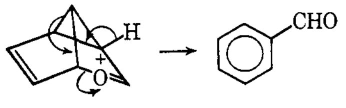
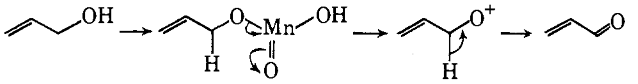
tion of a Lewis acid complex of the alcohol. In view of the proposed structure of the 7-norbornadienyl carbonium ion[3] and the tendency of 7-norbornadienyl derivatives to isomerize to the tricyclic structure (as in **2d**),[4] it is proposed that **2a** isomerizes to **2d** *via* the 7-norbornadienyl carbonium ion (**2b**, **2c**). Transformation of **2d** to **2f** is most readily understood in terms of heterolytic cleavage of the oxygen–manganese bond to donate electrons to manganese and thus effect its reduction. This leaves oxygen, at least formally, with a positive charge, and the resulting 1,2 shift gives **2f** in a manner analogous to the Baeyer–Villiger rearrangement.[5] The ion **2f** is particularly favorable, being both an oxonium ion and a cyclopropylcarbinylcarbonium ion. Addition of water to **2f** should lead exclusively to *endo*-hydroxy in **3**.[4] The ion, **2f**, can also give rise to benzaldehyde through a rearrangement involving loss of a proton.



2f

It should be noted that the type of rearrangement leading to **3** is not without precedent. Greene has reported the conversion of a cyclopropyl alcohol ring system[6] to a β-lactone. This type of rearrangement, again, suggests an ionic mechanism similar to the one we have proposed herewith, in the case of the cyclopropyl alcohol, initial rearrangement to a lactol followed by straightforward oxidation to the observed lactone product.

If, indeed, this mechanism is operative in our system and in Greene's, the implication is clear that manganese dioxide oxidations of ordinary allylic and benzylic alcohols may proceed in a similar fashion. However, in those cases where removal of an α proton is not difficult, as it would be in **2a** or **2d**, elimination takes place to form the conjugated carbonyl compound. We would



also suggest that product stability plays an important role in the reaction and accounts, at least in part, for the lack of reactivity of saturated alcohols. It is unlikely, of course, that a discrete electron-deficient oxygen is formed; it is likely, however, that cleavage of the oxygen–manganese bond leads in the transition state.

The interpretation offered here is perfectly consistent with the data of Pratt and Van de Castle,[7] who suggested a free-radical mechanism to explain the relative insensitivity of benzylic alcohols to changes in substituent when undergoing manganese dioxide oxidation. According to our mechanistic scheme, this insensitivity can be interpreted as arising from the fact that the positive charge in the transition state is on oxygen and not at the benzylic carbon. Other systems which may show the type of rearrangement encountered in this work are currently under investigation to test the general applicability of the mechanistic hypothesis outlined here.

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(3) P. R. Story, L. C. Snyder, D. C. Douglas, E. W. Anderson, and R. L. Kornegay, *J. Am. Chem. Soc.*, **85**, 3630 (1963).

(4) P. R. Story, *ibid.*, **83**, 3347 (1961); H. C. Brown and H. M. Bell, *ibid.*, **85**, 2324 (1963); H. Tanida, T. Tsuji, and T. Irie, *ibid.*, **88**, 864 (1966).

(5) P. A. S. Smith in "Molecular Rearrangements," P. de Mayo, Ed., John Wiley and Sons, New York, N. Y., 1964, Chapter 8.

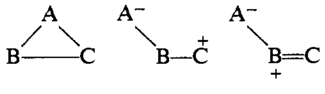
(6) Obtained from the intramolecular photodimerization of dianthracylcarbinol: F. Greene, *Bull. Soc. Chim. France*, 1356 (1960).

(7) E. F. Pratt and J. F. Van de Castle, *J. Org. Chem.*, **26**, 2973 (1961).

Di-*t*-butyloxadiaziridine, the Cyclic Form of an Azoxy Group. Ring–Chain Isomerism in Three-Membered Rings

Sir:

Observations that tertiary alkyl groups stabilize small rings[1] have directed our attention to the possibility of preparation of new ring systems and to the problem of ring–chain (I–II,III) isomerism in small rings.



I II III

Known examples embrace three-atom systems isolable only in the closed form (I,[2] A = B = C = carbon), only in the open form (III,[2] A = C = oxygen, B = nitrogen), or, much more rarely, in both forms (A = oxygen, B = nitrogen, C = carbon).[3] We wish to report the preparation of di-*t*-butyloxadiaziridine (V = I, A = oxygen, B = C = nitrogen), the first well-characterized[4] member of a new ring system and possibly unique in its lack of carbon as one of the three ring atoms.

