Table I. ν_{AB} Values for 1-Alkylaziridines (I)[a]

R	ν_{AB}, cps
Me	42
Et	39
i-Pr	36
t-Bu	3[b]

[a] 60-Mc/sec spectra recorded as 50% CCl_4 solutions. [b] Peak separation. A value of 5 cps was obtained from the deuterium-decoupled proton spectrum of 1-*t*-butylaziridine-2,2-d_2.

Table I reveals that the magnitude of the anisotropy shift decreases with the steric requirements of the N-substituent, *i.e.*, Me > Et > *i*-Pr ≫ *t*-Bu. The observed trend in ν_{AB} is surprising since one would have expected increased shielding from the anisotropy of the N-alkyl carbon–carbon bonds.[8] In light of our earlier studies,[7] however, we propose that intramolecular van der Waals (dispersion) interactions between the N-alkyl and ring protons account for the observed chemical shift trend.

Presumably, nonbonded interactions between the ring and N-substituent hydrogens cause a distortion of the electron cloud around the ring protons, *i.e.*, H_a in conformer Ib. These time-dependent distortions of the ring C–H bond symmetry lead to a reduction in shielding.[9] Such dispersion effects become especially important as the steric requirements of the N-alkyl group increase. Thus, the van der Waals contribution to ν_{AB} in 1-ethyl- and 1-isopropylaziridine relative to 1-methylaziridine is, as expected, rather small. On the other hand, the strong intramolecular dispersion effect due to the bulky *t*-butyl group in II (CCl_4) virtually *nullifies* the magnetic anisotropy contribution to ν_{AB}.

It is plausible that the magnitude of such intramolecular dispersion shifts in aziridines may be a sensitive function of the steric requirements of the N substituent. We are presently investigating this possibility.

[8] A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **83**, 231 (1961); **84**, 2784 (1962); F. A. Bovey and F. P. Hood, III, *ibid.*, **87**, 2060 (1965).

[9] For pertinent discussions see A. D. Buckingham, T. Schaefer, and W. G. Schneider, *J. Chem. Phys.*, **32**, 1227 (1960); T. Schaefer, W. F. Reynolds, and T. Yonemoto, *Can. J. Chem.*, **41**, 2969 (1963); V. M. S. Gil and W. A. Gibbons, *Mol. Phys.*, **8**, 199 (1964).

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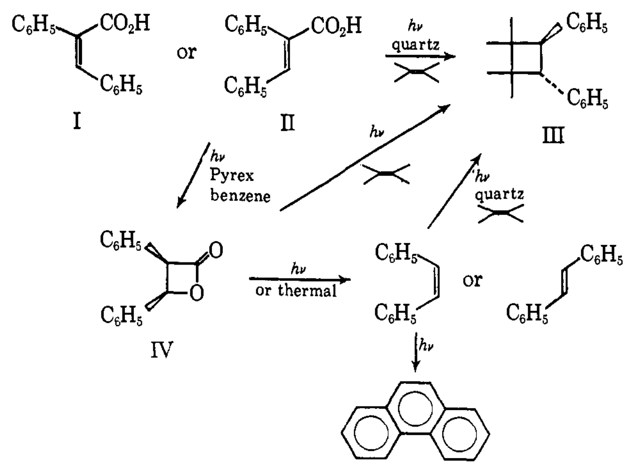
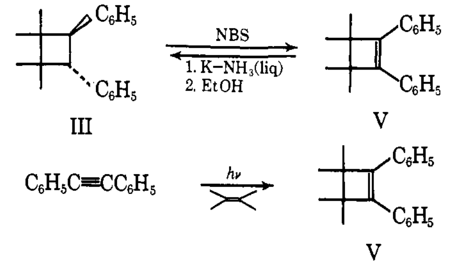
Received February 24, 1967

Photochemical Isomerization of α,β-Unsaturated Acids to β-Lactones and α,β-Unsaturated Amides to β-Lactams[1]

Sir:

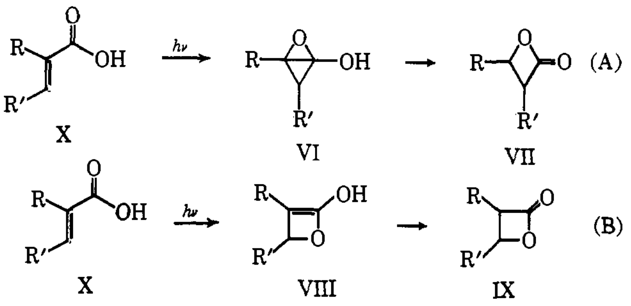
Attempts to add I or its isomer II to tetramethylethylene gave only *trans*-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane (III, mp 105–106°, 67%). The structure of the product was established by the molecular weight (mass spectrometry, mol wt 264), nmr (δ 7.07 (10 H, singlet), 3.55 (2 H, singlet), 1.12 (6 H, singlet), 0.77 (6 H, singlet)), and oxidation by N-bromosuccinimide to 1,2-diphenyl-3,3,4,4-tetramethylcyclobutene (V, 80%) which was identical with an authentic sample prepared by photocycloaddition of diphenylacetylene to tetramethylethylene (30%). Reduction of the cyclobutene with potassium in liquid ammonia gave the original cyclobutane III, which is thus assigned *trans* stereochemistry.





