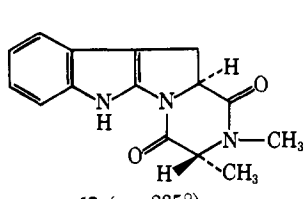
was reduced with deuterium. Acetylation of **9** with Ac_2O in pyridine gave **10**.

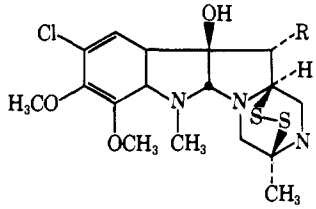
Further action of *t*-BuOCl on **4** at −10° gave the unstable 3a-chloroindolenine (**7**) in 57% yield. Analogously, 1 equiv of lead tetraacetate in CH_2Cl_2 gave the 3a-acetoxyindolenine (**8**) (23% yield) which was rapidly reduced by $NaBH_4$ in CH_3OH at 0° to the 3a-acetoxyindoline **11**, characterized as the diacetyl derivative **12**.

The diketopiperazine from L-tryptophyl-N-methyl-L-alanine reacted at 0° with 1.1 mol of *t*-BuOCl and Et_3N in a mixture of methylene chloride–dimethoxyethane (2:1, v/v) to yield 51% of the tetracyclic pyrroloindole **13**, a suitable model whence to explore approaches to sporidesmins A (**14**) and B (**15**).[4]

When the 3a-chloroindolenine **7** was refluxed in absolute ethanol with excess sodium acetate, the fully aromatic ethyl pyrrolo[2,3-*b*]indole-2-carboxylate (mp 186–188°, $\lambda\lambda_{max}^{EtOH}$ 330, 272 mμ) was obtained. This new tricycle, unlike **4**–**6**, is stable to acid. This great stability is also supported by preliminary delocalization energy calculations for the parent tricycle.[8]



13 (mp 235°)



14, R = OH
15, R = H

(8) We are obliged to Dr. K. Kirk for th s information.

(9) Associate in the Visiting Program of the U. S. Public Health Service, 1966–1968.

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Photocyclizations of Pharmacodynamic Amines. II. X-Ray Analysis of a Noncentrosymmetric Tetracyclic Indole

Sir:

The photolysis of N-chloroacetyl derivatives of aromatic amino acids and pharmacodynamic amines so far has led to tricyclic indoles, benzazepines, and azaazulenes.[1]

We have now found two novel photocyclizations of the N-chloroacetyl derivative of 3,4-dimethoxyphenethylamine, the catatonic compound implied as a metabolite in schizophrenia (I).[2] On irradiation *in ethanol–water solution* with a 100-W mercury lamp for 1.5 hr at room temperature, the cyclization reaction, in analogy with that of N-chloroacetyldopamine,[1] yielded the two isomeric benzazepines III and IV.

In addition a deep-seated photorearrangement gave a product, mp 123.5°, in 10–12% yield, for which structure V, *i.e.*, one arbitrarily chosen antipode, 1,2,-5a,7bβ-tetrahydro-5aβ,5bα-dimethoxy-5bH-cyclobuta-[1,4]cyclobuta[1,2,3-*gh*]pyrrolizin-4(5H)-one, of the racemic photoproduct, was established.

An X-ray diffraction analysis of a single optically active crystal, picked out of the racemic conglomerate, has established the structural formula and the configuration of the photoproduct. Eleven hundred independent reflections were recorded with Cu radiation by the multiple-film, equiinclination Weissenberg technique. The space group is $P2_12_12_1$ with four molecules per unit cell and the cell parameters are a = 11.75 Å, b = 6.27 Å, and c = 14.70 Å. Phases for the strong and moderately strong reflections were determined directly from the experimental intensities by the symbolic addition procedure[3] for noncentrosymmetric crystals. In the initial density map computed with 306 reflections whose phases had been determined, the positions of the 13 strongest peaks suggested an unusual arrangement of atoms. The coordinates of the 13 peaks were used as a partial structure in a recycling procedure employing the tangent formula, and the remaining three carbon atoms were located. Hydrogen atoms were found in a difference map. A least-squares refinement of the coordinates and thermal parameters has reached an agreement factor of 10.0%. In this way structure V was deduced with the bond lengths and angles illustrated in Figure 1.

