

I. TRISPIRO[4.0.4.0.4.0]PENTADECANE. PHOTOCHEMICAL
DECARBONYLATION OF POLYMETHYLENEKETENE TRIMERS

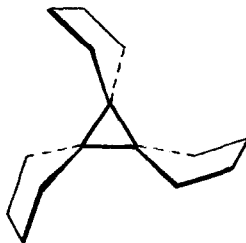
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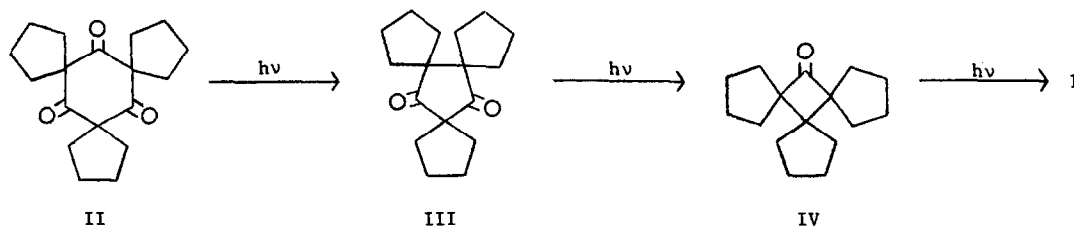
We wish to report the first synthesis of a "paddlewheel" system (2) which contains a central cyclopropane ring. This hydrocarbon, trispiro[4.0.4.0.4.0]pentadecane (I), is readily obtained in one operational step by a triple photodecarbonylation (3) of trispiro[4.1.4.1.4.1]octadecane-6,12,18-trione (II) (4).



I

Irradiation (5) of a degassed pentane solution of II (4.5 mg/ml) using quartz optics for 79.5 hours leads to a 14.1% yield of I (6). Compound I has the following properties: m.p. 34-35°; ν_{max} . (CCl₄) 2955 (s), 2865 (s) and 1455 (w) cm.⁻¹; nmr (CDCl₃) complex multiplet centered at δ 1.48; m/e⁺ 204.

Shorter irradiation periods yield the photo-labile intermediates trispiro[4.1.4.1.4.0]heptadecane-6,12-dione (III) (7,8) and trispiro[4.1.4.0.4.0]hexadecane-6-one (IV) (7,8). The mechanistic sequence outlined below allows for the formation of I.



The reactivity of I and the extension of this reaction to other polymethyleneketene trimers is under investigation.

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References

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2. (a) J. L. Ripoll and J. M. Conia, Tetrahedron Letters, 979 (1969).
(b) A. P. Krapcho and D. E. Horn, Tetrahedron Letters, 4537 (1969).
3. H. U. Hostettler, Tetrahedron Letters, 1941 (1965). A small amount of hexamethylcyclopropane was obtained upon photolysis of hexamethylcyclohexane-1,3,5-trione.
4. J. L. E. Erickson, F. E. Collins, Jr., and B. L. Owen, J. Org. Chem., **31**, 480 (1966).
5. A Rayonet RPR-100 chamber reactor fitted with sixteen RPR-2537Å lamps was used as a light source.
6. Compound I (Retention time: 15 minutes) was isolated by gas chromatography; 6' 20% Silicone GE-SS-96 on Firebrick column operated at 160° with injector 193° and flow rate of 75 ml/min. He.
Anal of I: Calcd for $C_{15}H_{24}$: C, 88.16; H, 11.84. Found: C, 88.31; H, 12.00.
7. Analytical and spectroscopic data are in agreement with the assigned structures.
8. Compound III and IV can be isolated in 7% and 8% yields, respectively.