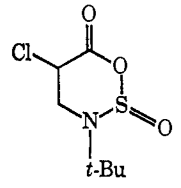
ilar behavior of both SOCl$_2$ and oxalyl chloride suggests that both reagents produce a common intermediate and argues against formation of intermediates such as **4** and **5**.[5] The previously established stability of various model aziridines toward acid halides and protons in the presence of Et$_3$N also excludes ring opening of some aziridinium species to an acyclic prescursor of **3**.[7] The possible intervention of symmetrical carbonium ion **6** can be ruled out by the stereospecific[8] conversion of **7a** and **7b** to **8a** and **8b**, respectively.[9]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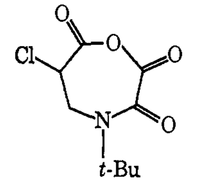
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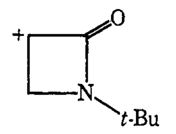
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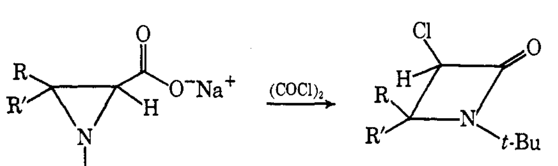
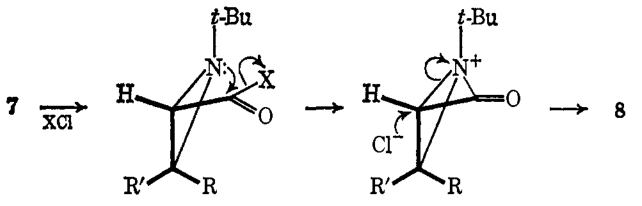


7a, R = CH$_3$; R′ = H
b, R = H; R′ = CH$_3$

8a, R = CH$_3$; R′ = H (79%)[10]
b, R = H; R′ = CH$_3$ (63%)

We believe that these results can only be explained in terms of ionization of mixed anhydride **9** to give the novel bicyclic ion **10**.[11] Capture of this remarkably strained intermediate by Cl$^-$ should occur in the manner shown to give **8** with the correct stereochemistry.



9 **10**

X = SOCl or COCOCl

The mild conditions, the good yields, and the stereospecificity make this ring expansion a potentially useful route to β-lactams. Further work is now in progress on the extension of this rearrangement to the synthesis of more complex molecules. Additional chemistry of **10** is also being studied.

Acknowledgment. Support of this research by National Science Foundation Grants GP-5531 and GP-8044 is gratefully acknowledged.

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Received May 29, 1969

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(5) The conversion of either intermediate to product under the reaction conditions seems unlikely.[6]

(6) *Cf.* J. A. Deyrup and C. L. Moyer, *J. Org. Chem.*, 34, 175 (1969).

(7) C. L. Moyer, Ph.D. Thesis, Harvard University, Cambridge, Mass., 1968; J. A. Deyrup and C. L. Moyer, *Tetrahedron Letters*, 6179 (1968).

(8) Stereochemistry was based on the relative (*cis* > *trans*) magnitude of J_{vic}.

(9) The formation of different products from 7a and 7b adds nonspectral evidence for the position of the Cl group.

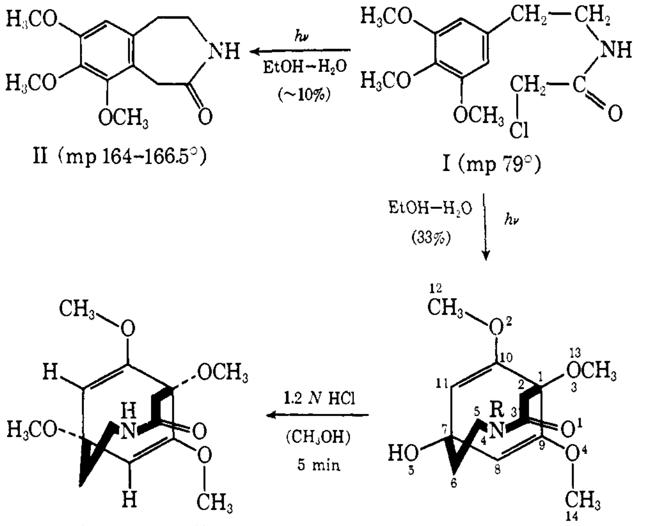
(10) Although ample spectral data were obtained for this structure, a satisfactory elemental analysis could not be obtained for **8a**.

