without success. However, when VIII is dissolved in strong acid, trifluoroacetic or sulfuric, the solution becomes a deep green, the typical color of the *trans*-15,16-dihydropyrene system. Furthermore, the absorption spectra of such solutions in trifluoroacetic acid show maxima at 470, 560, and 647 mμ, in good agreement with the spectra of *trans*-15,16-dimethyldihydropyrene derivatives.[10]

In view of the spectral correlations it is our belief that the solutions of VIII in strong acid contain pyrene 15,16-epoxide, the valence tautomer of VIII, presumably in its protonated form as shown by IX. The intensity of the green color increases to a maximum approximately 30 min after dissolving VIII in trifluoroacetic acid (temperature 30°); the intensity then decreases slowly with the rate showing first-order kinetics, suggesting IX is formed fairly rapidly and then undergoes slow decomposition. From this solution pyrene, 1,6-pyrenequinone, and 1,8-pyrenequinone have been isolated and identified chromatographically and spectroscopically.[11] We have found that a solution of pyrene in trifluoroacetic acid is stable, but the hydrocarbon is oxidized at room temperature by pertrifluoroacetic acid to yield a mixture containing the two quinones. These observations indicate that the cation IX forms pyrene by loss of OH$^+$ to form pertrifluoroacetic acid since it would be difficult to explain the formation of pyrene and the pyrenequinones from VIII.

[10] Since the absorption maxima of VIII are still present in the spectrum in trifluoroacetic acid, it is not possible to give exact values of the extinction coefficients. However, the relative intensities of the various maxima are in reasonable accord with those of the dihydropyrenes, the band at 560 mμ being extremely weak. No assignment of the ultraviolet bands could be made due to the presence of VIII initially and the formation of pyrene as the reaction progressed (see below).

[11] A. J. Fatiadi, *J. Chromatog.*, 20, 319 (1965).

[12] National Institutes of Health Postdoctoral Fellow, 1966–1967.

[13] Visiting Professor, on sabbatical leave from Oxford University.

[14] Aided in part by a grant from the National Science Foundation.

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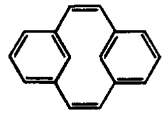
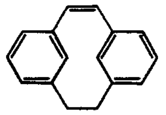
[2.2]Metacyclophane-1-ene[1] and Its Photoisomerization to 4,5,15,16-Tetrahydropyrene

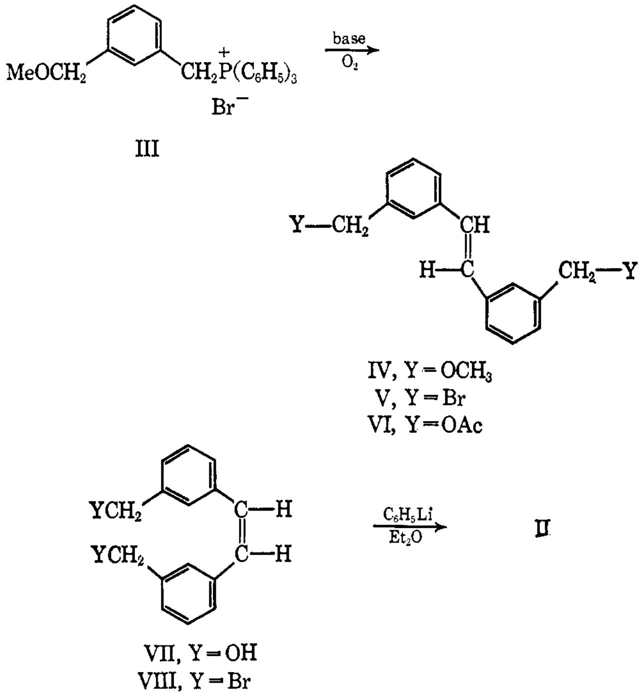
Sir:

Although Pellegrin[2] has claimed the synthesis of [2.2]-metacyclophane-1,9-diene (I), subsequent attempts to repeat his preparation have been unsuccessful.[3,4] Furthermore, even though the elegant studies of Dewhirst and Cram[5] have shown that [2.2]paracyclophane can be converted to the corresponding mono- and diolefins, attempts to utilize their procedure for introduction of unsaturation into the [2.2]metacyclophane molecule were quite unsuccessful.[4] In view of our recent studies[6] showing that [2.2]metacyclophane-1,9-diene derivatives undergo spontaneous valence tautomerization to the corresponding *trans*-15,16-dihydropyrene derivatives, it has become of interest to reexamine the synthesis of [2.2]metacyclophanes having unsaturation in the bridging atoms. We now report the successful preparation of [2.2]metacyclophane-1-ene (II).


