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TETRABROMOCYCLOPENTADIENOADAMANTANE, AN UNUSUAL PRODUCT FROM CHAIN BROMINATION OF 1,2-CYCLOPENTANOADAMANTANE WITH LIQUID BROMINE

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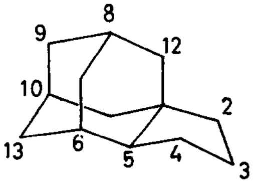
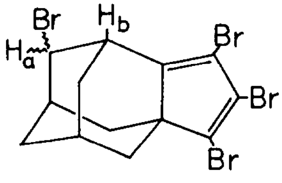
Like many other diamondoid hydrocarbons,[1] 1,2-cyclopentanoadamantane (1)[2] was expected to give bridgehead monobromide smoothly upon ionic bromination.[5] Quite unexpectedly, addition of (1) to stirred liquid bromine at room temperature ensued strongly exothermic reaction leading to spontaneous refluxing of bromine and evolution of a large amount of hydrogen bromide gas. After additional heating and work-up, a single product (2), mp 153.5°, was isolated in moderate yield.

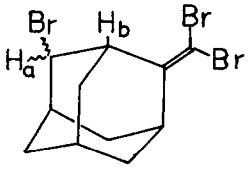
Mass spectrum (M^+, m/e 484, 14.6 %; M^+-Br, 405, 100 %) and elementary analysis (obs. C, 31.95; H, 2.47; Br, 64.95) revealed that the product (2) is a tetrabromide, $C_{13}H_{12}Br_4$ (calc. C, 32.00; H, 2.48; Br, 65.52). Dehalogenative hydrogenation over Pd/C under basic condition gave back (1), as confirmed by comparison of glc retention times and proton nmr spectra. Ir absorptions at 1614 (s) and 1540 (m) cm^{-1} as well as uv absorption at 274 nm (ε 3,300) suggest



(1)



(2)



(3)

the presence of conjugated double bonds. The strongest support for the proposed structure, tetrabromocyclopentadienoadamantane (2), came from the close similarity of proton nmr signals at δ 4.40 (broad s., 1H) and 3.13 (br. s., 1H) to those of H_a (δ 4.6 to 4.4, br. s.) and H_b (3.5 to 3.3, br. s.) of (3), obtained recently by liquid-bromine bromination of 2-methyladamantane.[6]

The mechanism for the formation of (2) should follow the similar steps to those proposed for the formation of (3) in the initial stages of reaction, namely generation of tertiary carbocation at C_5, followed by adamantane-protoadamantane-adamantane skeletal transformation that introduces one bromine atom at the bridge position C_7.[6] In the final stages the chain-like sequence of dehydrobromination-bromination proceeds along the periphery of cyclopentane ring until finally all the carbon atoms of the ring are dehydrogenated and bear bromine atom.

Renowned resistance of the adamantane skeleton against elimination[1] coupled with high thermodynamic stability of the fused cyclopentane ring appear to be responsible for the successful, first observation of exhaustive dehydrogenative bromination of cyclopentane ring. Preliminary liquid-bromine bromination of 1-bromo-1-methylcyclopentane gave pentabromide and tetrabromide retaining methylcyclopentane skeleton.[7]

REFERENCES AND NOTES

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(2) IUPAC Nomenclature: tetracyclo$[6.3.1.1^{6,10}.0^{1,5}]$tridecane. Obtained by Wolff-Kishner reduction of corresponding 3-ketone[3] or more conveniently by Lewis acid catalyzed isomerization of tetracyclo$[6.2.2.1^{3,6}.0^{2,7}]$tridecane,[4] E. Ōsawa, D. Farcasiu and P. v. R. Schleyer, unpublished results.

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