Tetrahedron Letters No. 36, pp 3229 - 3230, 1974. Pergamon Press. Printed in Great Britain.

A VINYLOG OF p-XYLYLENE. SYNTHESIS OF [2.6]PARACYCLOPHANE

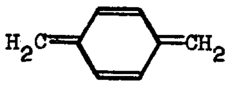
Lawrence G. Kaufman and Daniel T. Longone*

Department of Chemistry, The University of Michigan,
Ann Arbor, MI 48104

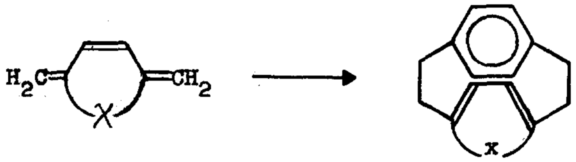
(Received in USA 22 March 1974; received in UK for publication 26 July 1974)

p-Xylylene (I) and substituted p-xylylenes both dimerize and react with related 1,4-quinodimethane intermediates to afford a variety of paracyclophane structures (II). The key role of I in the syntheses of bridged aromatic compounds[1] led us to seek comparable intermediates which would provide structural moieties of more than eight carbons and thereby expand synthetic capabilities in this area of study.

We report now a convenient route to a vinylog of I, the vinyl-p-xylylene III, and its conversion to new paracyclophane hydrocarbons.[2]

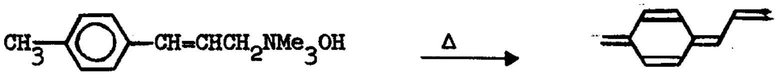


I



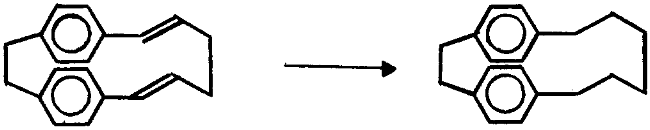
II

Pyrolysis in toluene[3] of the Hofmann base (IV) derived from p-methylcinnamyl bromide[4] affords, along with polymer, the dimer V (26% yield).[5] Catalytic hydrogenation of V provides (quantitative) the new hydrocarbon, [2.6]paracyclophane (VI).[6] Compound VI: mp 50-52°; NMR($CDCl_3$), τ3.31 (s,8H),

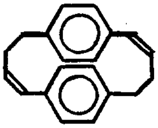


IV III

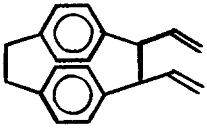
V



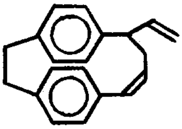
VI



VII



VIII



IX

6.98 (s,4H), 7.55 (m,4H), 8.63 (m,4H), and 9.38 (m,4H); UV (95% EtOH), 217 (4.15), 224sh (4.04), 265 (2.64), 270 (2.76), and 278 nm (2.64).[7]

The minor products from the pyrolysis of IV have not yet been identified; the formation of the head-to-tail dimer VII and the possible intermediacy[8] of VIII and IX are of synthetic and mechanistic interest. These considerations and the general usefulness of p-xylylene III in macrocyclic syntheses are being examined.

Acknowledgement. This work was supported in part by the Macromolecular Research Center of The University of Michigan

References and Footnotes

1. Vögtle and P. Neumann, Synthesis, 85 (1973).
2. Compounds V and VI give satisfactory elemental analyses; IR, NMR, UV, and mass spectra are in agreement with the assigned structures.
3. H. E. Winberg and F. S. Fawcett, Org. Syn., 42, 83 (1963).
4. H. Burton and C. K. Ingold, J. Chem. Soc., 904 (1928).
5. The double bonds appear to be trans (IR, 975 cm^{-1}).
6. Several derivatives of this ring system have been generated by a route not convenient for synthetic purposes: M. H. Delton and D. J. Cram, J. Amer. Chem. Soc., 94, 1669 (1972).
7. The UV spectrum of VI strongly resembles that of [3.6]paracyclophane: D. J. Cram and H. Steinberg, J. Amer. Chem. Soc., 73, 5691 (1951). Shielding of bridge methylene protons to values above τ9 has been observed in [1.n]paracyclophanes (n=8-12): D. J. Cram and L. A. Singer, ibid., 85, 1084 (1963).
8. See reference cited in Footnote 6.