

HEXAMETHYLENE BRIDGED CYCLOHEPTATRIENES. SYNTHESIS AND STRUCTURE

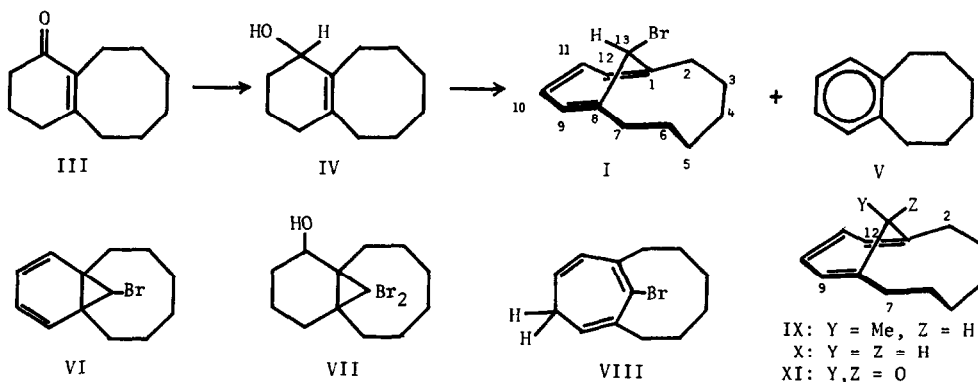
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The novel, bridged bromocycloheptatriene I has been obtained and characterized. The covalency of the C-Br bond was established and cycloheptatrienes IX and X, as well as the tropone XI, were derived therefrom.

Intramolecular aldol condensation of cyclododecane-1,5-dione (II)¹ was effected by means of sodium hydroxide (4%) in boiling methanol to afford the bicyclic enone III² (bp 100°/2.5 mm, ir 1661, 1629 cm⁻¹, 92% yield), which was reduced to the allylic alcohol IV² (bp 108°/2.5 mm, ir 3350 cm⁻¹, 90% yield) by the action of lithium aluminium hydride. Cycloaddition of dibromocarbene³ to IV, followed by thermolysis⁵ (150°/0.2 mm), afforded 13-bromobicyclo[6.4.1]trideca-8,10,12-triene (I)² (bp 125°/0.1 mm, ir 864, 739 cm⁻¹, 33% yield) along with V⁴ (ca. 10% yield). The assigned structure of I was supported by the pmr^{5,6} and cmr⁷, which clearly eliminated the possibility of the alternative norcaradiene structure VI. The anti-bromine stereochemistry on C(13) was based on the observed coupling pattern of the proton on the same carbon.⁸ Unexpectedly, attempts at obtaining the tropylium cation did not success upon treatment of I with Ag⁺ and I remained unchanged even after treatment with sodium hydroxide in boiling aqueous dioxane. The formation of I is explained by assuming that thermolysis of the dibromocarbene adduct VII gives initially the labile bromocycloheptatriene VIII which is transformed into the less strained isomer I by the suprafacial [1,5] shift of a hydrogen atom.⁹ The observed covalency of the C-Br bond of I is ascribed to the rigid structure constrained by the hexamethylene bridge.¹⁰

Reaction of I with methyllithium in ether/HMPA (10 : 1) gave syn-methyl substituted cycloheptatriene IX² (bp 120° (bath temp)/2 mm, ir 1623, 839, 729 cm⁻¹, 67% yield), whose 13-syn-methyl configuration was supported by the pmr.^{11,12} Reduction of I with lithium aluminium hydride gave the mother hydrocarbon X² (ir 3012, 1619, 734 cm⁻¹, 36% yield after tlc purification



on $\text{SiO}_2\text{-AgNO}_3$ ¹³ in addition to V (28% yield) and two unidentified products. The magnetic non-equivalence of the two hydrogens at C(13) indicated that the flipping of the hexamethylene chain was restricted. This suggests that the hexamethylene chain is not yet sufficiently long enough to induce the flipping up and down the tropyliene ring, even though the bond angle between C(1)-H and C(6)-H of tropyliene is smaller than that of meta hydrogens of a benzene ring. Hexamethylene bridged tropone (XI) (ir 1656, 727 cm^{-1} , a 16% yield)¹⁴ was obtained by oxidation of I with $\text{CrO}_3\text{-2Py}$ in dichloromethane. Unsuccessful transformation of XI into the hydroxytropylium cation¹⁵ by means of CF_3COOH also may be ascribed to the constraint of the system.

