Table II[a]

	$k_{rac} = k_a[Et_3N]/[Et_3N^+H] + k_b$			
Ester	k_a, min^{-1}	k_b, min^{-1}	$k_{coupling}$,[b] M^{-1} min^{-1}	$k_{coupling}/k_a$
Ia	1.4×10^{-3}	2.3×10^{-3}	8.7×10^{-1}	600
Ib	2.3×10^{-4}	2.3×10^{-5}	2.1×10^{-1}	930
Ic	2.9×10^{-5}	2.3×10^{-5}	4.8×10^{-2}	1600
II	3.8×10^{-3}	1.4×10^{-2}	19.3	5100

[a] Rates followed polarimetrically; $Et_3N = 0.2$ *M*, $Et_3N^+H + Et_4N^+ = 0.2$ *M*, temperature 25°, DMF, anion = BF_4^-, $0.01 \leq [Et_3N^+H] \leq 0.2$ *M;* k_a and k_b obtained as described in Table I, footnote *d.* [b] Rates of the reaction, ester + GlyOEt → ZGly-Phe-GlyOEt + phenol; rates followed by ultraviolet photometry in DMF, 30°; ester, $1\text{-}2 \times 10^{-4}$ *M;* GlyOEt, 0.01–0.5 *M;* reactions were first order in ester to at least three-half-lives, first order in amine over at least a 3-fold concentration range.

nolic esters can be slowed by as much as 50-fold by the addition of the corresponding ammonium fluoroborate salt.

Included in Table II are rates of combination of the esters Ia–c and II with ethyl glycinate in DMF. Since the value of *K* in (1) should not vary significantly for these esters, the values of k_a may be taken as measures of the relative reactivities of the esters Ia–c and II toward an internal oxygen nucleophile. Comparing these values with the rates of reaction with an external amine, one finds a surprisingly good correlation, despite considerable variation of reactivity and structure.

Acknowledgment. The support of the U. S. Public Health Service through Grants GM 13453-01 and -02 is gratefully acknowledged.

D. S. Kemp, S. W. Chien
Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

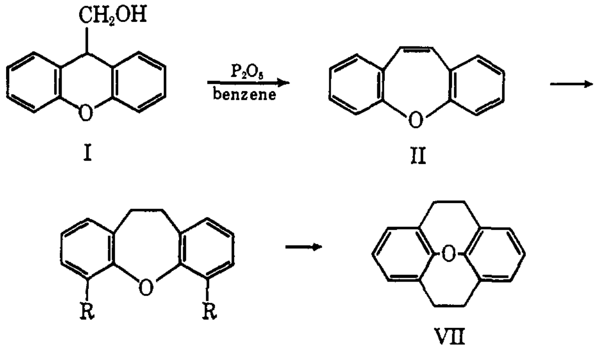
Received December 30, 1966

A Valence Tautomer of Pyrene *cis*-15,16-Epoxide

Sir:

Recently we reported the synthesis of *trans*-15,16-dimethyldihydropyrene[1] and its photoisomerization to the corresponding metacyclophane valence tautomer.[2] Since then, syntheses of other examples of *trans*-15,16-dihydropyrenes have been described,[3,4] but as yet no example has been reported of a *cis*-15,16-dihydropyrene derivative. We now wish to record the synthesis of 8,16-oxido[2.2]metacyclophane-1,9-diene (VIII), a valence tautomer of *cis*-pyrene 15,16-epoxide.

The starting material for this synthesis was xanthene-9-carbinol (I), which undergoes an acid-catalyzed rearrangement in essentially quantitative yield to give dibenz[b,f]oxepine (II).[5] Reduction of II gave the corresponding dihydro derivative III as a colorless oil, bp 100–103° (0.2 mm).[6] Treatment of III with *n*-butyllithium followed by carbonation, according to the procedure used by Gilman for carbonating diphenyl ether,[7] gave the corresponding dicarboxylic acid which, by reaction with diazomethane, led to the dimethyl ester IV as white crystals, mp 94.5–95.0°, in 39% over-all yield. Reduction of IV with lithium aluminum hydride provided the diol V as white crystals, mp 123–124°, in 98% yield. Conversion of V to the corresponding dibromide VI, white crystals, mp 124–125°, was accomplished in 90% yield using phosphorus tribromide. Cyclization of VI with phenyllithium to the corresponding metacyclophane VII, mp 94.0–95.5°, occurred smoothly in 75% yield.



