

HALOGENATION OF ADAMANTANE AND RELATED COMPOUNDS

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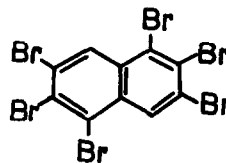
Although there has been speculation as to the mechanism of the aluminium halide-catalysed rearrangement of endo-trimethylenenorbornane (I) into adamantane little is known about this reaction beyond the fact that the first step involves the isomerization of (I) into its exo-isomer (II) (1). One way of studying this reaction is to trap and identify intermediate products of the rearrangement and with this possibility in mind we examined the aluminium bromide-catalysed bromination of (I) and (II) (2) at 0°. Even at this low temperature, however, the rearrangement proceeded right through to the adamantane stage giving about equal amounts of two tribromoadamantanes (63% yield) and 1,2,3,5,6,7-hexabromonaphthalene (29% yield) (3). No apparent intermediates were involved since g.l.p.c. analysis of the reaction mixture showed only starting material and the two tribromoadamantanes at intermediate times. The hexabromonaphthalene probably resulted from bromination of decalin, a recognised by-product in the preparation of adamantane from (I) under aluminium halide catalysis; in any event, bromination of decalin under similar conditions gave the same hexabromonaphthalene in 85% yield.



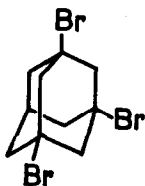
(I)



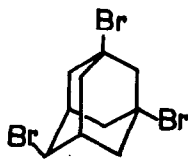
(II)



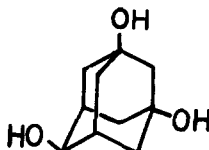
(III)



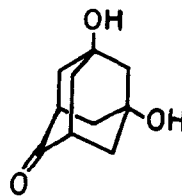
(IV)



(V)



(VI)

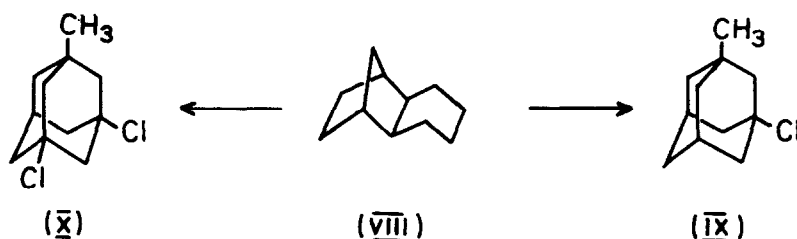


(VII)

One of the tribromides was readily identified as 1,3,5-tribromoadamantane (IV) (4). The presence of the adamantane skeleton in the second tribromide was established by hydrogenolysis over palladium and the one proton signal in the n.m.r. spectrum (100 MHz,  $\text{CDCl}_3$ ) at 5.53  $\tau$  indicated that one of the bromine atoms was attached to a non-bridgehead position. Hydrolysis employing silver sulphate and sulphuric acid gave a triol, m.p. 310-312 $^\circ$ , which was subsequently oxidised to a keto-diol, m.p. > 350 $^\circ$ . This compound was assigned structure (VII) since the n.m.r. spectrum ( $\text{CD}_3\text{SOCD}_3$ ) displayed an absorption at 7.64  $\tau$  attributable to the two protons on the bridgehead positions adjacent to the carbonyl group. Accordingly, the tribromide and the triol were assigned structures (V) and (VI).

While the results of the bromination reaction do not provide any information on the mechanism of adamantane formation, a number of points of interest arise. First, tribromide (V) cannot be the product of direct bromination of adamantane since, under the conditions employed, this reaction is known to produce bridgehead substitution exclusively (4). Rather, it must be formed by bromination of starting material or of an intermediate in the rearrangement which, however, continues on to the adamantane skeleton. Second, (V) provides a direct entry into the previously unreported 1,3,6-trisubstituted adamantane series; in this connection, the effect of temperature on the product ratio is important; bromination of (I) at -12 $^\circ$  gave (IV) and (V) in the ratio 1:3, and fractional crystallisation of the mixture gave (V), m.p. 169-170 $^\circ$ , in 39% yield.

