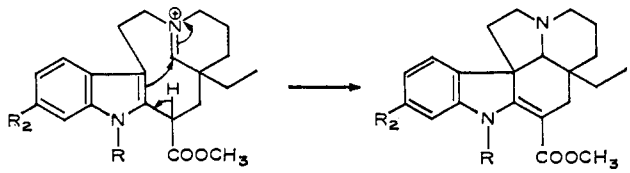
tra). Epivincadine was synthesized from the natural alkaloid by isomerization of the ester group.

The synthesis of *dl*-vincadine also completes the total synthesis of *dl*-vincaminoreine (VIII, R_3 = H) and *dl*-vincaminorine (IX, R_3 = H) in view of the known interconversions.[14]



X, R = H
XI, R = CH_3

An entry into the pentacyclic series exemplified by vincadifformine (X, R_2 = H)[15,16] and minovine (XI, R_2 = H)[11] was now possible by means of the transannular cyclization approach.[3] Reaction of vincadine and vincaminoreine with either mercuric acetate[3] or oxygen in the presence of a catalyst (5% platinum on charcoal)[17] provided vincadifformine and minovine identical in every respect (infrared, tlc) with authentic samples.[13]

An extension of the above sequence to encompass alkaloids bearing oxygen functions, particularly methoxyl groups, in the aromatic ring was now considered. For this purpose, 6-methoxytryptamine[18] was condensed with aldehyde I to afford in 70% yield the cyclic lactam as a mixture of diastereoisomers (II, R = CH_2-C_6H_5; R_1 = O; R_2 = H; R_3 = OCH_3): λ_{max}^{EtOH} 227, 264, 272 (sh), 297, 305 (sh), 321, and 336 mμ. Lithium aluminum hydride reduction of the latter, followed by catalytic debenzylation as described above, afforded the two isomeric alcohols. Separation of these compounds could be achieved by chromatographic techniques. The less polar alcohol II (R = R_2 = H; R_1 = H_2; R_3 = OCH_3) was obtained as a pale yellow oil which resisted crystallization; nmr signals: τ 2.74 (doublet, J_{ortho} = 8 cps, C_9-H), 3.26 (quartet, J_{ortho} = 8 cps, J_{meta} = 2.5 cps, C_{10}-H), 3.34 (doublet, J_{meta} = 2.5 cps, C_{12}-H), 6.00 (multiplet, C_3-H), 6.25 (singlet, OCH), 6.63 (-CH_2-OH), and 9.18 (triplet, CH_3). High-resolution mass spectrometry established the molecular formula $C_{20}H_{28}N_2O_2$ (found: 328.214; calculated: 328.215), while fragments were seen at *m/e* 214, 199, 186, etc. This compound is assigned the *cis* stereochemistry (C_3-H and ethyl group are *cis*). The *trans* alcohol[9] was obtained crystalline, mp 168–169°, and shown to be isomeric by mass spectrometry (found: 328.216).

Conversion of a mixture of these alcohols to the mesylates III (R = OCH_3) and reaction with potassium cyanide in the manner described above afforded two isomeric cyano compounds (IV and V, R_3 = OCH_3). One of these, IV, mp 186–187°, possessed an unresolved one-proton multiplet at τ 6.02 (-C*H*CN) and a methyl triplet at 9.07, while the other isomer, V, mp 191–192°, indicated a one-proton quartet at τ 4.02 (-C*H*CN) and a methyl triplet at 9.34 in the nmr spectra.

(14) J. Mokry and I. Kompis, *Lloydia*, **27**, 428 (1964).
(15) J. Mokry, I. Kompis, L. Dubravkova, and P. Sefcovic, *Experientia*, **19**, 311 (1963).
(16) M. Plat, J. Le Men, M. M. Janot, H. Budzikiewicz, J. M. Wilson, L. J. Durham, and C. Djerassi, *Bull. Soc. Chim. France*, 2237 (1963).
(17) D. Schumann and H. Schmid, *Helv. Chim. Acta*, **46**, 1996 (1963).
(18) R. B. Woodward, F. E. Boder, H. Bickel, A. J. Frey, and R. W. Kierstad, *Tetrahedron*, **2**, 1 (1958).