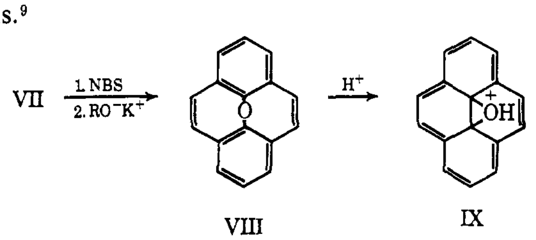
I

II

VII

III, R = H
IV, R = CO_2Me
V, R = CH_2OH
VI, R = CH_2Br

Although VII is a metacyclophane derivative, the oxygen bridge forces the two benzene rings into a *cis* relationship in contrast to the normal *trans* geometry of [2.2]metacyclophanes.[8] Further, it could be expected that the *cis* geometry of VII would allow normal benzylic substitution. This was found to be the case. Treatment of VII with 2 equiv of N-bromosuccinimide gave the corresponding dibromide as a mixture of two stereoisomers. Without separation, this mixture was then subjected to reaction with potassium *t*-butoxide in *t*-butyl alcohol to yield the desired unsaturated derivative, VIII, as white crystals, mp 119–120°. In support of its structural assignment, VIII showed an A_2B multiplet (6 H) at τ 2.66–3.30 and a singlet (4 H) at τ 2.92. Also, the ultraviolet absorption spectrum of VIII showed absorption maxima in cyclohexane at 239 (ε 15,700) and 302 mμ (ε 16,300), indicating conjugation between the aromatic rings and the unsaturated side chains.[9]



VIII

IX

Although the spectral data clearly establish that VIII is the correct structure of our product and that spontaneous valence tautomerization to the corresponding pyrene 15,16-epoxide structure does not occur, it was of interest to see whether conditions might be found for accomplishing this valence tautomerization. Our initial attempts employing light and heat have been

---

[1] V. Boekelheide and J. B. Phillips, *Proc. Natl. Acad. Sci. U. S.*, **51**, 550 (1964).

[2] H. Blattmann, D. Meuche, E. Heilbronner, R. J. Molyneux, and V. Boekelheide, *J. Am. Chem. Soc.*, **87**, 130 (1965).

[3] V. Boekelheide and T. Miyasaka, *ibid.*, **89**, 1709 (1967).

[4] H. B. Renfroe, L. A. R. Hall, and J. A. Gurney, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, Paper O-184.

[5] F. Anet, *Can. J. Chem.*, **35**, 1084 (1957).

[6] Satisfactory elemental analyses have been obtained for all of the compounds reported in this communication.

[7] K. Oita and H. Gilman, *J. Am. Chem. Soc.*, **79**, 339 (1957).

[8] W. S. Lindsay, P. Stokes, L. G. Humber, and V. Boekelheide, *ibid.*, **83**, 943 (1961).

[9] The mass spectrum of VIII shows the expected parent molecular ion at *m/e* 218, with an even more intense signal at 202 corresponding to loss of oxygen.

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.

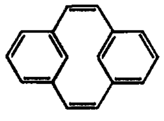
[14] Aided in part by a grant from the National Science Foundation.

B. Andes Hess, Jr.,[12] A. S. Bailey,[13] V. Boekelheide[14]
Department of Chemistry, University of Oregon
Eugene, Oregon 97403
Received April 4, 1967

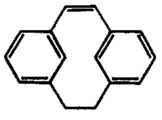
[2.2]Metacyclophane-1-ene[1] and Its Photoisomerization to 4,5,15,16-Tetrahydropyrene

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).

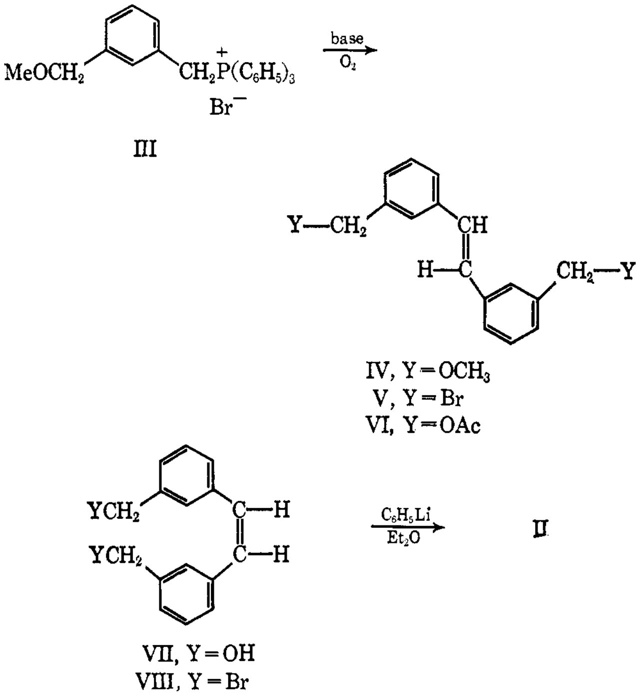


I



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).