Pentacyclo[4,4,0,$0^{2,10}$0,^{3,5},$0^{4,8}$]decane and Tetracyclo[4,4,0,$0^{2,10}$,$0^{4,8}$]decane

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Summary The 2,4,6,9- tetradehydroadamantane (pentacyclo[4,4,0,$0^{2,10}$,$0^{3,5}$,$0^{4,8}$]decane) (III), formed by thermolysis of adamantane-2,6-diaone bis(tosylhydrazone) (II), gives upon catalytic hydrogenation tetracyclo[4,4,0,$0^{2,10}$,$0^{4,8}$]decane (VI) as the main product.

THE alkaline decomposition of tosylhydrazones[1] can, in principle, yield strained polycyclic hydrocarbons.[2] We report the preparation, by this method, of a novel, strained $C_{10}H_{12}$ polycyclic hydrocarbon, the structure of which was established as that of the pentacyclo[4,4,0,$0^{2,10}$,$0^{3,5}$,$0^{4,8}$]decane (III). (2,4,6,9-tetradehydroadamantane.)

The decane (III) (m.p. 152—154°) was formed by the thermolysis of the di-lithium salt of adamantane-2,6-dione bis(tosylhydrazone) (II) obtained from (I)[3] by conventional methods.

Besides (III) another product was formed and isolated; the hitherto unknown 2-methylenebicyclo[3,3,1]nona-3,6-diene (IV) [λ_{max} (cyclohexane) 249 nm (ϵ 8800)]. The structure of (IV) was elucidated mainly from the ^{1}H n.m.r. spectrum by spin-decoupling techniques.

The structure of (III) was determined also by spectral analysis. The mass spectrum gave a molecular formula of $C_{10}H_{12}$. U.v., i.r., and Raman spectra suggested that double bonds were not present. Therefore (III) must be a pentacyclodecane. The i.r. spectrum (KBr disc and CCl_4 solution) showed a characteristic band at 3035 cm^{-1} attributed to cyclopropane CH stretching vibrations. The

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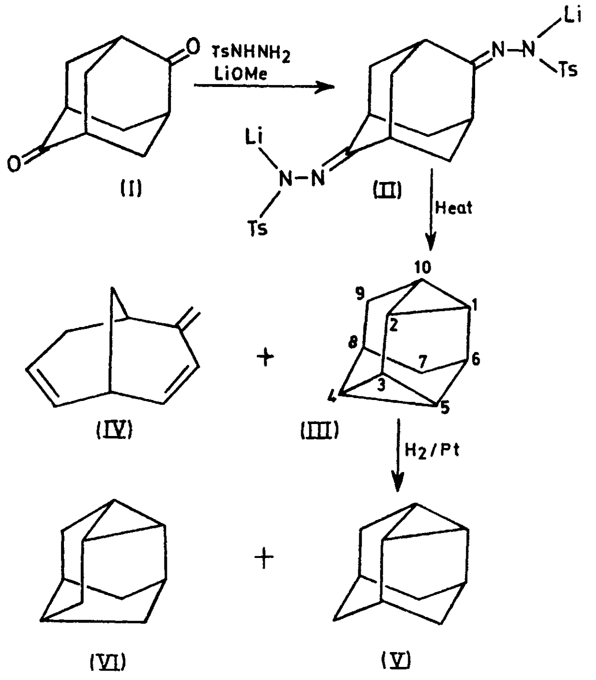
^{1}H n.m.r. spectrum (at 100 MHz) could only be interpreted partially, owing to the small differences between the chemical shifts of the protons and the apparently strong spin couplings, as well as second-order spin interactions. Measurements at 220 or 300 MHz did not lead to a simplification sufficient for interpretation. Unambiguous proof of the structure was obtained by a proton-noise-decoupled ^{13}C n.m.r. spectrum,‡ which revealed ten separate carbon resonances, indicating the absence of symmetry elements. Off-resonance techniques[4] showed that two of the signals originated from secondary carbon atoms (CH_2) and the remaining eight signals from tertiary carbon atoms (CH).



Chemical evidence for the structure of (III) was obtained by mild catalytic hydrogenation (PtO_2–THF–AcOH), which caused cleavage of only one cyclopropane ring, yielding a mixture of two $C_{10}H_{14}$ hydrocarbons. The minor component was identical with the known tetracyclo[4,3,1,$0^{2,4}$,$0^{3,8}$]decane (V).[2b] The main component was characterized (n.m.r.) as tetracyclo[4,4,0,$0^{2,10}$,$0^{4,8}$]decane (VI), another novel hydrocarbon.

Investigation of thermally induced valence isomerism of the pentacyclic hydrocarbon (III) by variable temperature ^{1}H n.m.r. analysis showed that the spectrum remained essentially unchanged between −67° and +80°. After heating of the pentacycle (III) at 250° for 10 min the substance was recovered unchanged. After heating at 400° for 10 min, the m.p. was lowered, but no contaminants could be detected (g.l.c.), and the starting material was still the major component.

Treatment of compound (III) in benzene solution with $AgBF_4$ did not change the ^{1}H n.m.r. spectrum at temperatures up to 80°, indicating that this polycyclic hydrocarbon with several strained σ-bonds did not isomerize under these conditions.[5]

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