The formation of III in high yield naturally raises questions concerning mechanism. Irradiation of I or II in degassed benzene gave the *cis*-β-lactone IV (mp 120–121°, isolated in 79% yield). The product showed $\lambda_{\max}^{\text{KBr}}$ 5.45 μ and $\nu_A = \delta$ 5.30, $\nu_B = \delta$ 5.84 (J_{AB} = 7.0 cps), δ 6.90–7.20 (10 H). Pyrolysis of the β-lactone gave *cis*-stilbene (up to 99%) and CO_2 (92%). Irradiation of the β-lactone in the presence of tetramethylethylene gave III. Irradiation of the β-lactone in the absence of tetramethylethylene gave a complex mixture from which phenanthrene (a photoproduct of *cis*-stilbene)[2] could be isolated. Irradiation of either *cis*- or *trans*-stilbene in the presence of tetramethylethylene gave only *trans*-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane (III).

Two structurally different paths may be considered for the formation of the β-lactone IV from the unsaturated acid I or II. Path A involves valence isomerization to a substituted oxabicyclobutane VI which can isomerize to β-lactone VII. Path B involves valence isomerization to hydroxy oxetene VIII which could keton-



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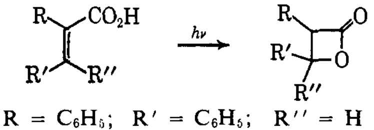
[1] Photochemical Transformations. XXI. All irradiations were carried out with degassed solutions.

[2] F. R. Stermitz in "Organic Photochemistry," Vol. 1, O. L. Chapman, Ed., Marcel Dekker, Inc., New York, N. Y., 1967, p 247.

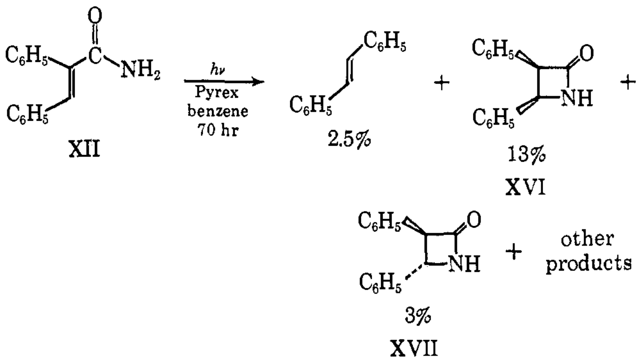
ize to β-lactone IX.[3] The isomerization of I to IV does not distinguish between paths A and B. Irradiation of X (R = C_6H_5; R′ = p-$CH_3C_6H_4$) gives IX (R = C_6H_5; R′ = p-$CH_3C_6H_4$). This result is consistent only with path B. The product shows λ_{max}^{KBr} 5.51 μ; $\nu_A = \delta$ 5.29, $\nu_B = \delta$ 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-$CH_3C_6H_4$) to phenylketene radical cation (m/e 118, 40.6% of base).

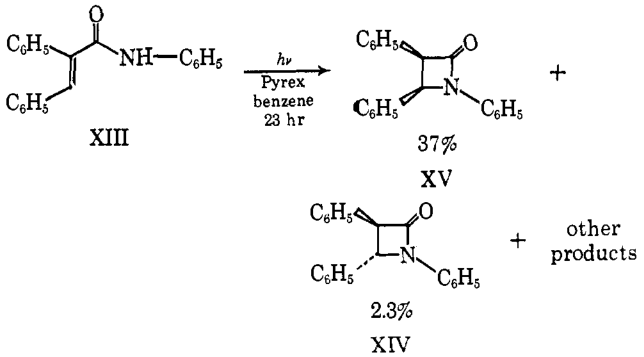
The isomerization of I and II to IV has some generality. A variety of α-substituted cinnamic and crotonic acids (XIa–e) give β-lactones. β-Lactones have not yet been isolated from cinnamic or crotonic acid. The photochemical synthesis of β-lactones has substantial advantages over other methods in ease 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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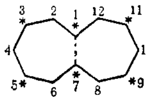
Received May 20, 1967

Pyracylene. A Pentalenoid System?

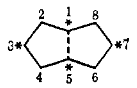
Sir:

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 nonbonding 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).