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THE REACTION OF CHLORINE WITH ADAMANTYLIDENEADAMANTANE

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Adamantylideneadamantane (I) has shown to be a reactive, though heavily hindered alkene, viz. its epoxidation (1) and its reaction with bromine (2). The latter reaction resulted in the isolation of a uniquely stable bromonium bromide. This prompted us to investigate the reaction of the olefin (I) with chlorine, a smaller molecule.

A white precipitate was formed when a hexane solution of adamantylideneadamantane was treated with a solution of chlorine in carbon tetrachloride at room temperature. This precipitate dissolved completely within a few minutes. After evaporation of the solvent starting material and polychlorinated products with a chlorine content up to four chlorine atoms remained, as shown by mass spectrometry. NMR evidence clearly shows that substitution at secondary positions has occurred, while some substitution at tertiary positions cannot be excluded. More chlorine could easily be incorporated by leading chlorine into a refluxing solution of adamantylideneadamantane in carbon tetrachloride. After four hours a white powder was obtained, containing 66,3 wght % chlorine. From the mass spectrum it could be deduced that substitution up to 15 chlorine atoms had taken place.

Further information on the course of the reaction was obtained when the reaction was carried out at lower temperature. At -20° the initial precipitate did not dissolve and could be filtered off easily. After washing with cold hexane and drying at -20° a white powder remained which was totally insoluble in non-polar solvents. This evidence once again points into the direction of an chloronium chloride structure for this white solid, similar to the bromonium bromide proposed earlier (2).

Allowing this powder to attain room temperature, hydrogen chloride and chlorine escaped and beautiful crystals were formed. Though melting sharp at 144-145°, they consisted mainly of starting material (I) and a monosubstitution product (III) to which, by reason of its NMR-spectrum, the structure of 4e-chloroadamantylideneadamantane must be assigned (fig. 1).

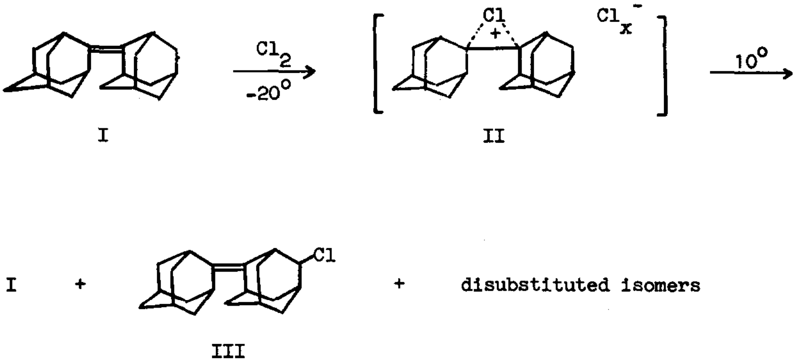

Fig. 1

The 2:5 ratio of these products is almost unaffected by the manner in which the salt was decomposed (e.g. in refluxing acetone or acetone of room temperature). In addition to the monosubstitution product a few percent of disubstituted isomers were always formed.

Because the main products (i.e. I and III) could not be separated, the original mixture was hydrolysed by means of silver nitrate in aqueous tetrahydrofuran, providing the unaffected adamantylideneadamantane and the two isomeric 4(a,e)-hydroxyadamantylideneadamantanes (IV) in a 1:1,8 ratio (fig. 2). The starting material was easily isolated by column chromatography on florisil. The axial alcohol isomerised under these conditons almost completely to the equatorial one. An analytically pure sample of the latter was obtained by recrystallisation from ether/carbon tetrachloride and subsequent sublimation, mp 214-215°.

Spectral properties:

<u>IR spectrum</u> (KBr): OH stretch frequency at 3400 cm^{-1} (broad).

<u>NMR spectrum</u> (CCl_4): $\underline{H}$COH τ=6.40 (1H), $\underline{H}$C-C=C τ=7.13 (4H), O$\underline{H}$ τ=8.76 (1H), remaining protons at τ=7,6-8,7 (22H).

<u>Mass spectrum</u>: M^+ at m/e 284 ($C_{20}H_{28}O$), M-H_2O at m/e 266.

The equatorial position of the hydroxyl group was assigned by the position of the geminal hydrogen atom in the NMR spectrum, which is upshielded relative to that of the axial isomer by the anisotropy of the olefinic linkage.

The postulated equatorial position of the chlorine atom in the initial monochlorinated product can now be verified by conversion of this alcohol into the equatorial chloride by means of thionyl chloride in dry ether.

Although 4e-chloroadamantylideneadamantane, obtained in this way, contains about 1% disubstituted isomers, all spectroscopic properties, of which the position of <u>H</u>CCl in the NMR spectrum at τ=5.85 (CCl_4) is decisive, find their reflection in those of the crude chlorination product. We may thus conlude that this easy chlorination of adamantylideneadamantane yields mainly 4e-chloroadamantylideneadamantane in addition to starting material and a minor quantity of disubstituted isomers.