(11) Although intermediacy of 1-azabicyclobutonium cations has been postulated previously,[7] the presence of the carbonyl group in a three-membered ring would be expected to contribute considerable added strain energy to **10**.

Photocyclizations of Pharmacodynamic Amines. III. Three-Dimensional Structure of 7-Hydroxy-1,9,10-trimethoxy-4-azabicyclo[5.2.2]undeca-8,10-dien-3-one from Mescaline[1]

Sir:

The presence of one or two methoxy substituents has greatly influenced the direction of cyclization and the nature of the products resulting from deep-seated rearrangements in the photolysis of N-chloroacetylphenethylamines.[2,3] The long-sought-after products of the photolysis of N-chloroacetylmescaline (I) have now finally been isolated and crystallized. One product, C$_{13}$H$_{17}$NO$_4$,[4] is 7,8,9-trimethoxy-1,2,4,5-tetrahydro-3(3H)-benzazepin-2-one (II), the first example of such a ring closure in the mescaline series in the absence of *ortho* or *para* activation by a phenolic hydroxyl group. The second photoproduct, after extensive purification by column chromatography over silica gel, was obtained as colorless prisms from methanol–ether in yields approaching 35%. The compound which had only end absorption in the uv had the composition C$_{13}$H$_{19}$NO$_5$. It was characterized by an acetylation product IV, colorless prisms, mp 188–189.5°.



II (mp 164–166.5°)

I (mp 79°)

V (mp 176–179°)

III, R = H (mp 230–232°)
IV, R = Ac (mp 188–189.5°)

An X-ray diffraction analysis of a single crystal established the structure and configuration III of this photoproduct. The compound crystallizes in the *orthorhombic space group Aba2* which does not have a

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(1) Presented in part at the Annual Meeting of the Japanese Pharmaceutical Chemistry Society, Nagoya, April 4–6, 1969.

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

(3) O. Yonemitsu, Y. Okuno, Y. Kanaoka, I. Karle, and B. Witkop, *ibid.*, **90**, 6522 (1968).

(4) Correct analyses for C, H, and N were obtained for all compounds reported.

center of symmetry and to which *symbolic addition procedure has been applied here for the first time.* Among the symmetry elements of the crystal there is a glide plane which acts as a mirror. Therefore, the photoproduct which has two asymmetric carbon atoms exists as a *racemate*, of which structure III represents one possible antipode.[5] Cell dimensions are: $a = 25.74 \pm 0.03, b = 13.88 \pm 0.02$, and $c = 7.49 \pm 0.02$ Å, $\alpha = \beta = \gamma = 90°$, and there are eight molecules in the unit cell. The X-ray data were collected photographically using the Weissenberg and precession cameras. A total of 1290 independent reflections were recorded with Cu Kα radiation. Phases for the reflections were determined directly from the structure factor magnitudes by the symbolic addition procedure[6] for noncentrosymmetric crystals and the positions of the heavy atoms were found in *E* maps. All but one hydrogen atom were found in a difference map. The final *R* factor was 6.8%. In the crystal there is one molecule of water of hydration for two organic molecules. Hydrogen bonds are formed between the water molecule and the OH and NH groups. In addition, the organic molecules are linked into infinite chains by hydrogen bonding between the OH and C=O groups. Bond distances and angles are shown in Figure 1.

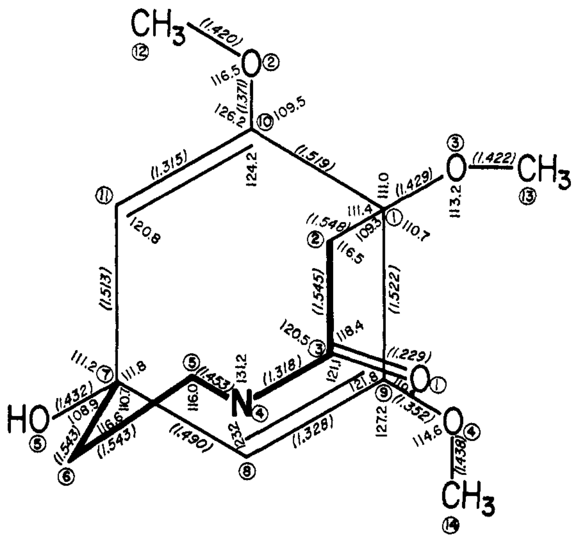
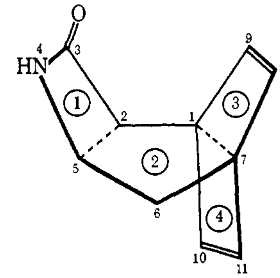