Alkaline hydrolysis of the cyano compounds followed by esterification of the resulting acids provided 16-methoxyvincadine (VI, R_3 = OCH_3) and 16-methoxyepivincadine (VII, R_3 = OCH_3). Methylation of these esters *via* the previously published procedure[14] provided the N-methyl derivatives VIII and IX (R_3 = OCH_3). These latter substances bear the skeletal features of a natural system, since vincaminoridine, an alkaloid isolated from *Vinca minor* L., has been assigned this structure.[14] Unfortunately, no stereochemical assignment is available in this publication, and a sample of the natural alkaloid could not be obtained for comparison.

Finally, the transannular cyclization reaction mentioned above provides an obvious synthesis of XI (R_2 = OCH_3) from the esters VIII and/or IX (R_3 = OCH_3). Although this pentacyclic structure has not as yet been isolated from a natural source, it is a valuable intermediate for the total synthesis of the monomeric alkaloid vindoline and thereby provides entry into the dimeric series as well. Results in this direction will be presented in future communications.

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Photochemical Rearrangement of 1,1,4-Triphenyl-2,3-benzoxazine. Formation of an Oxazirinodihydroisoindole

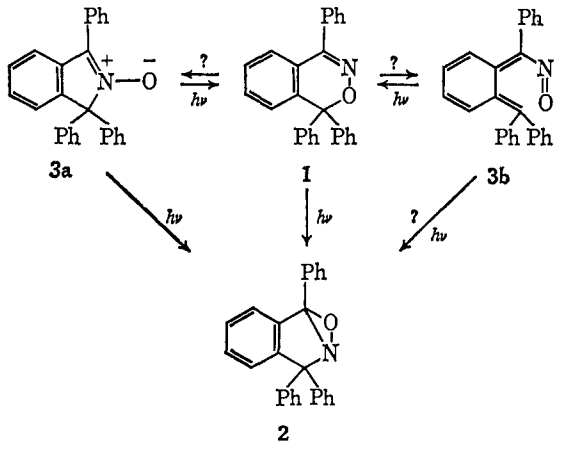
Sir:

Several conjugated cyclohexadienes and hexatrienes have been shown to undergo light-induced rearrangements to bicyclo[3.1.0]hexenes.[1] No structurally related heterocyclic diene has yet been shown to undergo an analogous rearrangement. This communication describes the first example of a facile photoisomerization of a 2,3-benzoxazine, **1**, to a fused oxazirane, **2**.

Irradiation of 1,1,4-triphenyl-2,3-benzoxazine[2] (**1**) [$\lambda_{max}^{CH_3CN}$ 288 (ε 4000), 230 mμ (20,000)] in benzene or acetonitrile solution with Pyrex-filtered light produced photoisomer **2** [mp 155–156°; λ^{CH_3CN} 290 (ε 115), 230 mμ (7800)] in nearly quantitative yield. The isomeric nature of **1** and **2** was established by mass spectral and combustion data.[3] Assignment of structure **2** to the photoisomer was based on spectral and chemical evidence, outlined below.

