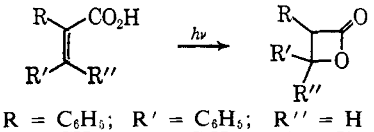
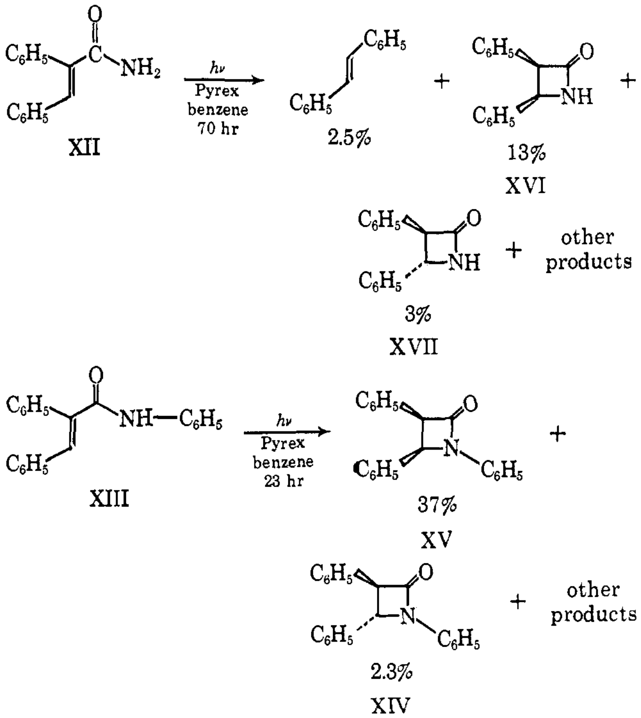
ize to β-lactone IX.[3] The isomerization of I to IV does not distinguish between paths A and B. Irradiation of X ($R = C_6H_5$; $R' = p\text{-}CH_3C_6H_4$) gives IX ($R = C_6H_5$; $R' = p\text{-}CH_3C_6H_4$). This result is consistent only with path B. The product shows λ_{max}^{KBr} 5.51 μ; $\nu_A = \delta\ 5.29$, $\nu_B = \delta\ 5.84$ ($J_{AB} = 7$ cps), and is identified as IX rather than VII by the fragmentation of the parent ion (*m/e* 238) of IX ($R = C_6H_5$; $R' = p\text{-}CH_3C_6H_4$) to phenylketene radical cation (*m/e* 118, 40.6% of base).

The isomerization of I and II to IV has some generality. A variety of α-substituted cinnamic and crotonic acids (XIa–e) give β-lactones. β-Lactones have not yet been isolated from cinnamic or crotonic acid. The photochemical synthesis of β-lactones has substantial advantages over other methods in ease and in producing the *cis*-lactone as the major product.



Xa, $R = C_6H_5$; $R' = C_6H_5$; $R'' = H$
b, $R = CH_3$; $R' = C_6H_5$; $R'' = H$
c, $R = C_6H_5$; $R' = CH_3$; $R'' = H$
d, $R = C_6H_5$; $R' = C_6H_5$; $R'' = C_6H_5$
e, $R = C_6H_5$; $R' = CH_3C_6H_4$; $R'' = H$

Irradiation of the α,β-unsaturated amides XII and XIII in degassed solution gives in each case the *cis*- and *trans*-β-lactams in the yields indicated, together with other products. The *trans*-β-lactam XIV (mp 127–128°), which has been identified by comparison with an authentic sample,[4] shows $\lambda_{max}^{CHCl_3}$ 5.73 μ; $\nu_A = \delta\ 4.25$, $\nu_B = \delta\ 4.94$ ($J_{AB} = 3.0$ cps). The *cis* isomer XV (mp 182–183°) shows $\lambda_{max}^{CHCl_3}$ 5.75 μ, $\nu_A = \delta\ 4.96$, $\nu_B = \delta\ 5.44$ ($J_{AB} = 7.0$ cps). Both *cis* and *trans* isomers give intense parent ions (*m/e* 299) and fragment ions at *m/e* 180 [(stilbene)·+]. The *cis*-β-lactam XVI (mp 154–155°)[5] shows $\lambda_{max}^{CHCl_3}$ 5.67 μ; $\nu_A = \delta\ 4.87$, $\nu_B = \delta\ 5.12$ ($J_{AB} = 6.0$ cps). The *trans* isomer XVII (mp 124–125°)[5] shows $\lambda_{max}^{CHCl_3}$ 5.67 μ; $\nu_A = \delta\ 4.15$, $\nu_B = \delta\ 4.62$, $J_{AB} = 3.0$ cps. Both XVI and XVII give intense parent ions (*m/e* 223) and fragment ions at *m/e* 180. The photochemical production of the *cis*-β-lactams in this series is of particular importance since these compounds are not easily available by other procedures.