On heating with alumina in toluene V aromatizes with loss of the elements of methanol to the lactam 2-oxo-8-methoxy-1,2,4,5-tetrahydropyrrolo[3,2,1-*hi*]indole (XI) which has almost the same chromophore [$\lambda\lambda_{max}$ mμ (ε): 301 (4630), 254 (6030); 219 (20,500)] as the indole alkaloid schizogalin.[4] Under the conditions of Fischer esterification the lactam V is opened to the ester hydrochloride X, from which base regenerates V.

On the other hand, irradiation of the amine I *in tetrahydrofuran solution* under the conditions described above gave the novel ten-membered lactam VI, 12-methoxy-2-oxa-6-azabicyclo[7.3.1]trideca-1(13),9,11-trien-5-one, as the major product, in addition to II, III, IV, V, and recovered I (Chart I). On heating in 48% hydrobromic acid at 140° for 2 hr, VI was converted to the tricyclic 9-hydroxy-2,3,5,6-tetrahydropyrano[2,3,4-*ij*]isoquinoline hydrobromide (VII).

The O-methyl ether VIII was also obtained from VI by cyclization with 6.0 *N* HCl at room temperature for

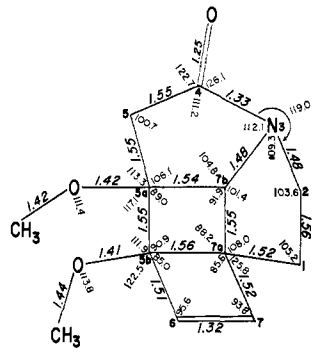


Figure 1. Bond distances and angles of compound V. Additional angles about atoms 5a, 5b, and 7a are as follows: 6–5b–5a, 114.6°; O–5b–7a, 126.0°; 5b–5a–5, 116.1°; O–5a–7b, 111.9°; 1–7a–5b, 127.0°; 7–7a–7b, 115.9°.

(1) *Cf.* O. Yonemitsu, T. Tokuyama, M. Chaykovsky, and B. Witkop, *J. Am. Chem. Soc.*, **90**, 776 (1968).

(2) *Cf.* C. R. Creveling and J. W. Daly, *Nature*, **216**, 190 (1967).

