

HEPTACYCLO[8.6.0.0^{2,8}.0^{3,13}.0^{4,11}.0^{5,9}.0^{12,16}]HEXADECANE

A BISETHANO-BISNORDIAMANTANE BY REARRANGEMENT

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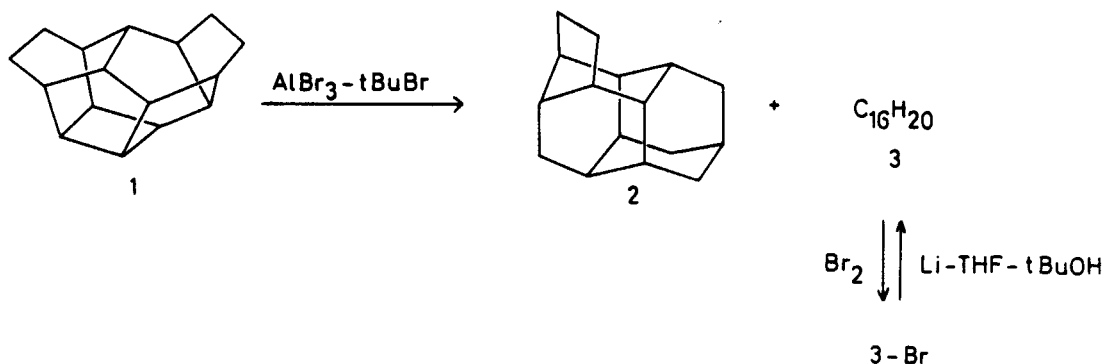
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Lewis acid-catalyzed rearrangements of polycyclic hydrocarbons² often give ethano-bridged diamond lattice molecules as the final products. Examples are 2,4- and 2,8-ethanonoradamantane (C₁₁R₄),^{3,4} 2,4-ethanoadamantane (C₁₂R₄),⁵ 1,3- and 3,14-ethanodiamantane (C₁₆R₆)⁶ and bastardane (C₂₂R₉).⁷ We report here the first synthesis of a bisethano-bridged diamond molecule by isomerization of a heptacyclic C₁₆H₂₀ hydrocarbon.

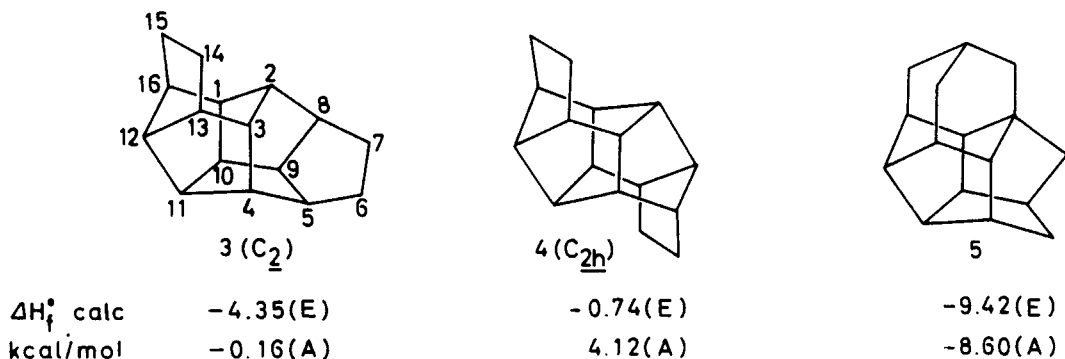
Hydrogenation of the 38.5⁰ dimer of cyclooctatetraene gave desired C₁₆R₇ precursor (1),⁸ which upon treatment with aluminum sludge catalyst⁹ at room temperature for five minutes afforded 1 : 4 mixture of solid and liquid products in 93 % yield. The solid minor product, mp 110-111.5⁰, has been shown to be hexacyclic (hence disproportionated) 3,14-ethanodiamantane (2) by x-ray method.⁶ The liquid main product (3),¹⁰ bp 263⁰, is an isomer of the starting material: mass spectrum, m/e (rel intensity) 212 (M⁺, 100) and 91 (26); ¹H nmr (CCl₄) δ 2.62(2H), 2.43(6H), 2.08(2H) and 1.75(10H), all broad singlets. Bromination of 3 with refluxing liquid bromine gave crystalline monobromide (3-Br),¹⁰ mp 94⁰, which gave back 3 upon reductive debromination with Li-THF-tBuOH.

