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ADAMANTYLIDENE ADAMANTANE GLYCOL

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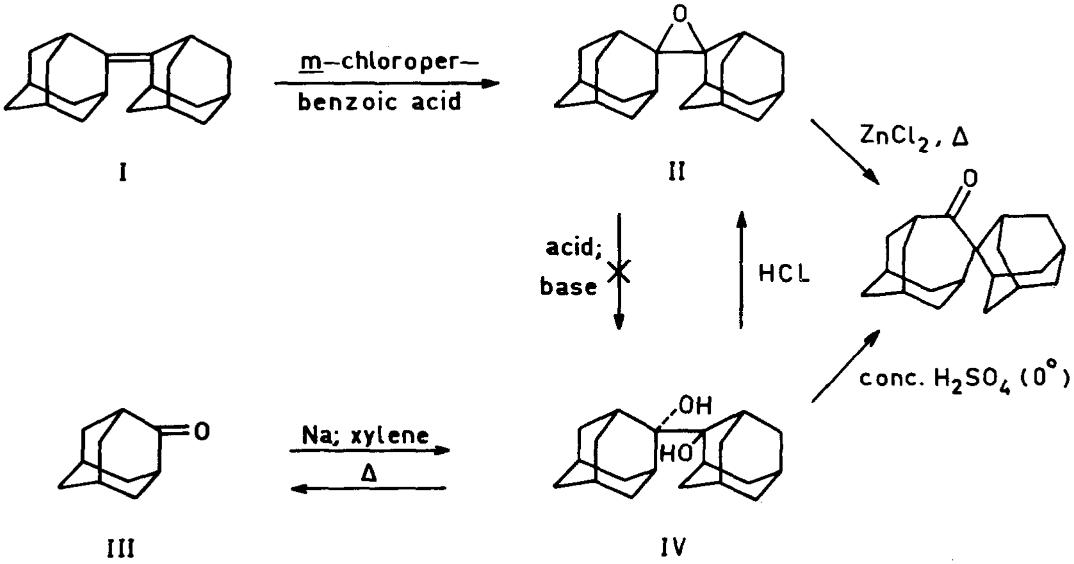
In a previous communication[1] we drew attention to the peculiar behaviour of the double bond in adamantylidene adamantane (I). The reaction of bromine with this olefin did not furnish a normal bromine adduct but led instead to the formation of a molecule whose structure we postulated as that of a bromonium ion. In order to obtain further insight into the nature of this unique double bond, epoxidation and hydroxylation of adamantylidene adamantane (I) were attempted. Epoxidation using m-chloro-perbenzoic acid in CH_2Cl_2 (24 hr at 6°) proceeded quantitatively indicating sufficient space between the adamantane moieties for attack by the oxidative species. However, neither acid (refluxing for 24 hr with 50% acetic acid) nor basic hydrolysis (24 hr refluxing with 30% NaOH solution and methanol) of this epoxide II, m.p. 181.5-183°, furnished the corresponding diol IV. Direct hydroxylation of adamantylidene adamantane I with alkaline permanganate (stirring for 5 hr in water-dimethoxyethane mixture at 20°) failed to provide the cis-diol.

In order to obtain the elusive 2,2'-dihydroxy-2,2'-biadamantane, adamantanone[2] (III) was allowed to react with finely divided sodium in refluxing xylene. Surprisingly this reaction furnished the hindered diol II[3], m.p. 267-269° (dec.), in 88% yield.

The slightly ramshackle nature of the latter molecule is demonstrated by the transformation[4] into the epoxide II by gaseous HCl in ethereal solution and by the pyrolysis to adamantanone (III), the latter reaction probably indicating a weak carbon-carbon bond between the two adamantane skeletons.



On the other hand the diol IV, when treated with concentrated sulfuric acid at 0^0 furnished in yield of 97% the normal pinacol rearrangement product V, m.p. 176-178^0, which is in fact the first representative of a spiro-connected adamantane-homoadamantane molecule.

It is noteworthy that the epoxide II is very unreactive (no reaction with $LiAlH_4$, n-butyllithium, or $\mathrm{P(\emptyset)_3}$). However, by heating using anhydrous zinc chloride IV was converted into the spiroketone V in high yield.

REFERENCES

1. J. Strating, J.H. Wieringa, and H. Wynberg, Chem. Comm., 1969, 907.
2. H.W. Geluk and J.L.M.A. Schlatmann, Tetrahedron, 24, 5361 (1968).
3. All new compounds gave satisfactory elemental analyses and spectral data. The diol IV showed a very sharp OH absorption at 3620 cm^{-1} in the i.r. due to a non-hydrogen bonded hydroxyl group; spiroketone V had a carbonyl absorption at 1680 cm^{-1}.
4. The trans configuration of the diol is supported by the facile epoxide formation.