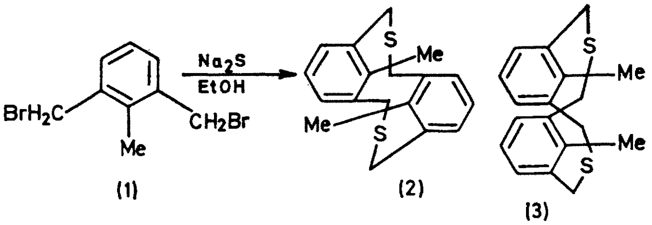
A Synthesis of *cis*-15,16-Dimethyldihydropyrene

By R. H. MITCHELL and V. BOEKELHEIDE*
(*Department of Chemistry, University of Oregon, Eugene, Oregon* 97403)

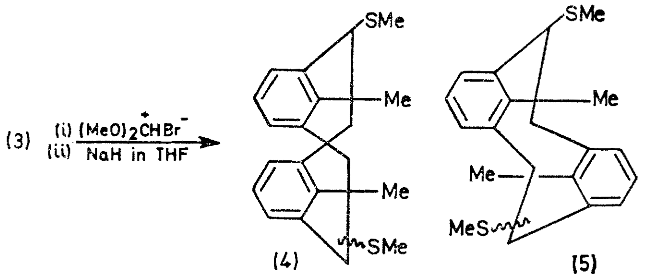
Summary The synthesis of *cis*-15,16-dimethyldihydropyrene (**7**), the first example of a *cis*-15,16-dihydropyrene derivative, has been accomplished starting from *syn*-2,11-dithia[3,3]metacyclophane (**3**) *via* a Stevens' rearrangement of the corresponding bis-sulphonium fluoroborate followed by a Hofmann elimination of the resulting bis-sulphide (**5**).

FOR some time we have studied the synthesis and properties of *trans*-15,16-dialkyldihydropyrenes as examples of rigid, planar [14]annulenes.[1] Recently we reported a convenient synthesis of *trans*-15,16-dimethyldihydropyrene *via* a procedure involving the transformation of the sulphide linkage in 2,11-dithia-9,18-dimethyl[3,3]metacyclophane into carbon–carbon double bonds.[2] This route is quite general and has permitted the synthesis of *trans*-15,16-dihydropyrene,[3] [2,2](2,6)pyridinophane-1,9-diene,[4] [2,2]-metaparacyclophane-1,9-diene,[5] and [2,2,2](1,3,5)cyclophane-1,9,17-triene.[6] We reported that the reaction of 2,6-bis(bromomethyl)toluene (**1**) with sodium sulphide gives both the *syn*- and *anti*-isomers of 2,11-dithia-9,18-dimethyl[3,3]metacyclophane which do not interconvert at temperatures below 200°.[2] The synthesis of *trans*-15,16-dimethyldihydropyrene was accomplished starting with the *anti*-isomer (**2**). We now report the conversion of the *syn*-isomer (**3**) into *cis*-15,16-dimethyldihydropyrene (**7**), the first example of such a *cis*-bridged derivative.

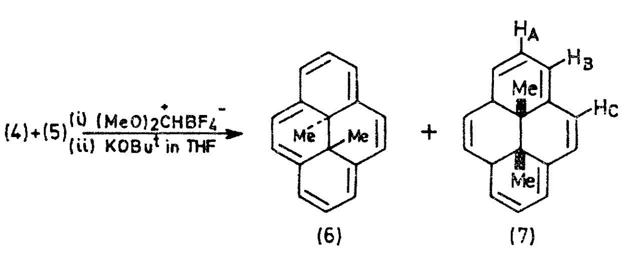


(**1**) (**2**) (**3**)

Treatment of (**3**) with dimethoxycarbonium fluoroborate readily gave the corresponding bis-sulphonium salt as white crystals, m.p. 200° (decomp.), in 83% yield.† When the bis-sulphonium salt was dissolved in tetrahydrofuran containing an excess of sodim hydride and left at room temperature with stirring for 20 h, a Stevens' rearrangement occurred to give in almost quantitative yield a mixture in which the ratio of *syn*- to *anti*-isomers was 3 : 1. As discussed previously,[2] the *syn*- and *anti*-isomers are readily distinguished by n.m.r. analysis in that the protons of the inner methyls at positions 8 and 16 of the *syn*-[2,2]metacyclophane isomers appear at τ 8·0, whereas in the corresponding *anti*-isomers they appear at τ 9·3. The fact that the Stevens' rearrangement of the *syn*-isomer (**3**) yields a mixture of *syn*- and *anti*-[2,2]metacyclophanes (**4**) and (**5**), whereas the Stevens' rearrangement of the *anti*-isomer (**2**) gives only the *anti*-[2,2]metacyclophane,[2] is probably due to the high degree of steric repulsion between the two aromatic rings in the *syn*-isomers which is relieved by inversion to the *anti*-geometry. That such a conformational inversion does occur is readily rationalized in terms of the currently-postulated diradical mechanism for the Steven's rearrangement of sulphonium ylides.[7] The ratio of *syn*- to *anti*-isomers formed during the Stevens' rearrangement is sensitive to both the nature of the base and the temperatures used.