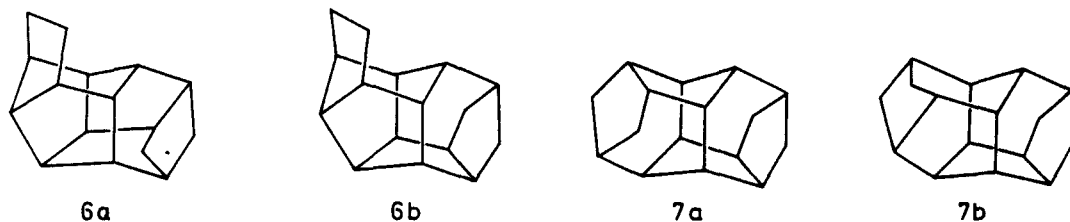
The structure of 3-Br was solved by single crystal x-ray analysis to be 5-bromoheptacyclo[8.6.0.0^{2,8}.0^{3,13}.0^{4,11}.0^{5,9}.0^{12,16}]hexadecane. The crystals are monoclinic, with four molecules in a unit cell with the dimensions of a = 6.562(2), b = 8.102(3), c = 23.058(6) Å, and β = 95.58(3)⁰; the space group is



$P2_1/c$. The arrangement of carbon atoms was elucidated by the heavy atom method on the basis of 2120 independent nonzero reflections collected on an automatic four-circle diffractometer with $\text{CuK}\alpha$ radiation, while hydrogen atoms were located in a difference Fourier map. The atomic coordinates were refined by the block-diagonal matrix least-squares method with anisotropic thermal parameters for the bromine and carbon atoms and with isotropic ones for the hydrogen atoms. The final R-value was 4.3 %. The carbon framework thus obtained is shown in Figure 1.

The bisethano-bisnordiamantane structure of 3 raises several questions. First, we must explain why the isomeric structure 4 did not form along with 3, despite the fact that all known bisnordiamantane derivatives have the carbon skeleton of C_{2h} point group.¹¹⁻¹³ According to empirical force field calculations¹⁴ (see below), 3 is about 4 kcal/mol more stable than 4. In view of the reported accuracy of ± 2 kcal/mol for these calculations,¹⁴ we believe that the predicted energy difference between 3 and 4 is significant.





Secondly, the force field calculations¹⁴ predict that one of six bisnor-triamantane isomers (5) is 5 to 7 kcal/mol more stable than the observed product 3, in apparent contradiction against the thermodynamic principle. We give the following explanation to this anomaly. Once 3 (or 4) is formed en route to the stabilomer,^{3b} the most likely subsequent steps are generation of secondary carbonium ion at the ethano-bridge, followed by 1,2-alkyl shifts to give 6a or 6b, and then 7a or 7b. If one takes only 1,2-alkyl shifts with reasonable bond alignment factor into accounts and excludes paths leading to highly strained structures having three- or four-membered rings,¹⁵ 3, 4, 6 and 7 form a closed graph (Figure 2) within which they readily interconvert. 3 is a prominent energy minimum and any pathway that leaks out of the graph and eventually leads to 5 must pass through high energy barriers. Actually, further treatment of 3 with fresh aluminum sludge catalyst at 100° C for two hours did not cause any change but the formation of small amounts of volatile by-products. 3 has more five-membered rings than six-membered rings and in this respect is unique in the

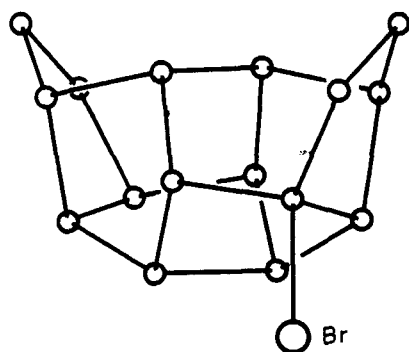


Fig. 1

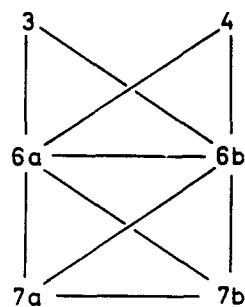


Fig. 2

diamondoid hydrocarbon family.

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