I


II

Treatment of the monophosphonium salt of *m*-xylyl dibromide with methanol readily gives the corresponding methoxy derivative III, mp 242–242.5°.[7] The reaction of III with oxygen in the presence of base, following the procedure of Bestmann,[8] yielded a mixture of the *cis*- and *trans*-stilbenes, IV. Cleavage of the benzylic ether linkages of IV with hydrogen bromide gave the corresponding *trans*-dibromide V, mp 161–162°, which by reaction with sodium acetate led to the *trans*-diacetate VI, mp 97–98°. Irradiation converted VI to a mixture of stereoisomers whose nmr spectrum indicated the ratio of *cis* to *trans* isomers was 3:1. On addition of ethanol the *trans* form of VI crystallized out. Hydrolysis of the remaining *cis* isomer of VI gave the corresponding diol VII as an oil, which was characterized by its analytical and spectral data. Treatment of VII with phosphorus tribromide followed by chromatography of the product gave the pure *cis*-stilbene dibromide VIII as a colorless oil.



In devising this scheme it had been anticipated that the presence of a bridging double bond, if it were in the *cis* configuration, would not interfere but might even help in a cyclization to the corresponding metacyclo-

[1] The nomenclature used in this communication follows the suggestion of B. H. Smith, "Bridged Aromatic Compounds," Academic Press Inc., New York, N. Y., 1964, p 88.

[2] M. Pellegrin, *Rec. Trav. Chim.*, **18**, 457 (1899).

[3] W. Baker, J. F. W. McOmie, and J. M. Norman, *J. Chem. Soc.*, 1114 (1951).

[4] W. S. Lindsay, P. Stokes, L. G. Humber, and V. Boekelheide, *J. Am. Chem. Soc.*, **83**, 943 (1961).

[5] K. C. Dewhirst and D. J. Cram, *ibid.*, **80**, 3115 (1958).

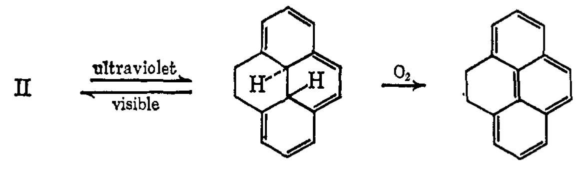
[6] H-R. Blattmann, D. Meuche, E. Heilbronner, R. J. Molyneux, and V. Boekelheide, *ibid.*, **87**, 130 (1965).

[7] Satisfactory elemental analyses and supporting spectral data have been obtained for all new compounds reported in this communication.

[8] H. J. Bestmann, *Angew. Chem.*, 72, 34 (1960); H. J. Bestmann and O. Kratzer, *Chem. Ber.*, **96**, 1899 (1963).

phane. When VIII was treated with sodium in the presence of tetraphenylethylene, the usual conditions for cyclization to form metacyclophanes, cyclization occurred, but it was accompanied by aromatization to give 4,5-dihydropyrene (X) in 50% yield. However, an investigation of other cyclization procedures led to the discovery that the treatment of VIII with phenyllithium in ether gives the desired [2.2]metacyclophane-1-ene (II) as white crystals, mp 82–83°, in 45% yield. It is of interest that in the nmr spectrum of II the signal for the two internal aromatic protons at the 8 and 16 positions is a broad singlet at τ 4.38. In [2.2]metacyclophane itself the internal 8 and 16 protons appear at τ 5.75. Thus, the orientation of the bridging double bond is such that it has a strong deshielding effect on the internal aromatic protons.

Ultraviolet irradiation of stilbene solutions in the absence of oxygen has been shown by a number of investigators to lead to 4a,4b-dihydrophenanthrenes.[9–13] When a solution of II in benzene or carbon tetrachloride was irradiated with ultraviolet light, the solution rapidly became colored, showing the appearance of absorption bands at 237, 305, 318.5, and 500 mμ (broad).[14] This spectrum is in good accord with that reported for the hexamethyldihydrophenanthrene[13] and suggests the formation of the 4,5,15,16-tetrahydropyrene (IX). As would be expected, the formation of IX is readily reversible by visible light. Furthermore, the solutions resulting from irradiation of II are extremely sensitive to traces of oxygen and, in its presence, the product found is 4,5-dihydropyrene (X).



IX X

Thus far, attempts (catalytic dehydrogenation and NBS) to effect a dehydrogenation of IX to give *trans*-15,16-dihydropyrene have been unsuccessful and have invariably yielded pyrene. However, in the case where the internal substituents are other than hydrogen, the corresponding irradiation products should be more stable both toward oxygen and toward aromatization to pyrene. Studies on such derivatives are in progress.

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[9] W. M. Moore, D. D. Morgan, and F. R. Stermitz, *J. Am. Chem Soc.*, **85**, 829 (1963).

[10] M. V. Sargent and C. J. Timmons, *ibid.*, **85**, 2186 (1963).

[11] F. B. Mallory, C. S. Wood, and J. T. Gordon, *ibid.*, **86**, 3094 (1964).

[12] G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *ibid.*, **86**, 3197 (1964).

[13] K. A. Muszkat, D. Gegiou, and E. Fischer, *Chem. Commun.*, 447 (1965). We are indebted to Professor Fischer for his kindness in making a preprint of their detailed paper on this subject available to us prior to publication.

