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OLIGOMERIZATION OF 2,4-DEHYDROADAMANTANE

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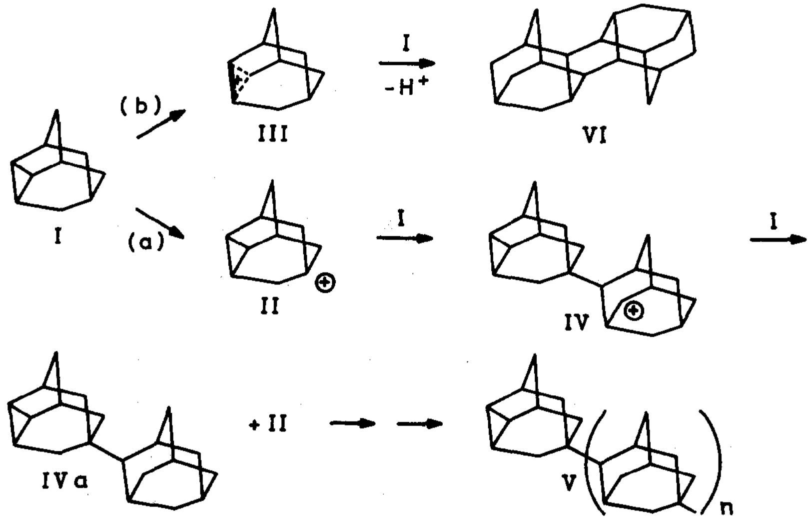
After the discovery of the hydride-halide exchange reaction[1], it was reasonable to assume that the isomerization of saturated hydrocarbons catalysed by Lewis acid halides in the presence of cocatalysts proceeds by an ionic chain mechanism, analogous to the radical chain reactions well known by that time. The cocatalysts are normally small amounts of alkyl halides, olefins or water, the mechanism of activation by the latter being not so straightforward. Isomerization of alkylcyclobutanes[2] and alkylcyclopentanes[3], i.e., ring expansions, has been shown to occur to a fairly large extent. However, isomerization of alkylcyclopropanes has been found not to take place[2]. Extensive polymerization occurred instead, producing evidence for a preferred cleavage of the three-membered ring by an external carbonium ion rather than hydride abstraction from a side chain followed by ring enlargement from alkyl shift.

As aluminium halide catalysed reactions of this kind are thermodynamically controlled processes the occurrence of alkyl shifts in the carbonium ion generated by the action of moist aluminium chloride on 2,4-dehydroadamantane (I), must be regarded as most unlikely. Hydride abstraction from (I) can occur preferentially from either (a) the tertiary positions outside the cyclopropane ring (II) or (b) inside the three-membered ring, i.e., ring opening. The ion (III) (case (b)) may well be considered as a protonated 2,4-dehydroadamantane.

The expected products in case (a) would be polymers of type (V) arisen by electrophilic attacks by ions (II) on products having a cyclopropane ring. The chain-propagation step will be the hydride transfer from (I) to cations of type (IV). (Scheme 1)



Scheme 1

On the other hand, in case (b), the reaction between (III) and (I) would lead to the highly symmetrical adamantane dimer (VI) (isomeric to (IVa)) as the sole product. However, because of the assumed[4] greater stability of the 1-adamantyl cation as compared with the corresponding 2-ion, the former reaction path (case (a)) ought to be favoured.

In order to clarify this 2,4-dehydroadamantane (I) was synthesised by pyrolysis of the lithium salt of adamantanone benzenesulphonylhydrazone[5] and freed from adamantane and other side products by preparative g.l.c. On treatment of (I) with 50% $AlCl_3$ (by weight) in anhydrous carbon disulfide in a glove box (N_2) at 20 °C, the solution became immediately brown. After a reaction time of *ca.* 12 hrs. (the solution was still coloured brown) unreacted (I) (*ca.* 30%) was removed by sublimation *in vacuo* leaving behind a slightly yellow substance which contained only minor amounts of monomeric material by g.l.c. The mass spectrographic data (direct insertion, 70 eV, 220 °C (ionisation temperature)) of the product are given below. (Table 1)

Evaporation temp. (°C)	Basic peaks (m/e)
20	268,135
105	402,269,268,267,135
195	536,403,402,401,269,268,267,135
290	670,537,536,535 " " " "

Table 1

At all temperatures the adamantyl ion radical (m/e=135) was 5-10 times more intense than the molecular ions, or the higher fragments. At 20 °C only dimeric product vaporized the m/e = 135 being *ca.* 5 times more intense than the molecular ion, m/e = 268. The dimer can not be the adamantane dimer (VI) for the following reasons:

1. Like adamantane, (VI) ought to be uniquely stable and thus give a molecular ion of great intensity. It may be compared with congressane (diadamantane)[6] where the molecular ion is *ca.* 3 times more intense than any other ion.
2. The fragmentation of (VI) to m/e = 135 should not be important.
3. The occurrence of higher oligomers.
4. The detection of cyclopropane ring in the products.

The latter criterion was produced as it was possible, by preparative g.l.c., to isolate the dimeric product (together with small amounts of assumed 1,2'-biadamantane (m/e = 270)[7]) which showed an infrared band at 3020 cm^{-1}, characteristic of cyclopropanes. The presence of a three-membered ring in the compound was verified as the oily product, obtained on treatment of the dimer with acetic acid for 15 hrs. at 100 °C, showed carbonyl-absorbtion and *no* 3020 cm^{-1} band in infra-red. With the exception of the peak, assumed to be due to 1,2'-biadamantane, <u>no</u> dimeric hydrocarbons could be detected in the solvolysis products by g.l.c.

A m.s. analysis of the assumed acetate did not give the molecular ion (m/e = 328) but M-44 (loss of CO_2).

On increasing the evaporation temperature in m.s. to 105 °C, the molecular ion of the trimer (V, n = 2) appeared (m/e = 402). Its fragmentation pattern, M-133 (m/e = 269) and M-135 (m/e = 267), corresponds to rupture of the bond between the 2,4-dehydroadamantyl-adamantyl units and the adamantyl-adamantyl units, respectively. The same nice correlation between the fragmentation pattern for the tetramer and pentamer and what is expected for the proposed structures (V, n = 3,4) is seen from Table 1.

Due to reduced solubility in carbon disulfide and low volatilities, higher oligomers (V, n > 4) may have been present, undetected.

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