The mixture of isomers (4) and (5) was again treated with dimethoxycarbonium fluoroborate to give the corresponding bis-sulphonium salts as a mixture of isomers in 88% overall yield. This mixture was then dissolved in tetrahydrofuran (THF) containing potassium t-butoxide to effect elimination of dimethyl sulphide. The products were separated by chromatography over alumina and the two green crystalline compounds, so isolated, were identified as *trans*-15,16-dimethyldihydropyrene (6), (28% yield) and *cis*-15,16-dimethyldihydropyrene (7), (10% yield). Sublimation of (7) readily gave emerald-green crystals, m.p. 90—95°.



In contrast to *trans*-15,16-dimethyldihydropyrene which, both from molecular models and *X*-ray studies[8] is known to have a planar ring skeleton, molecular models of *cis*-15,16-dimethyldihydropyrene suggest that the ring portion of the molecule has a shallow, saucer-shaped geometry. Thus, it would be expected that the internal methyl protons of (**7**) would not be embedded so deeply in the cavity of the π-electron cloud as the corresponding methyl protons of (**6**) and so should exhibit a smaller ring current effect. This is supported by the n.m.r. spectrum‡ of (**7**) which shows the internal methyl protons at τ 12·06, whereas the internal methyl protons of (**6**) occur at τ14·25. Likewise, the peripheral aromatic protons of (**7**) are at higher field and more cleanly separated than is the case with (**6**). Thus, the H_C protons of (**7**) appear as a 4H singlet at τ 1·26, the H_B protons as a 4H AB_2 doublet at 1·76 (J 8 Hz), and the H_A protons as a 2H triplet at 2·50.

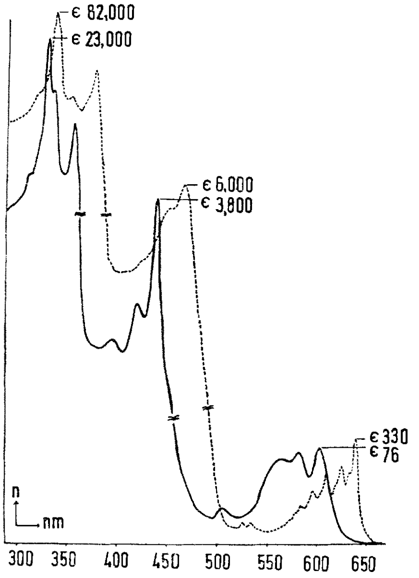
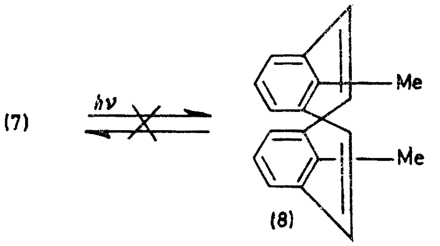


FIGURE. *U.v. and visible spectra of* (6) (------) *and* (7) (———) *taken in cyclohexane using a Carey* 15 *spectrophotometer.*

The mass spectrum of (7) shows the expected parent molecular ion at 232 with signals of stronger intensity at $M^+ - 15$ and $M^+ - 30$, corresponding to the loss of one and two methyls, respectively.

The u.v. and visible spectra of (6) and (7) are compared in the Figure. Although the two spectra are quite similar, there is less fine structure in the spectrum of (7) and its absorption bands are both shifted to shorter wavelength and are of lower intensity than those of (6).



---

† The composition and empirical formulae assigned to all new compounds are supported by satisfactory elemental analyses and/or high resolution mass spectra.

‡ The n.m.r. spectrum of (7) was taken with deuteriochloroform as solvent using a Varian 100 MHz spectrometer.

An interesting property of *trans*-15,16-dimethyldihydropyrene is its reversible photoisomerization to the corresponding valence tautomer, *anti*-[2,2]metacyclophane-1,9-diene.[9] Attempts to effect a similar photoisomerization of *cis*-15,16-dimethyldihydropyrene (**7**) to *syn*-[2,2]metacyclophane-1,9-diene (**8**) have been unsuccessful. Destruction of (**7**) occurs on irradiation with visible light but, as yet no recognizable products have been isolated from such irradiation experiments.

We thank the National Science Foundation for support of this work.

(*Received, September 2nd,* 1970; *Com.* 1477.)

[1] V. Boekelheide and T. Hylton, *J. Amer. Chem. Soc.*, 1970, **92**, 3669. For a review on dihydropyrenes, see V. Boekelheide, *Proc. Welch Foundation*, 1968, **XII,** 83; for a review on annulenes, see F. Sondheimer, *Proc. Welch Foundation*, 1968, **XII,** 125.

[2] R. H. Mitchell and V. Boekelheide, *Tetrahedron Letters*, 1970, 1197.

[3] R. H. Mitchell and V. Boekelheide, *J. Amer. Chem. Soc.*, 1970, **92**, 3510.

[4] V. Boekelheide and J. Lawson, *Chem. Comm.*, 1970, 1479.

[5] V. Boekelheide and P. H. Anderson, *Tetrahedron Letters*, 1970, 1207.

[6] V. Boekelheide and R. A. Hollins, *J. Amer. Chem. Soc.*, 1970, **92**, 3512.

[7] J. E. Baldwin, W. F. Erickson, R. E. Hackler, and R. M. Scott, *Chem. Comm.*, 1970, 576.

[8] A. W. Hanson, *Acta Cryst.*, 1965, **18**, 599.

[9] H.-R. Blattmann, D. Meuche, E. Heilbronner, R. J. Molyneux, and V. Boekelheide, *J. Amer. Chem. Soc.*, 1965, **87**, 130; *cf.* H.-R. Blattmann, Doctoral Dissertation, Eidg. Tech. Hochschule, Zürich, 1967.