

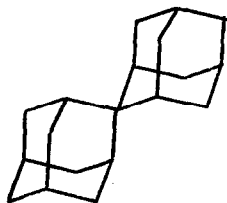
DIAMOND LATTICE HYDROCARBONS. SPIRO[ADAMANTANE-2,2'-ADAMANTANE]

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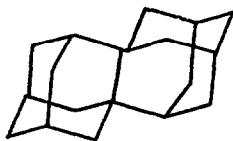
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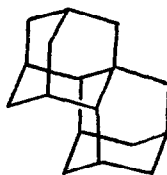
The four "di-adamantanes" consisting of two adamantane units sharing, respectively, one, two, three, and six carbon atoms are I-IV. Of these, only IV (diamantane) is known.¹ We report here the synthesis of I, spiro[adamantane-2,2'-adamantane].²



C₁₉H₂₈
I



C₁₈H₂₆
II

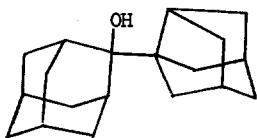


C₁₇H₂₄
III

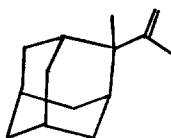


C₁₄H₂₀
IV

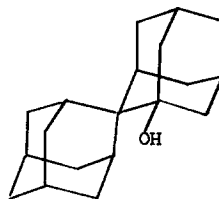
Baeyer-Villiger oxidation of 3-noradamantyl methyl ketone³ followed by lithium aluminum hydride reduction of the resulting acetate gave 3-noradamantanol.⁴ The latter with 47% aqueous HI in a sealed tube at 130° for 30 hours yielded, after column chromatography on silica gel, 3-noradamantyl iodide (40% yield) as a pale yellow viscous oil (60 MHz nmr peaks at δ 0.89, 1.25, 1.62, 2.01, 2.35, 2.85; ir: bands at 2940, 2870, 2850, 1460, 1315, 1245, 1107, 975, 905 cm⁻¹).⁵ Reaction of a twofold excess of *t*-butyl lithium (Alfa Inorganics) in 1:2 diethyl ether-pentane at -78° generated 3-noradamantyl lithium from the iodide *in situ* by lithium-iodine exchange. No 3-noradamantyl iodide was detected by glc after 10 minutes. Addition of 2-adamantanone yielded a mixture of 2-*t*-butyl-2-adamantanol⁶ and 2-(3-noradamantyl)-2-adamantanol, V. Treatment of this crude mixture with 48% aqueous HBr-H₂SO₄ at room temperature yielded a readily separable mixture of 2-methyl-2(2-isopropenyl)adamantane, VI,⁶ and a C₁₉H₂₈O alcohol (m.p. 221.6-222.7°), assigned structure VII, since it differed in glc retention time (10', 10% Carbowax 20M, 200°) from that of V. VII (nmr δ 1.21 (OH), 1.42, 1.59, 1.76, 2.02, 2.21, 2.39, 2.64, 2.85; ir 3580cm⁻¹ (OH); mass spectral base peak m/e 254, others M⁺ 272, 135, 95, 79) would be expected from thermodynamically favorable ring expansion of V



V



VI



VII

Treatment of VII in methyl cyclohexane with concentrated H_2SO_4 at room temperature for thirty minutes gave I, spiro[adamantane-2,2'-adamantane], nearly quantitatively by hydride exchange. I melted (completely submerged sealed capillary) at $249-251^\circ$; the 100 MHz nmr spectrum displayed the expected seven peaks - singlets at δ 1.67, 1.80, 2.24, and a pair of AB doublets at δ 1.49 and 1.99 with J_{AB} 12 cps. The ir had bands at 2940, 2900, 2880, 1455, 1090 cm^{-1} ; while the mass spectral base and parent peak was at m/e 256, other intense peaks were observed at m/e 135, 106, 105, 91. Undepressed mixed m.p. and spectral comparison with sample from Groningen² confirmed the identity of the two compounds.

Our next objective is the synthesis of II.

Acknowledgments. This work was supported by NIH and PRF-ACS Grants, and by Hoffmann-La Roche, Inc., Nutley, New Jersey. The synthesis of I was completed first (Nov. 1971) by Boelema, Strating and Wynberg.² We are much indebted to these authors for informing us of their results and agreeing to delay their publication in order that our paper would appear simultaneously.

Notes and References

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