Irradiation of azoxy-*t*-butane[5,6] (IV) in pentane at 10° with a Hanovia Type L lamp resulted in the disappearance of the ultraviolet absorption. Removal of solvent, trap-to-trap distillation of the residue, and chromatography on Woelm alumina at 10° with pentane eluent afforded an oil of composition $C_8H_{18}N_2O$ (*Anal.* Calcd: C, 60.72; H, 11.47; N, 17.70; mol wt, 158. Found: C, 60.62; H, 11.33; N, 17.70; mol wt, 166 [cryoscopic in benzene]); infrared (CCl_4)[7] 2980, 2930, 2860, 1475, 1450, 1385, 1365, 1235, and 1210 cm^{-1}; nmr (CCl_4) singlet at 1.0 ppm; major species in the mass

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(1) F. D. Greene and J. C. Stowell, *J. Am. Chem. Soc.*, **86**, 3569 (1964); J. C. Sheehan and J. H. Beeson, *ibid.*, **89**, 362, 366 (1967); J. F. Pazos and F. D. Greene, *ibid.*, **89**, 1030 (1967).

(2) For I, II, and III, the appropriate number of substituents are assumed to be attached to A, B, and C, corresponding to the usual valence states of these atoms.

(3) W. D. Emmons, *J. Am. Chem. Soc.*, **79**, 5739 (1957). See also E. Schmitz, *Advan. Heterocyclic Chem.*, **2**, 83 (1963).

(4) The nitrogen–nitrogen–oxygen three-membered ring frequently has been postulated in the older literature. It has also been proposed as an intermediate in the Wallach rearrangement by M. M. Shemyakin, V. I. Maimind, and Ts. E. Agadzhanyan, *Chem. Ind.* (London), 1223 (1961). However, see also C. S. Hahn, K. W. Lee, and H. H. Jaffé, *J. Am. Chem. Soc.*, **89**, 4975 (1967), and references cited therein.

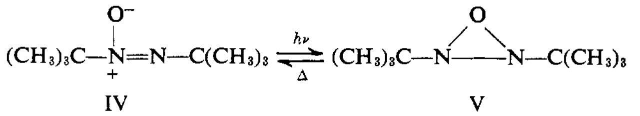
(5) J. P. Freeman, *J. Org. Chem.*, **28**, 2508 (1963).

(6) Ultraviolet maximum at 221 mμ.

(7) Azoxy-*t*-butane has strong bands at 1285 and 1490 cm^{-1}.

spectrum at 70 ev: m/e (relative intensity) 103 (1.8), 102 (3.8), 87 (6.8), 57 (100), and 41 (45).

The compound is thermally labile, reverting quantitatively to the azoxy derivative IV (at 20° $t_{1/2}$ ~8 hr in CCl_4, ~3 hr in CH_3NO_2). It is unreactive toward water and moderately stable in acidic media.[8] In carbon tetrachloride the only observed effect of dichloroacetic acid (1.7 M) is a fivefold increase in rate of isomerization of the photoproduct to the azoxy compound. The available physical and chemical data afford a strong basis for assignment of the three-membered ring structure V to the photoproduct.



$$(CH_3)_3C-\overset{O^-}{\underset{+}{N}}=N-C(CH_3)_3 \underset{\Delta}{\overset{h\nu}{\rightleftharpoons}} (CH_3)_3C-N\overset{O}{\frown}N-C(CH_3)_3$$

IV V

Compound V is far less stable than corresponding oxaziridines (I, A = oxygen, B = nitrogen, C = carbon).[3] In the latter series aryl-substituted derivatives are less stable than those with alkyl groups.[3,9] On this analogy, aryl-substituted oxadiaziridines may be expected to be highly unstable species. The dependence of stability of oxadiaziridines on the nature of *alkyl* substituents, however, is a more open question.

[8] A possible open-chain isomer, $RN{=}O^+{-}\bar{N}R$ (III, A = C = nitrogen, B = oxygen), is rendered unlikely by these observations.

[9] See J. S. Splitter and M. Calvin, *J. Org. Chem.*, **30**, 3427 (1965), and references cited therein.

[10] National Institutes of Health Predoctoral Fellow, 1965–1967.

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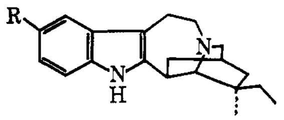
The Total Synthesis of *dl*-Ibogamine

Sir:

The seven-membered ring and isoquinuclidine moiety[1] of the iboga alkaloids (I) give them a unique position among the indole alkaloids.[2] Attention has been focused on them because one of the building blocks of *vincaleukoblastine*,[3] an antileukemic agent, and of *voacamine*,[4] a cardiotonic dimeric indole, also possesses the iboga skeleton.

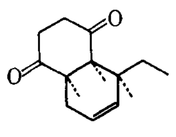
In view of the interest in structure and physiological activities[2c] of the iboga alkaloids, their synthesis was initiated in our laboratory.[5] While this work was in progress, Büchi and his co-workers[6] reported the first total synthesis of *dl*-ibogamine (Ia) and *dl*-ibogaine (Ib),[7] while others achieved partial[8a] or part structure[8b–e] syntheses.



