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CHEMICAL STUDIES OF CAGED COMPOUNDS. II[1]
THE SYNTHESIS OF PENTACYCLO $[6,3,0,0^{2,6},0^{3,10},0^{5,9}]$ UNDECANE: TRISHOMOCUBANE

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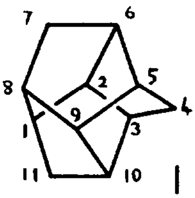
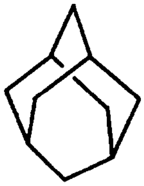
In a continuation of our previous studies[1] of the chemistry of rigid polycyclic hydrocarbons and their derivatives, we have synthesized the highly symmetrical hydrocarbon, pentacyclo $[6,3,0,0^{2,6},0^{3,10},0^{5,9}]$ undecane I for which we propose the trivial name trishomocubane. To our knowledge only one compound (the ketone) having this skeleton has been reported previously[2]. In this paper we wish to describe the synthesis in good yield of this hydrocarbon and draw attention to some of the interesting similarities between I and adamantane II as well as to some significant differences between the two.

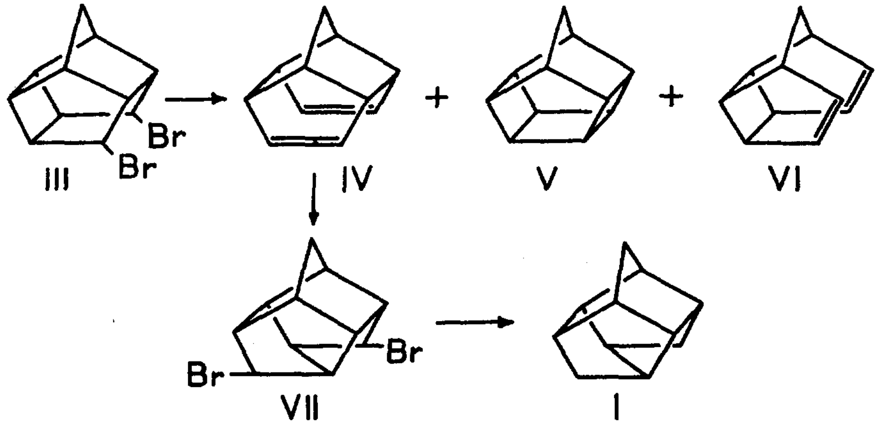


I



II

The dibromide III was synthesized as previously described[1]. Debromination of III with zinc dust in ethanol produced the diene IV along with substantial amounts of homopentaprismane V and a small amount of VI. The diene IV could be isolated by column chromatography over 20% silver nitrate on silica gel. During this process, it appears that VI isomerizes to IV and that homopentaprismane V isomerizes to another, as yet unidentified, compound. These isomerizations are of particular interest in view of recently reported silver ion catalyzed isomerizations of similar compounds[3]. The diene sublimes readily at 70-75°/760 mm.; m.p.: 143.5 - 144.5° (sealed tube); infrared (CCl_4): 3025, 2950, 2870, 850 cm^{-1}; nmr (CCl_4): broad singlets at τ 4.15 (4H), τ 7.75 (4H), τ 8.4 (2H), and a poorly resolved multiplet at τ 6.85 (2H); mass spectrum, m/e (%):144 (55); 129 (21); 128 (18); 79 (100); 78 (33); 77 (36).



Treatment of IV with bromine in carbon tetrachloride gave an essentially quantitative yield of the dibromide VII, m.p.: 146-148°. This unusual 1,4 - addition reaction of IV appears to involve a transition state which is considerably less strained than the transition states leading to the alternative products. There is no spectroscopic evidence for twisting in the diene IV however. Mass spectral and elemental analysis of VII require that it contains two bromine atoms. The infrared spectrum confirms the presence of a methylene group (ν = 2875 cm^{-1}) but nmr shows both these hydrogens to be equivalent. In the series of compounds preceeding IV, these hydrogens are distinctly nonequivalent. Debromination of VII with lithium in t-butanol further supported this structural assignment for VII. The reaction proceeded smoothly to yield a mixture of I and IV which were separated by column chromatography over 20% silver nitrate on silica gel. The hydrocarbon I is a white crystalline solid having m.p. 147 - 149° (sealed tube). The nmr spectrum of I consisted of two broad singlets at τ 8.85 (8H) and τ 8.65 (6H) consistent with the high symmetry of the molecule. The infrared spectrum showed absorptions at 2951(s), 2875(s), 1250(s), 1295(s), 860(s) cm^{-1}. The major peaks in the mass spectrum were: m/e (%): 146 (27); 118 (7); 117 (11); 81 (13); 80 (100); 79 (35); 77 (12); 68 (16); 67 (19); 66 (16).

An examination of a model of compound I shows that this compound may be regarded as resulting from the fusion of six equivalent cyclopentane rings or three norbornanes. Adamantane by comparison consists of four equivalent fused cyclohexanes. It can also be seen that trishomocubane has three C_2 axes of symmetry each passing through a methylene carbon (e.g., C_4) and the center of an opposite C-C bond (e.g., C_1-C_8), a skew C_3 axis of symmetry passing through C_2 and C_9 and that the molecule is chiral. In view of the various biological applications of adamantane derivatives[4], this property should present some interesting effects in the study of derivatives of I. Work is currently in progress to synthesize, and examine the properties, of these derivatives[5].

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