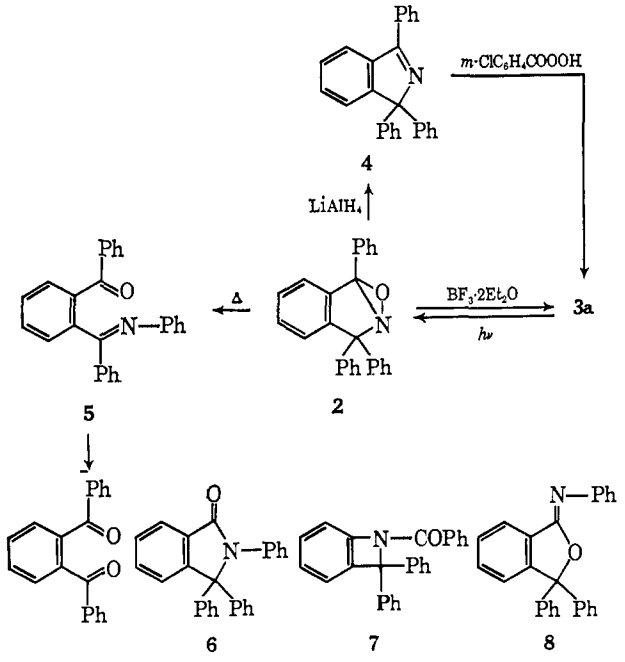
In agreement with structure **2**, the photoproduct showed only benzenoid absorption in the ultraviolet.

(1) For leading references see (a) W. G. Dauben and W. T. Wipke, *Pure Appl. Chem.*, **9**, 539 (1964); (b) J. Meinwald and P. H. Mazzocchi, *J. Am. Chem. Soc.*, **88**, 2850 (1966); (c) W. G. Dauben and J. H. Smith, *J. Org. Chem.*, **32**, 3244 (1967); (d) M. Pomerantz, *J. Am. Chem.Soc.*, **89**, 694 (1967); J. Meinwald and P. H. Mazzocchi, *ibid.*, **89**, 696 (1967); (e) K. R. Huffman and E. F. Ullman, *ibid.*, **89**, 5629 (1967), and references therein.
(2) A. Mustafa, W. Askar, M. Kamel, A. F. A. Shalaby, and A. E. A. E. Hassen, *ibid.*, **77**, 1612 (1955).
(3) Satisfactory elemental analyses were obtained for all new compounds described here.



The infrared spectrum lacked the 11.0-μ band (N–O stretch due to the PhC(Ar)=NO– moiety) characteristic of the starting material and possessed a strong band at 7.49 μ, well within the range expected for an oxazirane structure.[4] The mass spectrum (71 eV) of **2** showed its parent peak at *m/e* 361, together with other major fragments at 345, 331, 285 and 77.

Reaction of **2** in benzene solution with boron trifluoride diethyl ether followed by decomposition with cold aqueous sodium bicarbonate yielded the nitrone[5,6] **3a** (87%): mp 198°; $\lambda_{max}^{CH_3CN}$ 335 (ϵ 8000), 317 (7100), 252 mμ (29,500); ir (Nujol) 6.30, 6.59, 6.95, 8.70 μ; *m/e* 361 (parent), together with other fragments at 345 and 77. Ultraviolet irradiation of **3a** transformed it quantitatively to the oxazirane **2**. The latter transformation is quite characteristic of the nitrones.[7]



As expected, reduction of **2** with $LiAlH_4$ in refluxing ether produced[5,6,8] **4** (90%): mp 145–146°; $\lambda_{max}^{CH_3CN}$ 270 (ϵ 5100), 243 mμ (11,600); ir (Nujol) 6.25, 6.42, 6.70, 6.90 μ; *m/e* (parent) 345. Further proof for structure **4** was provided by its quantitative conversion to the nitrone **3a** when treated with *m*-chloroperbenzoic acid in dry dichloromethane.[6,9]

Additional insight into the oxazirane structure **2** was provided by its nearly quantitative (91%) thermal isomerization[11] (170–180°, 0.5 hr) to the monoanil **5** of *o*-dibenzoylbenzene: mp 95–97°; $\lambda_{max}^{CH_3CN}$ 330 (ϵ 2780), 250 mμ (28,300); ir (Nujol) 6.02 (C=O), 6.19 μ (C=N);[12] *m/e* 361 (parent), 180, 103. Compelling evidence in favor of structure **5** and against possible structures **6**, **7**, or **8** was furnished by its hydrolysis (5% aqueous methanolic H_2SO_4) to *o*-dibenzoylbenzene (86%), mp 146–147°, identified by comparison with an authentic sample (melting point, mixture melting point, ir, uv).