[14] Since the concentration of IX in the irradiated solutions is not known, extinction coefficients for their absorption bands could not be determined.

[15] We thank the Office of Naval Research for their support under Contract Nonr-2771(OR),NR-055-468, which made this investigation possible.

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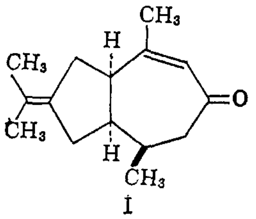
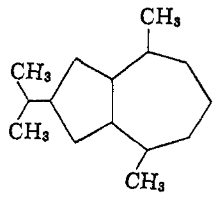
A Stereoselective Synthesis of Hydroazulenes. Grounds for Structure Revision of the Vetivane Sesquiterpenes

Sir:

With a view toward the total synthesis of β-vetivone, a constituent of the essential oil of vetiver,[1] we formulated a new stereoselective route to substituted hydroazulenes and thereby prepared the three 6,10-dimethyl-*cis*-decahydroazulen-8-ones **12a–c**. In this report we describe these synthetic studies and show that none of the aforementioned hydroazulenones corresponds to either of the epimeric desisopropylidenedihydro-β-vetivones prepared from β-vetivone. This finding invalidates not only the structure (I) heretofore accepted[1,2] for β-vetivone but, by virtue of reported chemical correlations, the proposed carbon framework (II) of the entire class of bicyclic vetivane sesquiterpenes as well.[2e,3]



I



II

Methylation (KO-*t*-Bu, CH_3I)[4] of the known hydrindanone **1**[5] afforded the dimethyl derivative **2** [λ_{max}^{film} 3.28 (C=CH), 5.84 (CO), 6.09 (C=C), 8.78, 9.21, 9.58, 9.82, 9.92, and 10.05 μ; $\delta_{TMS}^{CCl_4}$ = 5.36 (H-3, four lines, $J_{3,2}$ = 2 Hz, $J_{3,7a}$ = 2 Hz), 1.21, and 1.20 ppm (C-4 dimethyl)]. This substance yielded principally the *cis*-hydrindanone **3a** [λ_{max}^{film} 5.86 (CO), 10.14, 10.86, and 11.59 μ, purified *via* the semicarbazone derivative, mp 207–208°] upon hydrogenation over palladium on carbon in ethanol. The minor hydrogenation product was identified as the *trans*-hydrindanone **3b** by comparison with an authentic sample.[6] Bromination followed by dehydrobromination[4] converted hydrindanone **3a** to the conjugated ketone **4** [λ_{max}^{film} 5.96 (CO), 6.18 (C=C), 8.91, 10.82, 11.80, and 12.41 μ]. Hydrogenation (Pd–C) regenerated the *cis*-hydrindanone **3a** thus confirming our expectation[4] that isomerization of the ring fusion had not occurred en route to the conjugated ketone **4** (Chart I).

Addition of methylmagnesium iodide to hydrindanone **4** in the initial presence of cupric acetate[4] afforded the 1,4 adduct **5** [λ_{max}^{film} 5.84 (CO), 8.90, 9.10, 9.63, and 9.95 μ; $\delta_{TMS}^{CCl_4}$ = 1.27, 0.97 (C-4 dimethyl, two singlets), and 1.01 ppm (C-7 methyl doublet, J = 5.0 Hz)]. This

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[1] J. Simonsen and D. H. R. Barton, "The Terpenes," Vol. III, Cambridge University Press, London, 1952, pp 224–232.

[2] (a) A. S. Pfau and P. A. Plattner, *Helv. Chim. Acta*, **23**, 768 (1940), and previous papers; (b) Y. R. Naves and E. Perrottet, *ibid.*, 24, 3 (1941); (c) Y. R. Naves, *Bull. Soc. Chim. France*, 369 (1951); (d) M. Romaňuk and V. Herout, *Collection Czech. Chem. Commun.*, 25, 2540 (1960); (e) I. Yosioka and T. Kimura, *Chem. Pharm. Bull.* (Tokyo), **13**, 1430 (1965).

[3] Notably hinesol: W. Z. Chow, O. Motl, and F. Šorm, *Collection Czech. Chem. Commun.*, **27**, 1914 (1962); I. Yosioka, H. Hikano, and Y. Sasaki, *Chem. Pharm. Bull.* (Tokyo), **9**, 84 (1961), and previous papers. Bicyclovetivenol: G. Chiurdoglu and J. Decot, *Tetrahedron*, **4**, 1 (1958). α-Isovetivenene and β-isovetivenene: ref 2d.

[4] *Cf.* J. A. Marshall and N. H. Andersen, *J. Org. Chem.*, **31**, 667 (1966).

[5] G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Am. Chem. Soc.*, **85**, 207 (1963).

[6] G. Stork, P. Rosen, H. Goldman, R. V. Coombs, and J. Tsuji, *ibid.*, **87**, 275 (1965).