
An analogous but incompletely described catalyst has been used by Schleyer and his co-workers (5).


I


III



II R = H
IV R = 1,3-Me_2
VI R = 1,3,5,7-Me_4
VIII R = 1,3,5-Me_3,7-Et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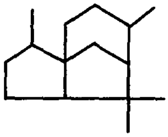
VII

Isomerisation of saturated tricyclic hydrocarbons to adamantane and its methyl derivatives by the action of aluminium and t-butyl bromides at 50-60°.

Substrate (g)	$AlBr_3$ (g.)	t-BuBr (ml.)	Time (hr.)	Product (%)	Bp (Mp)
I(100)	85	3.5	5	II(25-30)[a]	(260-262°)
	40	1.5	5		
III(70)	90	4	1	IV(60-65)[b]	200-203°
V(115)	120	5	50	VI(40-60)[a]	(64°)
	50	2	50		
VII(40)	35	1.5	2	VIII(60-65)	111-116° (10 mm)

[a] Two treatments with catalyst required. [b] If the catalyst is used a second time the reaction requires up to 12 hr.

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