References and Footnotes

1. S. Fujita and H. Nozaki, Bull. Chem. Soc. Japan, **44**, 2827 (1971).
2. All the new compounds gave expected parent peaks in mass spectra and/or satisfactory analyses.
3. S. Hirano, T. Hiyama, S. Fujita, and H. Nozaki, Chemistry Letters, 707 (1972).
4. Ms m/e 160 (M^+). IRDC Cards, No 5344, Nankodo, Tokyo, Japan.
5. Pmr (CDCl_3) δ 6.60 (dd, C(10,11)-H), 6.03 (m, C(9,12)-H), 3.85 (s, C(13)-H), 2.93, 2.41 (m, allylic 4H).
6. The observed parameter N of an A_2B_2 system was 5.9 Hz. Cf. H. Günther and H. Hinrichs, Tetrahedron Letters, 787 (1966); H. Günther, Angew. Chem., **84**, 909 (1972).
7. Cmr (CDCl_3 , 15.1 MHz, TMS as a standard, taken by Mr. Kushida, Varian Associates) chemical shift (intensity) 132.3 (90), 130.1 (173), 120.7 (148) ppm due to the vinylic carbons. The peak of C(13) appeared at 58.8 (92) ppm, and the methylene chain carbons at 32.4 (190), 28.5 (176), and 25.1 (152) ppm. Cf. H. Günther and T. Keller, Chem. Ber., **103**, 3231 (1970).
8. In the compound X the C(13)-H (anti, Z) couples with hydrogens on C(9) and C(12),¹³ while the C(13)-H (syn, Y) does not. This supports the anti-bromine structure, explaining the magnetic non-equivalence of the allylic hydrogens on C(2) and C(7). The stereochemical deduction is further supported by its uv to be recorded in a full report. For the stereochemical determination of bridged cycloheptatrienes, see E. Vogel, W. Wiedemann, H. D. Roth, J. Eimer, and H. Günther, Liebig Ann. Chem., **759**, 1 (1972).
9. K. W. Egger, J. Amer. Chem. Soc., **89**, 3688 (1967).
10. Ms m/e 254, 252 (M^+ , both 1.2%), 173 (100%). The detection of the molecular ions also confirms the covalency of the C-Br bond. Cf. W. Tochtermann, H. O. Horstmann, C. Degel, and D. Drauss, Tetrahedron Letters, 4719 (1970).
11. Pmr (CDCl_3) δ 6.32 (dd, C(10,11)-H), 5.96 (m, C(9,12)-H), 3.23 (q of t, C(13)-H, J = 7.2, 1.5 Hz), 2.43 (m, allylic 4H), 0.63 (d, CH_3 , J = 7.2 Hz). See K. Conrow, M. E. H. Howden, and D. Davis, J. Amer. Chem. Soc., **85**, 1929 (1963).
12. No deuterium incorporation was observed upon quenching with deuterium oxide. The observed inversion of the configuration on C(13) must be ascribed to a push-pull concerted mechanism involving two molecules of methyl lithium or alternatively to a radicalic one.
13. Pmr (CDCl_3) δ 6.43 (dd, C(10,11)-H), 5.94 (m, C(9,12)-H), 2.95 (d of t, C(13)-H (anti), J = 11.9, 1.5 Hz), 2.47 (m, allylic 4H), 1.78 (d, C(13)-H (syn), J = 11.9 Hz).
14. Pmr (CDCl_3) δ 6.62 (s, 4H), 3.28, 2.48 (m, allylic 4H); pmr ($\text{CDCl}_3\text{-1.5 eq of CF}_3\text{COOH}$) δ 6.76 (s), 3.29, 2.55 (m, allylic 4H).
15. T. Hiyama, Y. Ozaki, and H. Nozaki, Chemistry Letters, 963 (1972).