ADAMANTENE

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The possibility of existence of 1,2-dehydroadamantane or adamantene II is an intriguing question in adamantane chemistry (1). Adamantene is expected to be highly strained because the p-orbitals of the 1,2-double bond cannot overlap without considerable deformation of the rigid skeleton. Few attempts have been made to demonstrate the occurence of adamantene (2,3) and recently a dimer was isolated in high yield (4,5). The existence of the monomer was not proved in any of the cases cited above.

We report now direct evidence for the occurence of adamantene by trapping the latter as a Diels-Alder adduct using 2,5-dimethylfuran and diphenylisobenzofuran. It is known that strained bridgehead olefins, e.g. norbornene (6), form Diels-Alder adducts with ease (7,8). We observed (9) that the adamantene ion is the base peak in the mass spectra of 1,2-adamantane carboxylic acid and its anhydride. The method (10) we **chose** to generate adamantene consisted in degradation of the bis-t-butylperester I. The latter was prepared from the diacid chloride, isolated as an oil from the diacid with PCl_5 ($\nu_{c=o}$ 1800 cm^{-1}), with sodium t-butylperoxide (11). I was purified by chromatography over florisil with dichloromethane and crystallized from pentane at $-70^{\circ}C$ (m.p. 78-80°, ν_{co} 1790 cm^{-1}, correct elemental analysis).
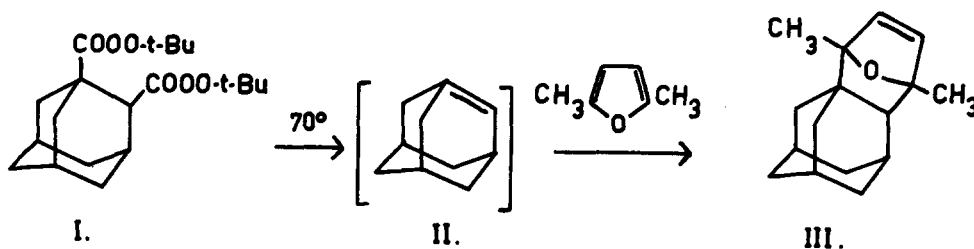
When a dilute solution of I in 2,5-dimethylfuran was gradually heated to 70° a colour-

less crystalline solid, m.p. 135-150°, was obtained in 9% yield after chromatography of the reac-

tion mixture with florisil/hexane/benzene 1:1 and crystallization from methanol. We assigned struc-

ture III to the adduct on the basis of following evidence: The mass spectrum gives the molecular

ion at 230. In the PMR spectrum the methylsinglet of 2,5-dimethylfuran at τ = 2,2 (6H) is found

at τ = 1,9 in the region of adamantylprotons at τ = 1,6-2,7 (20H); the signal of the 3,4-hydrogen

atoms at τ = 5,7 (2H) is shifted to τ = 6,2 clearly demonstrating the formation of a Diels-Alder

adduct. The correct analysis of the solid with m.p. 135°-150° indicated that III consists of a

mixture of exo and endoisomer (confirmed by gc analysis). The polar fraction of the crude mixture

is mainly polymeric and contains the t-butyl moiety and carbonylgroups shown by IR and PMR spec-

troscopy.

When the bis-t-butylperester is warmed in benzene in the presence of diphenylisobenzo-

furan -after destroying excess of this furan with maleic anhydride (7) and repeated thin layer

chromatography of the apolar fraction on Silicagel with hexane- a compound was obtained in 2,5%

yield which showed in the masspectrum a molecular ion at 404 and gave PMR signals of 1:1 ratio

of aromatic and adamantyl protons. Photolytic degradation of I in furan resulted in excessive

polymer formation so that the Diels-Alder adduct could not be isolated.

The low yields of Diels-Alder adducts formed during the decomposition of I can be rationalized. It is reasonable to propose (12) that a high concentration of monoradical precursor to adamantene is present. Adamantene itself would then be formed from this monoradical. Since the latter, depending on its lifetime can undergo many side reactions none leading to Diels-Alder adduct formation only a tiny fraction of highly reactive adamantene is present at any one time in solution. It is noteworty that none of the previous experiments assuming intermediacy of adamantene for the formation of the dimer (4,5), led to Diels-Alder trapping of this olefin. This together with the amazingly (90%) high yield of dimer leads one to suggest that the latter is formed via a different pathway **probably** not involving adamantene.

References.

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12. According to our own preliminary kinetic measurements on the monosubstituted and 2 t-butyl-perester, decomposition of the former is about ten times faster than that of the latter. Although this result need not be exactly valid for the 1,2-disubstituted derivative it may point to the preference of decomposition.