

SYNTHESES DIRECTED TOWARD SATURATED "FLAT" CARBON

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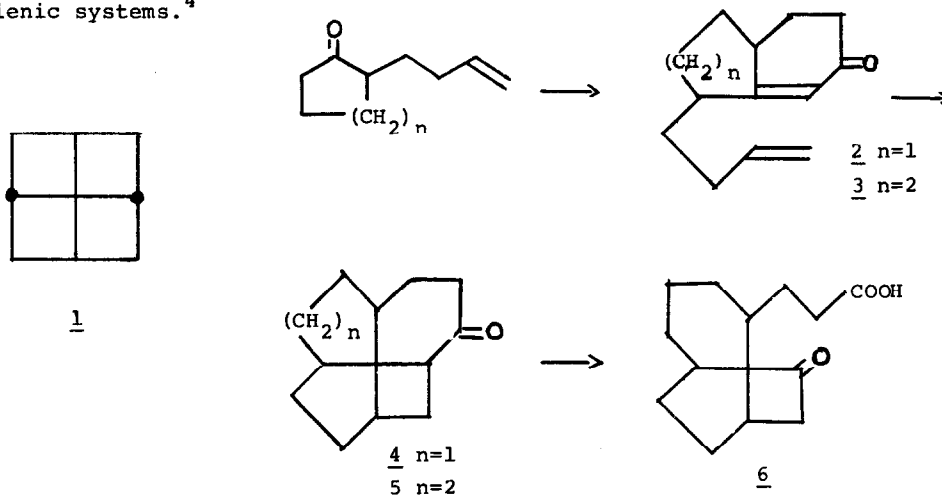
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(Received in USA 31 August 1972; received in UK for publication 19 September 1972)

Although many highly distorted geometries have been achieved at a saturated carbon atom,¹ there has been no attempt at imposing a "flat" condition thereon.² Such is the constraint on the central carbon atom in the structure of tetracyclo[3.3.1.0^{3,9}.0^{7,9}]nonane (1), for which we suggest the name fenestrane.³

We report herein the syntheses of two compounds, tetracyclo[5.5.1.0^{3,13}.0^{10,13}]tridecan-4-one (4) and tetracyclo[6.5.1.0^{4,14}.0^{12,14}]tetradecan-11-one (5), each containing an analogous rosette of four carbocyclic rings with a central distorted tetrahedral carbon, as models for establishing a synthetic approach to 1. Compounds 4 and 5 are conveniently prepared from bicyclic precursors 2 and 3 via 2+2 photochemical cycloaddition, the bicyclo[3.2.0]heptane moiety in 4 and 5 being the known exclusive result in the photolysis of 1,6-dienic systems.⁴



The pyrrolidine enamine derivatives of the respective 2-(3-butenyl)-cycloalkanones ⁵ prepared satisfactorily only by the alkylation of the Grignard derivatives of the N-cyclohexyliminocycloalkanes ⁶ with 3-bromo-1-butene [2-(3-butenyl)-cyclopentanone semicarbazone, mp 186-7^o], reacted with 3-buten-2-one ⁷ to produce 7-(3-butenyl)- $\Delta^{1,8}$ -2-tetrahydroindanone (2) [50%, bp 103-6^o/0.3mm; $\nu_{\text{max}}^{\text{film}}$ 1675, 1640, 1610 cm^{-1} ; $\lambda_{\text{max}}^{\text{EtOH}}$ 241 (ϵ 12,000); $\delta_{\text{ppm}}^{\text{CDCl}_3}$ 0.9-2.9, 4.8-5.1, 5.85; m/e 190; semicarbazone, mp 198-9^o] and 8-(3-butenyl)- $\Delta^{1,9}$ -2-octalone (3) [49%, bp 114-18^o/0.4mm; $\nu_{\text{max}}^{\text{film}}$ 1675, 1640, 1610 cm^{-1} ; $\lambda_{\text{max}}^{\text{EtOH}}$ 240 nm (ϵ 13,600); $\delta_{\text{ppm}}^{\text{CDCl}_3}$ 1.2-2.7, 4.8-5.1, 5.85; m/e 204; semicarbazone, mp 148-50^o]. Products 2 and 3 are judged to be 75:25 (\pm 5) mixtures of $\alpha, \beta: \beta, \gamma$ unsaturated ketones from comparison of ϵ values with that of $\Delta^{1,9}$ -2-octalone.

Photolysis ⁸ of 1-2% hexane solutions of 2 and 3 produced the tetracyclo structures 4 [4.5 hrs irradiation, 62%, bp 86-8^o/0.3mm; m/e 190; semicarbazone mp 198-200^o] and 5 [1.5 hrs irradiation, 76%, bp 108-10^o/0.4mm; m/e 204]. These structures no longer show uv or ir absorption attributable to unsaturation and now possess $\nu_{\text{max}}^{\text{film}}$ 1710 cm^{-1} (saturated C=O). Additionally, the nmr spectra show an absence of vinylic protons and a characteristic absorption at $\delta_{\text{ppm}}^{\text{CDCl}_3}$ 2.63 (t, J=6Hz) indicative of a methinyl proton α to the carbonyl in the bicyclo[3.2.0]octanone ⁹ component of the photoproducts. Further evidence was obtained by treatment of 5 with trifluoroperoxyacetic acid followed by hydrolysis and oxidation (CrO₃/acetone) of the hydroxy acid to yield a keto acid 6 showing $\nu_{\text{max}}^{\text{film}}$ 1768 and 1706 cm^{-1} compatible with the proposed structure.

Modifications in the plan of synthesis of a rosette of four rings to allow for ring contractions toward fenestrane (1) are in progress.

Acknowledgment of appreciation is made to the National Science Foundation for support of this investigation through its program of Research Participation for College Teachers (Grant No. GY-6933)

References

1. In addition to many others, see reviews: K. Wiberg, Adv. Alicyclic Chem. 2, 185 (1968); D. Ginsburg, Accts. of Chem. Research, 5, 249 (1972); K. Wiberg, E.C. Lupton, Jr., and G. J. Burgmaier, J. Am. Chem. Soc., 91, 3372 (1969).
2. For a theoretical treatment of planar tetracoordinate carbon: R. Hoffmann, R.W. Adler, and C.F. Wilcox, J. Am. Chem. Soc., 92, 4992 (1970).
3. Lat., fenestra, window + alkane.
4. R. Srinivasan and K. H. Carlough, ibid., 89, 4932 (1967); J.R. Scheffer and M.L. Lungle, Tetrahedron Letters, 845 (1969).
5. Correct microchemical analyses obtained for all new compounds.
6. G. Stork and S.R. Dowd, J. Am. Chem. Soc., 85, 2178 (1963).
7. G. Stork, A. Brizzolara, H. Landesman, J. Smuszkovicz, and R. Terrell, ibid., 85, 207 (1963).
8. All irradiations were performed in a water cooled immersion well apparatus nitrogen flushed, using a 450 watt Hanovia lamp and a Pyrex filter.
9. P. Singh, Tetrahedron Letters, 4089 (1970).