

PENTACYCLO[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]DECANE

AND

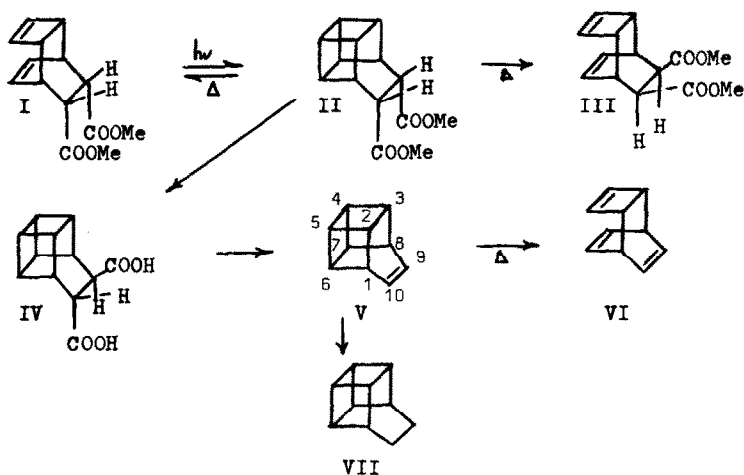
PENTACYCLO[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]NONANE

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Recently, Masamune, Cuts, and Hogben (1) reported the
preparation of pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decane (VII)(2)



of the olefin V, Masamune has assigned $J_{4,6} = J_{5,6}$ and $J_{1,6} = J_{1,7}$. The correctness of this assignment or whether there is virtual coupling (10) leading to an apparent averaging of the coupling constants will have to be determined by obtaining additional $^{13}\text{C-H}$ coupling constants.

Hydrogenation of olefin V with prereduced platinum oxide in 95% ethanol resulted in the uptake of one equivalent of hydrogen to yield the parent saturated hydrocarbon VII in 62% yield; m.p. $102-104^\circ$ (capillary), on a hot stage a phase change was noted at $55-65^\circ$ but the material became liquid at $102-104^\circ$; $\epsilon_{205}^{\text{EtOH}}$ 175; mol. wt. 132 (mass spectrum); n.m.r., τ 6.6-7.1 (6H, multiplets), τ 7.30 (2H, unresolved), τ 8.55 (4H, triplet, total separation of outermost lines is 2.5 c.p.s.). This last triplet structure for the resonance band of the four equivalent methylene protons would be expected on the basis of the direct coupling with one bridgehead proton and the virtual coupling with the other bridgehead proton (9). The low intensity of the ultraviolet end absorption and the absence of vinyl proton absorption in the n.m.r. spectrum establish the saturated nature of VII and its formation by absorption of one mole of hydrogen establishes its structure in relation to V.

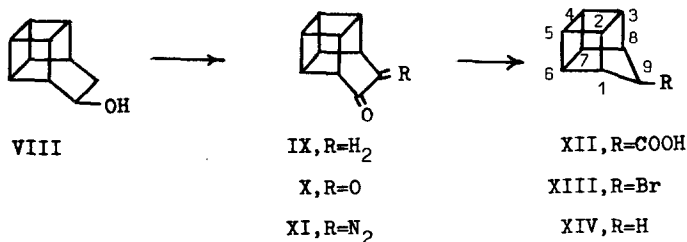
The identical saturated hydrocarbon VII also was obtained in the following manner. Hydroboration (11) of the olefin V yielded the alcohol VIII, m.p. $136-137^\circ$, in an overall yield of 40% from the diacid IV when the intermediate V was not purified. The methanesulfonate ester was prepared by treatment of VIII with methanesulfonyl chloride and triethylamine in benzene (12). The ester was unstable but when reduced

and its related 9,10-dicarboxylic acid (II) and 9-ene (V). Their proof of structure rested mainly on the n.m.r. spectrum of the 9-ene. We should like to report a similar but more extensive study of this ring system as well as the preparation of the related pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane (homocubane) which establishes, unequivocally, the assigned structures.

The known cis-endo diester I (3) when photosensitized by acetone (4) afforded the saturated pentacyclic isomer II, m.p. 81-82°, in 35% yield. The spectral properties of II are: $\epsilon_{205}^{\text{isooctane}}$ 210; n.m.r., τ 6.36(6H, singlet), τ 6.80(8H, broad), and τ 7.20(2H, broad)(5). II when heated at 275° for 20 min. in an evacuated tube yielded the precursor I and the cis-exo diester III. This latter material may be envisioned as arising by rupture of the 2,5 and the 3,4 bonds in II. Hydrolysis of cis-photodiester II with potassium hydroxide in methanol yielded the trans-photodiacid IV, m.p. 226-228° [dimethyl ester, m.p. 57-58°] (6).