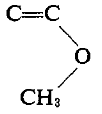
Figure 1. Bond lengths and angles of the photoproduct III from N-chloroacetylmescaline. Additional angles are C(2)C(1)O(3), 103.9°; C(9)C(1)C(10), 110.4°; C(6)C(7)C(11), 107.6°; C(8)C(7)C(5), 106.6°.



VI

There are three features of interest. (i) The nine-membered ring formed from four atoms of the six-membered ring, C(7), C(8), C(9), and C(1), and five atoms from the chain of the original molecule assumes a boat conformation (VI). Atoms C(1), C(7), C(8), and C(9) are coplanar to within ±0.015 Å while atoms C(2), C(3), N(4), and C(5) are coplanar to within ±0.008 Å. Dihedral angles between planes 1 and 2 and between planes 2 and 3 are 118 and 105°, respectively. Intra-ring distances between atoms separated by two other atoms are fairly short, *e.g.*, C(3)···C(9) is 2.78 Å and C(1)···C(7) is 2.95 Å. There is another nine-membered ring containing C(10) and C(11) instead of C(8) and C(9) which has a chair conformation.

(ii) The orientation of the methoxy groups is of interest. The two OCH_3 groups adjacent to the double bonds of the six-membered rings lie so that each set of four heavy atoms in the grouping



are coplanar to within ±0.02 Å. The CH_3 groups are *cis* with respect to the double bonds resulting in the short C(11)···C(12) and C(8)···C(14) separations which are only 2.79 and 2.77 Å, respectively. The hydrogen atoms on the CH_3 groups are oriented so that one H atom is in the plane of the heavy atoms and directed away from the double bond. As a consequence, the other two H atoms are symmetrically disposed above and below the plane maximizing the distance of closest approach of a hydrogen atom to the carbon atoms in the double bond. The middle OCH_3 group lies in the approximate mirror plane (except for atoms N(4), C(3), and O(1)) of the molecule.[7]

This *preferred conformation of the O-methyl groups* is the first direct evidence confirming the observation on similar enol or phenol ethers in solution that the O-methyl and vinyl protons *cis* to the ethylenic bond show long-range coupling which can be studied by the nuclear Overhauser effect.[8,9]

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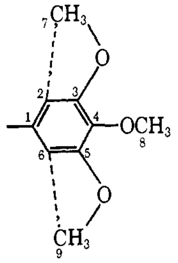
(5) This is in contrast to the photoproduct from N-chloroacetyl-3,4-dimethoxyphenethylamine[2] which was a *conglomerate* from which a single optically active crystal of 1,2,5a,7bβ-tetrahydro-5aβ,5bα-dimethoxy-5bH-cyclobuta[1,4]cyclobuta[1,2,3-*gh*]pyrrolizin-4(5H)-one, one arbitrarily chosen antipode, was picked.

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

(7) In the reserpine molecule, the OCH_3 groups in the trimethoxyphenyl moiety are disposed in a similar fashion as in the present molecule; that is, the middle OCH_3 group is approximately perpendicular to the ring while the other two OCH_3 groups are nearly coplanar with the ring, although the ring in reserpine is a planar aromatic ring while the ring in the present molecule has a fold of 156° at C(1)···C(7). In reserpine the values for the C(2)···C(7) and C(6)···C(9) separations are similarly very low, 2.80 and 2.82 Å: I. L. Karle and J. Karle, *Acta Cryst.*, **B24**, 81 (1968).



(8) M. C. Woods, Department of Chemistry, Tohoku University, Sendai, Japan, personal communication.

(9) M. C. Woods and I. Miura, *Tetrahedron Letters*, 2009 (1968). *Cf.* J. E. Baldwin and J. E. Brown, *Chem. Commun.*, 167 (1969).

