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TETRASPIRO[5.0.2.0.5.0.2.0]OCTADECANE

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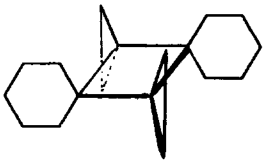
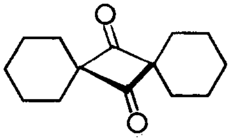
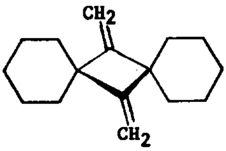
We wish to report a facile two-step synthesis of the "paddlewheel" system I (tetraspiro[5.0.2.0.5.0.2.0]octadecane). This represents the first synthesis of a compound of this type in which the central four-membered ring contains four spiro linkages. The first member of this intriguing class of compounds has recently been synthesized by Ripoll and Conia (1). These authors have suggested the general designation "rotanes" for these systems because of their paddlewheel-like structures.


I


II



III

It has been reported that reaction of tetramethyl-1,3-cyclobutanedione with triphenylphosphinemethylene (methyltriphenylphosphonium bromide, n-butyllithium in tetrahydrofuran) leads to the ring-opened triphenyl-2,2,4-trimethyl-3-oxovalerylmethylene (2). However, we have found that the readily available (3) dispiro[5.1.5.1]tetradecan-7,14-dione (II) in the Wittig reaction (methyltriphenylphosphonium bromide using potassium t-butoxide or n-butyllithium in benzene) led to 7,14-dimethylenedispiro[5.1.5.1]tetradecane (III) in about a 20% yield. Compound III (4) had the following properties: m.p. 57.0-57.5°; $\nu_{max.}$ (CCl_4) 3060 (w), 1640 (w) and 870 (s) cm.$^{-1}$; nmr (CCl_4) δ 1.55 (broad singlet, 20H) and 4.82 (sharp singlet, 4H) (5).

The reaction of III with CH_2I_2 and a Zn/Cu couple (6) led to I (4,7) in a 75-80% yield; m.p. 45-46°; $\nu_{max.}$ (CCl_4) 2050 (s) and 905 (m) cm.$^{-1}$; nmr (CCl_4) δ 0.50 (sharp singlet, 8H) and 1.30 (broad singlet, 20H). A 0.25 ppm upfield shift of the cyclohexane ring protons is found in the nmr comparison of I to III due to the effect of the adjacent spiro cyclopropane rings in I (8).

The extension of this reaction sequence to other ketene dimers and trimers is being pursued along with a more detailed nmr study of potential ring interactions and other properties of these interesting systems.

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References

1. J. L. Ripoll and J. M. Conia, Tetrahedron Letters, 979 (1969).
2. E. A. Lancette, J. Org. Chem., **29**, 2957 (1964).
3. J. L. E. Erickson, F. E. Collins, Jr., and B. L. Owen, J. Org. Chem., **31**, 480 (1966).
4. Satisfactory elemental analysis have been obtained.
5. D. P. G. Hamon, J. Am. Chem. Soc., **90**, 4513 (1969); a synthesis of 1,3-dimethylene-2,2,4,4-tetramethylcyclobutane is reported along with spectroscopic data.
6. R. S. Shank and H. Shechter, J. Org. Chem., **24**, 1825 (1959).
7. The name shelburnane has been adopted by us for I to commemorate the operational paddlewheel at the Shelburne Müseum in Shelburne, Vermont.
8. a) D. J. Patel, M. E. H. Howden and J. D. Roberts, J. Am. Chem. Soc., **85**, 3218 (1963).
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