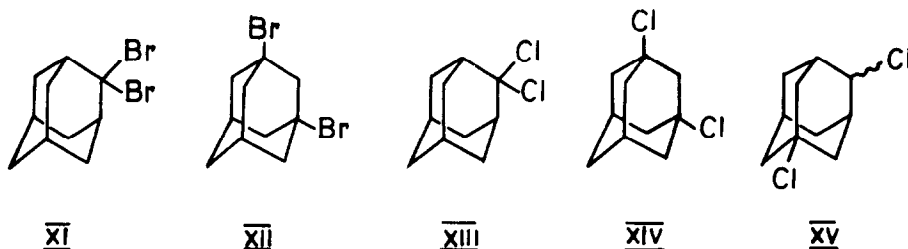
Following these experiments we investigated other methods for effecting the rearrangement of suitable tricyclic hydrocarbons into adamantanes and the introduction of functional groups in a single operation. This approach has already been successfully applied to the preparation of several aminoadamantanes from tricyclic precursors and trichloramine under aluminium chloride catalysis (5). Two reactions using *exo*-tetramethylenenorbornane (VIII) (6) are shown below. A solution of (VIII) in dichloromethane containing aluminium chloride was



heated under reflux while the progress of the reaction was monitored by g.l.p.c. analysis. After 15 minutes, the mixture contained about equal amounts of 1- and 2-methyladamantane, but after two hours the product was almost exclusively composed of the 1-methyl isomer. At this point the solution was cooled to 0 $^\circ$  and acetyl chloride was added. Distillation gave 1-chloro-3-methyladamantane (IX), m.p. 39-41 $^\circ$ , in 82% yield. This structural assignment is based on the spectral data (7) and on Koch carboxylation which gave 3-methyl-1-adamantanecarboxylic acid (8) in 85% yield. Adaption of the rearrangement-functionalisation procedure to the introduction of two chlorine substituents proved unexpectedly simple; if instead of acetyl chloride paraformaldehyde and additional aluminium chloride were added, the product isolated in 74% yield was

5-methyl-1,3-dichloroadamantane (X), m.p. 45-46°.

Other examples of rearrangement and bridgehead halogenation were observed during a study of the behaviour of 2,2-dihaloadamantanes under aluminium halide catalysis. For example, 2,2-dibromoadamantane (XI), m.p. 162-163°, (9) is smoothly converted into 1,3-dibromoadamantane (XII) by aluminium bromide in dibromomethane. Similarly, 2,2-dichloroadamantane (XIII), m.p. 203-204°, (9) rearranges into 1,3-dichloroadamantane (XIV) in the presence of aluminium chloride



in carbon tetrachloride. By changing the solvent to nitromethane in the latter reaction it was possible to observe five intermediate dichlorides. The two major components were isolated and identified as the cis- and trans-isomers of 1,4-dichloroadamantane (XV) (10). These rearrangements probably proceed by way of intermolecular hydride transfer reactions (11) (12).

#### References

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- (2) exo-Trimethylenenorbornane (II) was prepared in high yield by isomerisation of (I) over a palladium on silica catalyst at temperatures in the range 200-360°. For the details of this and related reactions see H. Quinn, M.A. McKervey, W.R. Jackson, and J.J. Rooney, *J. Amer. Chem. Soc.*, in press.
- (3) We are indebted to Professor G. Ferguson, University of Guelph, Guelph, Ontario, who performed an X-ray analysis of this compound.
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- (9) These dihalides were prepared from adamantanone and the appropriate phosphorus pentahalide-phosphorus trihalide mixture.
- (10) H.W. Geluk and J.L.M.A. Schlatmann, *Tetrahedron*, **24**, 5369 (1968).
- (11) Cf. P. von R. Schleyer, *Angew. Chem.*, **81**, 539 (1969).
- (12) All new compounds gave satisfactory analytical and spectral values.