Oxidative bisdecarboxylation (7) of IV with lead tetraacetate in pyridine and acetonitrile gave pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]deca-9-ene V, m.p. 61-62°, in 40% yield. This cage olefin was thermally unstable and rapidly decomposed at 110° to the known tricyclic triene VI (8). The n.m.r. spectrum of V was identical with that reported by the other workers (1). The ¹³C-H coupling constant for the vinyl protons was 160 c.p.s., a value which indicates a normal C-C=C angle of 120° (9). For this angle to be maintained in the olefin, the two adjacent cyclobutane rings must be puckered considerably. From the n.m.r. spectrum

with sodium in liquid ammonia yielded the starting alcohol, showing that no structural rearrangement had occurred during the preparation of the ester. The methanesulfonate ester upon reduction with lithium aluminum hydride afforded VII, m.p. 102-104°. Masamune and his coworkers have reported a m.p. of 58-61° for their saturated material assigned the structure VII. Professor Masamune kindly supplied us with a copy of their n.m.r. and mass spectra of their material and the spectra were identical with those obtained with our material. The melting point behavior is complicated due to the extreme volatility of the compound and the value reported depends upon the method used for the determination and the rate of heating. These workers have called the saturated hydrocarbon "basketane"; we should like to suggest the name 1,1'-bishomocubane for this series of compounds since such a name more directly related the structure to other series of materials.



Proof of the pentacyclic nature of V, VII, and VIII was obtained in the following manner. Oxidation of VIII by the Jones procedure (13) gave the ketone IX, m.p. 84.5-86.0°, $\nu_{\text{max}}^{\text{CCl}_4}$ 1730, 1710 cm^{-1} , in 80% yield. Selenium dioxide oxidation of the ketone yielded the diketone X in 80% yield,

m.p. 243-244°, $\lambda_{\text{max}}^{\text{CHCl}_3}$ 490 m μ (ϵ 16); $\nu_{\text{max}}^{\text{CHCl}_3}$ 1740, 1720 cm^{-1} ; n.m.r., τ 6.0-6.5 (complex). The diazoketone XI was prepared from X via the monotosylhydrazone and irradiation (14) of XI in aqueous tetrahydrofuran gave the ring contracted homocubane carboxylic acid (XII), m.p. 156-157°, in 47% yield. The absence of olefinic proton absorption in the n.m.r. spectrum of XII provided evidence for the structure assigned, and X-ray analysis (15) of the *p*-bromoanilide of XII confirmed its structure. The value of 97-98° obtained for the angle C₁-C₉-C₈ in the two crystallographically different molecules in the unit cell of XII compares favorably with the values of 93-95° for the C₁-C₇-C₄ angle of several [bicyclo 2.2.1]heptane derivatives (16). However, the angle C₂-C₁-C₆ of 83-87° in XII differs largely from the 108-114° found in the bicyclic system. The X-ray data also show that the homocubyl system XII consists of two cyclobutane rings, C₂-C₃-C₄-C₅ and C₄-C₅-C₆-C₇, which are essentially planar, and two cyclobutane rings, C₁-C₂-C₅-C₆ and C₃-C₄-C₇-C₈, which are puckered by an angle of approximately 20°. The bond length of C₄-C₅ is 1.56Å and of C₂-C₃ is 1.62Å.

The modified bromodecarboxylation reaction (17) when run with XII readily afforded homocubyl bromide XIII, in addition to some polybrominated material. This mixture, without further purification, was debrominated (18) with sodium and *t*-butanol to the parent hydrocarbon XIV, m.p. 104-105°; $\epsilon_{205}^{\text{EtOH}}$ 250; mol. wt. 118 (mass spectrum). The isolated yield (GLC) of homocubane based on XII was 30%. The n.m.r. spectrum of XIV possessed absorptions at τ 6.6-7.0 (8H) and τ 8.35 (2H, unresolved). The infrared spectrum of XIV remained unchanged after heating XIV at 240° for 5 min., and therefore indicated

a remarkable stability of this ring system.



XV



XVI

From the debromination reaction, a minor product also was isolated in 4% yield and its n.m.r. spectrum was identical to the spectrum of XV, a compound recently synthesized from cyclopentadiene and cyclobutadiene (19). A second synthesis of homocubane was accomplished by dechlorination of nonachlorohomocubane XVI (20) with sodium in *t*-butanol. A 20% yield of a mixture of at least eight compounds was obtained. Two compounds, in a 2:3 ratio, accounted for 65% of the material and when these materials were separated (GLC) they were shown to be XIV and XV, respectively. A very minor product was shown to be indane.

In this study all n.m.r. spectra were taken in CCl_4 solution (TMS external) using a Varian A-60 spectrometer.

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