Irradiation of II or XII in the presence of iodine or oxygen gives the corresponding phenanthrene.[6,7]

Acknowledgment. This research was supported by a grant from the National Science Foundation (GP 6740).

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[3] Ketonization of the enol must be kinetically controlled to produce the *cis*-β-lactone. The hydroxy oxetene VIII could be formed by addition of either oxygen of the carboxyl group to the β carbon.

[4] W. Kirmse and L. Horner, *Chem. Ber.*, **89**, 2759 (1956); R. Pfleger and A. Jäger, *ibid.*, **90**, 2460 (1957).

[5] The *cis* and *trans* assignments are based on comparison of J_{AB} in each case with J_{AB} for the *cis* and *trans* isomers XIV and XV.

[6] C. S. Wood and F. B. Mallory, *J. Org. Chem.*, **29**, 3373 (1964).

[7] M. V. Sargent and C. J. Timmons, *J. Chem. Soc.*, 5544 (1964).

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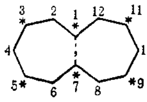
Received May 20, 1967

Pyracylene. A Pentalenoid System?

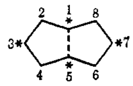
Sir:

Although Hückle's $4n + 2$ rule strictly applies only to monocyclic systems, polycyclic unsaturated $4n + 2$ systems also appear to possess the properties attributed to aromatic hydrocarbons. To account for the similarities in properties of the two types of unsaturated species Platt[1] proposed that the polycyclic system can be treated in terms of their $4n + 2$ peripheries in which the cross-links only cause a small perturbation. We wish to consider the extension of such a model to molecules possessing $4n$ perimeters. In particular, we were interested in that subclass of these latter types that maintain a nonbonding energy level.

HMO theory predicts that $4n$ monocyclic systems possess a degenerate pair of nonbinding levels occupied by two electrons. Application of the first-order perturbation treatment of Dewar and Pettit[2,3] indicates that cross-linkage between alternate atoms only (*i.e.*, from starred to starred or unstarred to unstarred in I and II) removes this degeneracy but maintains one of the nonbonding levels. Cross-linkage to yield polycyclic systems possessing rings of 3, 7, 11, 15, etc., members, such as between atoms 1 and 7 in I, produces a compound possessing a filled nonbonding level (a heptalenoid system), whereas cross-linkage to yield polycyclic systems possessing rings of 5, 9, 12, 17, etc., members, such as between atoms 1 and 5 in II, produces a compound possessing an empty nonbinding level (a pentalenoid system). In general, this cross-link may be a simple bond between the atoms or a carbon–carbon double bond inserted between them. More than one



I



II

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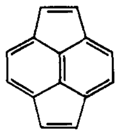
[1] J. R. Platt, *J. Chem. Phys.*, **22**, 1448 (1954).

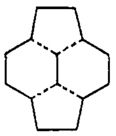
[2] M. J. S. Dewar and R. Pettit, *J. Chem. Soc.*, 1617 (1954).

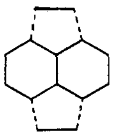
[3] Upon completion of this work a similar treatment of bicyclic $4n$ systems appeared. See G. V. Boyd, *Tetrahedron*, **22**, 3409 (1966).

cross-link, introduced as described above, may exist with no alteration in the above conclusions.

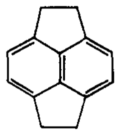
A particularly interesting pentalenoid system is pyracylene III which, in terms of the above discussion, can be treated as a cyclododecahexaene with a vinyl cross-link (IIIa). On the other extreme, a naphthalene core with two vinyl bridges (IIIb) is a reasonable model. To examine these possibilities, we began to explore the chemistry of pyracylenes.[4] We wish now to report the synthesis and spectral properties of the parent hydrocarbon.

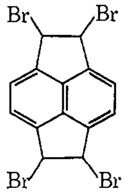

III

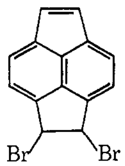

IIIa


IIIb

Controlled bromination of pyracene IV with 3.7 equiv of NBS for 15 min in refluxing CCl$_4$ produced a colorless tetrabromide, decomposing at 150°, whose spectral and analytical (*Anal.* Found: C, 34.06; H, 1.70; Br, 64.40) properties identify it as 1,2,5,6-tetrabromopyracene (V). The ultraviolet spectrum[5] showed maxima [λ (mμ) (log ϵ)] at 232 (4.68), 318 (4.08), and a shoulder at 332 (3.97). Its nmr spectrum[6a] showed only two singlets of equal intensity at 6.00 and 7.65 ppm fully confirming the assignment of the symmetrical tetrabromide. The mass spectrum[6b] showed no molecular ion peak. The highest and most intense peak in the spectrum appeared at m/e 176 and the second most intense peak appeared at $m/2e$ 88. These peaks correspond to the pyracylene molecular ion and its dication, respectively, and the spectrum corresponds to that of pyracylene. The fragmentation pattern is remarkably similar to that of acenaphthylene.