Rearrangement during chlorination can be excluded since reduction of the crude chloronation product with sodium and ethereal liquid ammonia furnished adamantylideneadamantane as the only product.

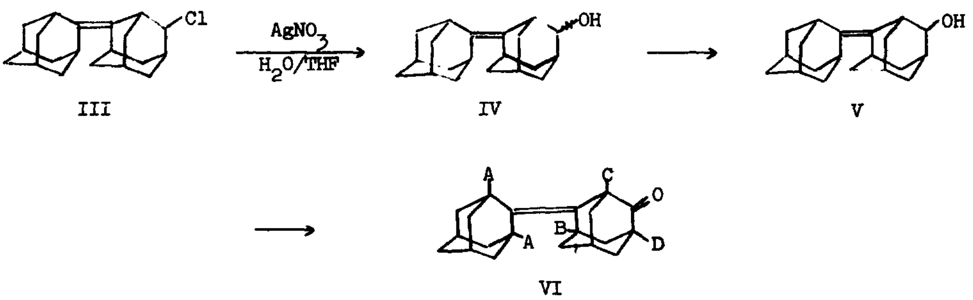

Fig. 2

Chemical evidence for the position of the substituent was obtained by oxidation of V to adamantylideneadamantane-4-one (VI) with exactly one equivalent of Jones reagent, a procedure by which simultaneous oxidation of the olefinic linkage is prevented.

An analytically pure sample of the unsaturated ketone VI was obtained by column chromatography of the crude oxidation product over a colmn of florisil with chloroform as eluent and subsequent sublimation, mp 158-160°.

Spectral properties:

<u>IR spectrum</u> (KBr): C=O stretch frequency at 1720 cm^{-1}.

<u>NMR spectrum</u> (CCl_4): (see VI, fig. 2) H_a, H_b τ=7.15 (broad, 3H), H_c τ=6.62 (1H), H_d τ=7.60 (1H), remaining protons τ=7.8-8.7 (21H).

<u>Mass spectrum</u>: M^+ at m/e 282 ($C_{20}H_{26}O$), M-CO at m/e 254.

UV spectrum (C_2H_5OH): λ_{max}=227 mμ (ε=3500), λ_{max}=300 mμ (ε=564).
The ketone formation indicates an OH function at a secondary carbon atom; the UV spectrum suggests considerable spatial overlap of the π-bonds of the chromophores, which is only consistent with a keto group at the 4-position.

The reaction proceeds presumably via a mechanism analoguous to the one proposed by McKervey for the explanation of the abnormal products he obtained from bromination of 2-methyladamantane (3). The key step (step 3, fig. 3) of the reaction is the formation of the protoadamantene-like intermediate. Naturally a radical mechanism is not rigidly excluded by the evidence presented here; however, when I was irradiated in benzene solution at 60° for 8 hrs. in the presence of bromotrichloromethane, starting material was recovered unchanged, thus effectively eliminating hydrogen abstraction as a mechanistic alternative under these conditions.

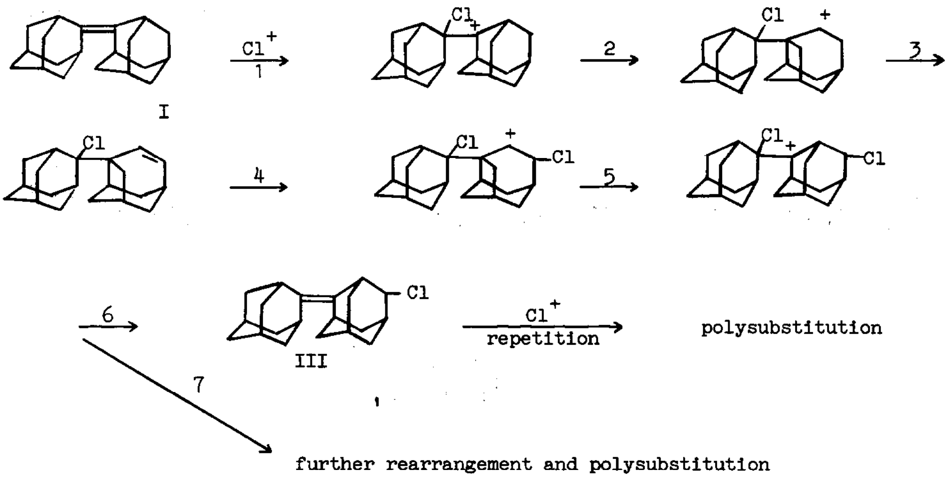

Fig. 3

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