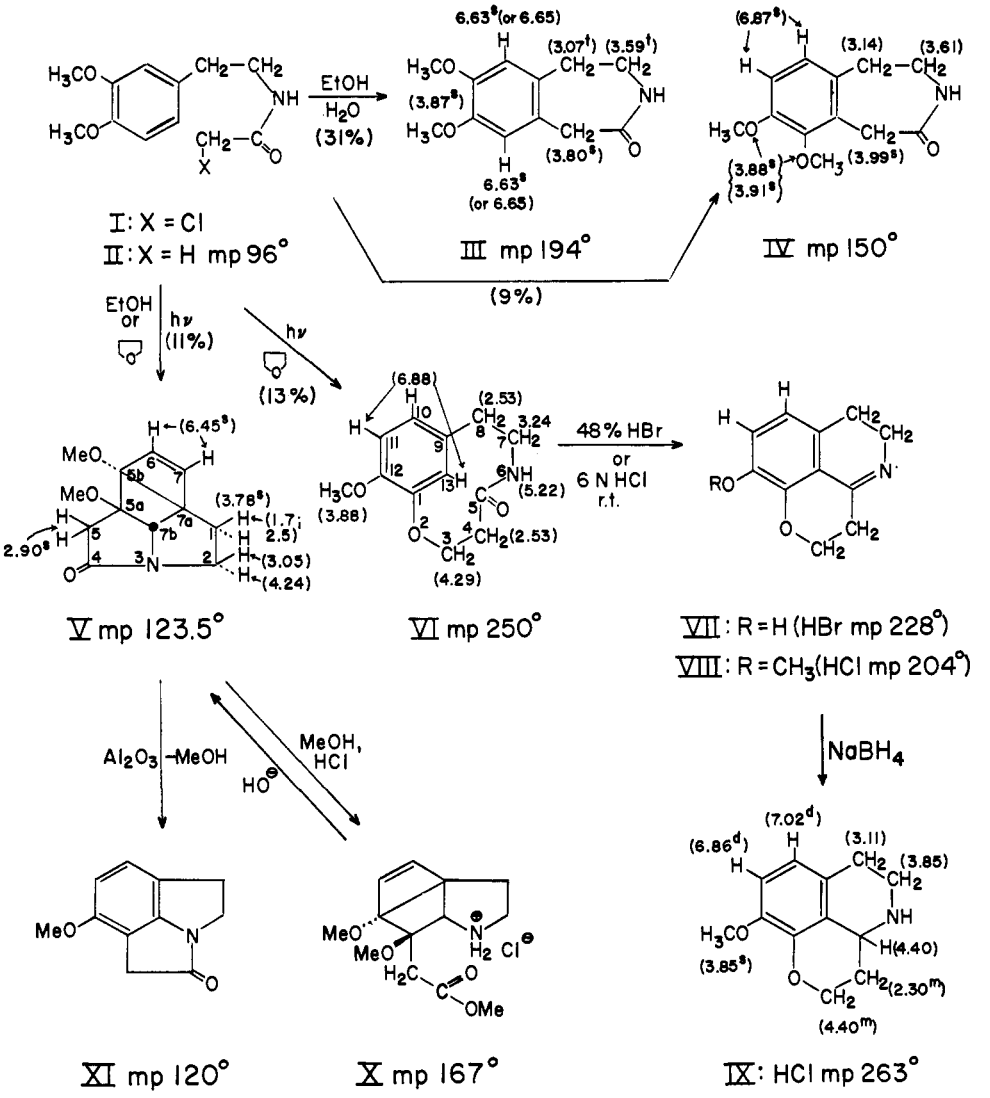
(3) I. L. Karle and J. Karle, *Acta Cryst.*, 17, 835 (1964); J. Karle and I. L. Karle, *ibid.*, 21, 849 (1966); **B24**, 182 (1968).

(4) U. Renner and P. Kernweisz, *Experientia*, **19**, 244 (1963).

a few minutes, an example of an unusually facile *transannular Bischler–Napieralski reaction.*

mation of VI. Such a dualism of photolysis has recently been observed for α-sulfonyloxy ketones.[7]

Chart I. Photocyclizations of N-Chloroacetyl-3,4-dimethoxyphenethylamine. The figures in parentheses refer to nmr values (δ, $CDCl_3$; IX in D_2O).



There is precedent for the participation of an aromatic methoxy substituent in the photocyclization of quercetin pentamethyl ether.[5] The $-OCH_2\cdot$ radical may be formed by abstraction of H· through Cl· generated in the photoinduced homolysis of the C–Cl bond which is known to depend on the nature of the solvent.[6] The results presented here point to two simultaneous primary reactions. The n,π* activation of the carbonyl group of I may lead to elimination of the α substituent, Cl^-, as an anion, and a positive fragment which is capable of electrophilic aromatic substitution to give photoproducts III, IV, and possibly V. In nonpolar aprotic solvents a radical mechanism would favor for-

(5) A. C. Waiss, Jr., R. E. Lundin, A. Lee, and J. Corse, *J. Am. Chem. Soc.*, **89**, 6213 (1967).

(6) G. A. Russell, *ibid.*, **80**, 4987, 4997 (1958); *cf.* J. A. Barltrop and A. Thomson, *J. Chem. Soc., C*, 155 (1968).

(7) S. Iwasaki and K. Schaffner, *Helv. Chim. Acta*, **51**, 557 (1968).

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The Role of Arene Oxide–Oxepin Systems in the Metabolism of Aromatic Substrates. II. Synthesis of 3,4-Toluene-4-^{2}H Oxide and Subsequent "NIH Shift" to 4-Hydroxytoluene-3-^{2}H[1]

Sir:

Arene oxides have been postulated as intermediates in the oxidative metabolism of aromatic substrates.[2]