IV


V


VI

Debromination of V with iodide ion[4] in DMF, acetonitrile, or acetone proceeded smoothly to produce a solution of pyracylene III. This compound had an ultraviolet spectrum[5] very similar to that of dibromopyracylene[4]—maxima (in mμ) at 385, 378, 341, 332, and 220 with extensive tailing to 650 mμ. The nmr spectrum[6a] showed two singlets of equal intensity at 6.01 and 6.52 ppm. Hydrogenation of a deep red ethyl acetate solution of III utilizing platinum oxide produced a quantitative yield (based on V) of pyracene —fully confirming the structure. Attempts to isolate pyracylene in the solid state produced only amorphous yellow polymers.

The full ppm upfield shift of the proton in the nmr spectrum is inconsistent with any $4n + 2$ aromatic model (*e.g.*, IIIb). Recently, Pople and Untch[7] provided a theoretical basis for the presence of a paramagnetic ring current in 4n monocyclic systems. Nmr studies of the [16]-[8] and [24]annulenes[9] provided experimental verification. Although no satisfactory model for a [12]annulene such as is present in III exists,[10] it appears a similar explanation is required to explain the large shift. Thus, the periphery model best accounts for these properties.

An excellent correlation of the energy of the first unoccupied molecular orbital with half-wave potentials exists.[11] Such a correlation predicts a first half-wave potential of -0.924 ± 0.109 v for a system in which the electron enters a nonbonding level.[12] Triphenylmethyl radical, which is such a system, exhibits its first wave at -1.05 v *vs.* sce. Pyracylene shows two one-electron waves at -1.056 and -1.635 v *vs.* sce[13] in DMF, in excellent agreement with the theoretical prediction of the presence of a nonbonding level.

Following the debromination reaction by nmr revealed the presence of an intermediate which eventually is completely converted to pyracylene. The nmr in acetone[14] showed an AB pattern for four protons with H_A at 7.96 ppm and H_B at 7.66 ppm and $J_{AB} = 7.0$ cps, a singlet for two protons at 7.24 ppm, and a singlet for two protons at 6.12 ppm, in complete accord with structure VI. The presence of VI as a detectable intermediate suggests that proceeding to the fully unsaturated system does not produce a substantial increase in stability.

Acknowledgment. We express our gratitude to the National Institutes of Health, Grant No. GM-13587-01, and the Wisconsin Alumni Research Foundation for partial support of this work.

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[4] This paper forms part V in our series of studies in this area. For part IV see B. M. Trost and D. R. Brittelli, *Tetrahedron Letters*, 119 (1967); for part III see S. F. Nelsen, B. M. Trost, and D. H. Evans, *J. Am. Chem. Soc.*, **89**, 3034 (1967).

[5] Determined as a solution in ethanol.

[6] (a) Determined as a solution in CCl$_4$. (b) We are deeply indebted to Professors Lawrence A. Singer and Joseph Ciabattoni for this determination.

[7] J. A. Pople and K. G. Untch, *J. Am. Chem. Soc.*, **88**, 4811 (1966).

[8] G. Schroeder and J. F. M. Oth, *Tetrahedron Letters*, 4083 (1966).

[9] I. C. Calder and F. Sondheimer, *Chem. Commun.*, 904 (1966).

[10] Two models may be considered. *s*-Indacene exhibits absorptions at somewhat lower field than III (see K. Hafner, *Angew. Chem.*, **75**, 1041 (1963)). Cyclododecatrienetriyne shows an upfield shift of its protons in its nmr spectrum (see K. G. Untch and D. C. Wysocki, *J. Am. Chem. Soc.*, **88**, 2608 (1966), and F. Sondheimer, R. Wolovsky, P. J. Garratt, and I. C. Calder, *ibid.*, **88**, 2610 (1966)).

[11] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1962, pp 173–201.

[12] This predicted value is for aqueous dioxane; however, it has been shown that the first half-wave potential varies at most by only a few hundredths of a volt for changes from aqueous dioxane to anhydrous DMF. See ref 11 and P. H. Given, *J. Chem. Soc.*, 2684 (1958).

[13] We wish to thank Professor Dennis H. Evans for this determination.

[14] In these series of compounds, acetone causes a downfield shift of 0.1–0.2 ppm relative to carbon tetrachloride.

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Received February 24, 1967

A New Stereospecific Synthesis of Trisubstituted Olefins. Stereospecific Synthesis of Farnesol

Sir:

This note describes a new synthetic method which allows the stereospecific conversion of propargylic alcohols to either 2-alkylated or 3-alkylated allylic alcohols (eq 1) and its application in the isoprenoid field.