(iii) We have tried to detect a special lability in the proximity of the amide group to the enol ether bond. Brief treatment (5 min) of the photoproduct III with methanolic HCl led only to V by etherification of the allylic hydroxyl. But on standing overnight with methanolic HCl at room temperature the lactam easily opened to a (rearranged) basic compound characterized by a hydrochloride (mp 118–124°), perchlorate (mp 163–165°), and N-trifluoroacetyl derivative (mp 125°), all containing a new chromophore ($\lambda\lambda_{max}$ 245 (ϵ 3370), 294 nm (ϵ 885)) on the structure of which we hope to report soon.

Studies with different solvents involving oxygen quenching point to a novel type of cage effect directing the *intra*- and *inter*molecular subsequent reactions of the photoexcited intermediates.

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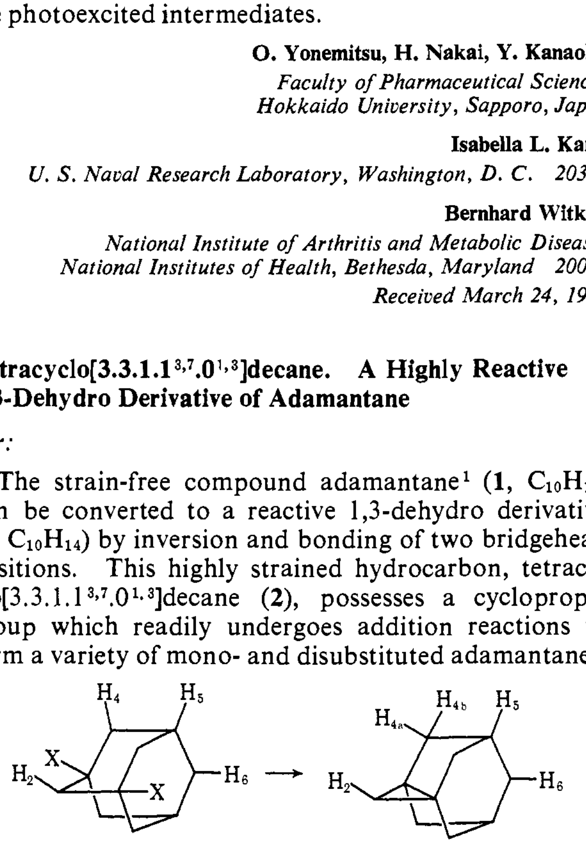
Received March 24, 1969

Tetracyclo[3.3.1.1^{3,7}.0^{1,3}]decane. A Highly Reactive 1,3-Dehydro Derivative of Adamantane

Sir:

The strain-free compound adamantane[1] (**1**, $C_{10}H_{16}$) can be converted to a reactive 1,3-dehydro derivative (**2**, $C_{10}H_{14}$) by inversion and bonding of two bridgehead positions. This highly strained hydrocarbon, tetracyclo[3.3.1.1^{3,7}.0^{1,3}]decane (**2**), possesses a cyclopropyl group which readily undergoes addition reactions to form a variety of mono- and disubstituted adamantanes.



1 2

Reaction of 1,3-dibromoadamantane[2] (**1**, X = Br) with a Na–K dispersion in refluxing heptane produces **2** accompanied by *ca.* 10% of adamantane. Moderate thermal stability of compound **2** is shown by its analysis and separation using gas–liquid partition chromatography (Carbowax columns at 150°, detector at 250°). Degassed solutions of **2** (0.04 *M* in heptane) are essentially unchanged after 3 days at 100°. However, even in dilute solutions at room temperature, reaction of **2** with air occurs promptly ($t_{1/2}$ = *ca.* 6 hr) and results in precipitation of peroxide containing material (white solid, explosion point *ca.* 160°).[3] The peroxide obtained from heptane solutions was reduced with $LiAlH_4$ to yield 1,3-dihydroxyadamantane (**1**, X = OH) as the major product. Analysis of the benzene-insoluble fraction from the peroxide precipitate corresponds to polymeric 1,3-dioxyadamantane, $[-O-C_{10}H_{14}-O-]_x$. *Anal.* Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.55; H, 8.28.