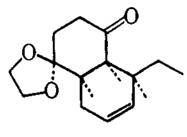
Ia, R = H
b, R = OCH_3

The present work represents a different, completely stereocontrolled approach that is more versatile by virtue of forming the seven-membered ring first and completing the isoquinuclidine and indole ring closures at the end of the synthesis. This scheme is devoid of undesired rearrangement[6] and the several steps produce good yields.

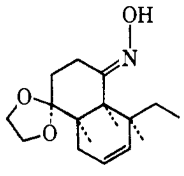
The *cis*-enedione II[5a] afforded an excellent starting point. The stereochemically unstable II was monoketalized at C_1 to III with the retention of its *cis* configuration (80%); bp 104° (0.01 mm);[9] ν_{max}^{neat} 5.83 (>C=O), 9.0 μ (ketal); nmr δ 4.10 ppm (ketal, 4 H, singlet).[10] Then the *cis,anti*-oxime ketal IV was prepared (90%); mp 126.5–127.5°; ν_{max}^{KBr} 3.1 (–OH), 5.97 (>C=N–), 6.05 μ (>C=C<); nmr δ 4.06 (ketal, 4 H, singlet), 5.65 (2 vinylic H, singlet), 8.8 ppm (hydroxyl, 1 H, broad). A Beckmann rearrangement of IV by tosyl chloride in hot pyridine readily produced the seven-membered *cis*-lactam ketal V (80%); mp 146–147.5°; ν_{max}^{KBr} 3.15 (–NH–), 6.03 μ (lactam).[11]



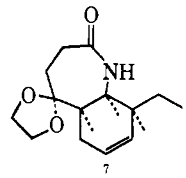
II



III

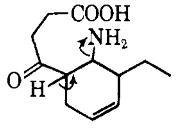


IV

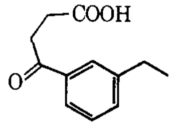


V

The structure of V was proved by consecutive acidic and alkaline treatment, which cleaved the ketal and lactam groups, respectively. The intermediate β-amino ketone XVII lost ammonia and the cyclohexadiene structure aromatized to 3-(m-ethylbenzoyl)propionic acid (XVIII; 95%); ν_{max}^{KBr} 3.73 (–OH), 5.83 (–COOH), 5.92 μ (ketone); nmr δ 7.64 ppm (4 aromatic H, multiplet). Finally, nitric acid oxidation of XVIII led to isophthalic acid, mp 334–337°.



XVII



XVIII

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[1] M. F. Bartlett, D. F. Dickel, and W. I. Taylor, *J. Am. Chem. Soc.*, **80**, 126 (1958).

[2] (a) L. Marion, *Alkaloids*, **2**, 450 (1952); (b) J. E. Saxton, *ibid.*, **7**, 143 (1960); (c) W. I. Taylor, *ibid.*, **8**, 203 (1965).

[3] N. Neuss, M. Gorman, H. E. Boaz, and N. J. Cone, *J. Am. Chem. Soc.*, **84**, 1509 (1962).

[4] J. LaBarre and L. Gillo, *Compt. Rend. Soc. Biol.*, **149**, 1075 (1955); A. Quevauviller and O. Blaupin, *Ann. Pharm. Franc.*, **15**, 617 (1957).

[5] (a) S. I. Sallay, *Tetrahedron Letters*, 2443 (1964); (b) S. I. Sallay, U. S. Patent 3,294,817 (1966).

[6] G. Büchi, D. L. Coffen, K. Kocsis, P. E. Sonnet, and F. E. Ziegler, *J. Am. Chem. Soc.*, **87**, 2073 (1965); **88**, 3099 (1966).

[7] Shown in their absolute configuration; *cf.* footnote 11 of ref 6.

[8] (a) J. P. Kutney, R. T. Brown, and E. Piers, *J. Am. Chem. Soc.*, **86**, 2287 (1964); (b) M. P. Cava, C. K. Wilkins, Jr., D. R. Dalton, and K. Bessho, *J. Org. Chem.*, **30**, 3772 (1965); (c) J. W. Huffman, C. B. S. Rao, and T. Kamiya, *J. Am. Chem. Soc.*, **87**, 2288 (1965); *J. Org. Chem.*, **32**, 697 (1967); (d) Y. Ban, T. Oishi, M. Ochiai, T. Wakamatsu, and Y. Fujimoto, *Tetrahedron Letters*, 6385 (1966); (e) W. Nagata, S. Hirai, K. Kawata, and T. Okumura, *J. Am. Chem. Soc.*, **89**, 5046 (1967).

[9] Satisfactory elemental analyses were obtained for all compounds for which melting point or boiling point values are cited. These measurements are uncorrected.

[10] All samples were measured in $CDCl_3$ at 60 Mc on a Varian Model A-60 spectrometer and expressed as parts per million shift (δ) downfield from tetramethylsilane.

[11] The model study[5a] has shown that the related *trans*-oxime ketal does not undergo Beckmann rearrangement under the same conditions.