With regard to the mechanism of the photoisomerization **1** → **2**, direct transformation of the benzoxazine **1** to the oxazirane **2** appears likely, though intervention of intermediates such as **3a** or **3b** cannot be excluded. Further studies directed toward the mechanistic details of this reaction are in progress.

Acknowledgment. I wish to thank Dr. A. Zweig for his critical comments.

(4) Several alkyl-substituted oxaziranes have been reported to show a strong band in the 7-μ region which has been attributed to the oxazirane ring [H. Krimm, *Ber.*, **91**, 1057 (1958)]. Also 2,2,5-trimethyl-6-oxa-1-azabicyclo[3.1.0]hexene shows an infrared absorption band at 7.44 μ not present in the parent 2,5,5-trimethyl-1-pyrroline.[7d]

(5) For a summary of oxazirane reactions see E. Schmitz, *Advan. Heterocyclic Chem.*, **2**, 83 (1963).

(6) W. D. Emmons, *J. Am. Chem. Soc.*, **79**, 5739 (1957).

(7) (a) M. J. Kamlet and L. A. Kaplan, *J. Org. Chem.*, **22**, 576 (1957); (b) J. S. Splitter and M. Calvin, *ibid.*, **23**, 651 (1958); (c) R. Bonnett, V. M. Clark, and A. R. Todd, *J. Chem. Soc.*, 2102 (1959); (d) L. S. Kaminsky and M. Lamchen, *ibid.*, 2295 (1967).

(8) Treatment of **2** with potassium iodide in aqueous–ethanolic acetic acid solution produced **4** and iodine.

(9) Ordinarily most imines yield oxaziranes with peracids,[6,10] but formation of nitrone in the present case may be due to the lowered basicity of the C=N bond due to extensive substitution. The oxazirane **2** was found not to rearrange under the experimental conditions in the presence of the peracid.

(10) R. G. Pews, *J. Org. Chem.*, **32**, 1628 (1967).

(11) The failure of **2** to yield the amides **6** or **7** (or the nitrone **3a**) may be due to steric crowding (which minimizes the orbital overlap between the migrating centers) of the transition states leading to their formation.

(12) A band of comparable intensity was also observed at 6.18 μ in the infrared spectra of *o*-methylbenzophenone anil and *o*-(α-isopropylidenebenzyl)benzophenone anil and was assigned to the C=N bond in these molecules (K. R. Huffman, unpublished work).

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Photolytic Isomerization of Aromatic Species. Poly-*t*-butylfurans

Sir:

Recent investigators[1–4] have observed that various five-membered aromatic heterocycles undergo specific light-induced rearrangements involving over-all transposition of annular atoms, similar to the irradiation-induced interconversions of poly(alkylbenzenes) involving valence bond isomers.[5] With a singular exception,[1] no intermediates in such processes have been isolated, identified, and studied, and the general mechanism of such photoisomerizations has remained correspondingly uncertain. By employing means which

(1) E. F. Ullman and B. Singh, *J. Am. Chem. Soc.*, **88**, 1844 (1966); **89**, 6911 (1967).

(2) H. Wynberg, R. M. Kellogg, H. van Driel, and G. E. Beekhuis, *ibid.*, **89**, 3501 (1967), and earlier papers.

(3) H. Tiefenthaler, W. Dörscheln, H. Göth, and H. Schmid, *Helv. Chim. Acta*, **50**, 2244 (1967).

(4) P. Beak, J. L. Miesel, and W. R. Messer, *Tetrahedron Letters*, 5315 (1967).

(5) For an account of the early history of this phenomenon, see E. E. van Tamelen, *Angew. Chem.*, 77, 759 (1965).