1,3-Dehydroadamantane in heptane solutions was further characterized by the following rapid reactions:[4] catalytic hydrogenation to yield greater than 92% adamantane, hydration with 1 *M* H_2SO_4 to 1-adamantanol, acetolysis to 1-adamantyl acetate, and bromination to 1,3-dibromoadamantane. Compound **2** is thus a readily available intermediate in the production of many bridgehead-substituted adamantanes; *e.g.*, titration of **2** with iodine in heptane produced 1,3-diiodoadamantane (**1**, X = I), mp 110–111°; nmr (benzene) δ 3.19 (H-2), 2.24 (H-4), 1.24 (H-5 and H-6). *Anal.* Calcd for $C_{10}H_{14}I_2$: C, 30.95; H, 3.64; I, 65.41. Found: C, 31.30; H, 3.71; I, 65.11.

Isolation of 1,3-dehydroadamantane by glpc gave an unstable crystalline solid with characteristic infrared absorptions at 3040 (cyclopropyl C–H stretching),[5] 2900, 1450, 1285, 1085, and 895 cm^{-1}. Its nmr spectrum (in degassed benzene) showed absorptions at δ 2.73 (broad singlet, two protons of H-5), 2.05 (triplet, J_{5-6} = 1.2 Hz, two protons of H-6), 1.66 (closely spaced multiplet for two protons of H-2), and a pair of doublets centered at 1.15 and 1.91 (for the four protons each of H-4a and H-4b, J_{ab} = 11 Hz). The large chemical-shift difference (0.76 ppm) of the geminal C-4 hydrogens is consistent with their positions above (H-4a) and nearer the side (H-4b) of the anisotropic cyclopropyl ring.[6] The protons on C-5 and C-6 lie in deshielded positions with respect to the cyclopropyl ring and they appear at unusually low fields.[7] *Anal.* Calcd for $C_{10}H_{14}$: mass, 134.1095. Found: mass, 134.1086 ± 0.001.

The great activity of 1,3-dehydroadamantane is no doubt due to its highly constrained structure and its relaxation to strainless adamantanes as the 1,3 bond is broken. Models suggest that compound **2** possesses carbon atoms (C-1 and C-3) with all four bonds almost extended from one side of each of these atoms. This rare[8] and unstable carbon configuration allows easy access to the approach of reagents from the other side. Inversion of atoms C-1 and C-3, with breakage of the weak internal cyclopropyl bond, completes the transformation to strain-free adamantyl structures.

Acknowledgment. This work was supported by the National Research Council of Canada. We are grateful for technical assistance from Mr. R. Burton and Mr. G. Gunn.

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(1) R. C. Fort, Jr., and P. von R. Schleyer, *Chem. Rev.*, **64**, 277 (1964).
(2) H. Stetter and C. Wulff, *Ber.*, **93**, 1366 (1960).
(3) In the presence of the free-radical inhibitor, 2,6-di-*t*-butyl-*p*-cresol, precipitation of peroxide does not occur and loss of **2** proceeds at a slower pace ($t_{1/2}$ = 30 hr with 3×10^{-2} *M* inhibitor).
(4) For some similar reactions of 2,4-dehydroadamantanes see A. C. Udding, J. Strating, and H. Wynberg, *Tetrahedron Letters*, 1345 (1968); J. E. Baldwin and W. D. Fogelsong, *J. Am. Chem. Soc.*, **90**, 4303 (1968).
(5) H. E. Simmons, E. P. Blanchard, and H. D. Hartzler, *J. Org. Chem.*, **31**, 295 (1966).
(6) The nonequivalent protons on C-4 of 1,3-disubstituted adamantanes ordinarily do not show different chemical shifts; see R. C. Fort, Jr., and P. von R. Schleyer, *ibid.*, **30**, 789 (1965).
(7) For some examples and references see J. Haywood-Farmer, R. E. Pincock, and J. I. Wells, *Tetrahedron*, **22**, 2007 (1966).
(8) K. B. Wiberg, J. E. Hiatt, and G. Burgmaier, *Tetrahedron Letters*, 5855 (1968); K. B. Wiberg and G. J. Burgmaier, *ibid.*, 317 (1969); see also K. B. Wiberg, E. C. Lupton, Jr., and G. T. Burgmaier, *J. Am. Chem. Soc.*, **91**, 3372 (1969).
(9) Alfred P. Sloan Foundation Fellow.

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Received April 24, 1969