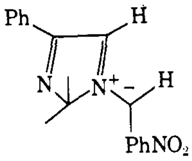
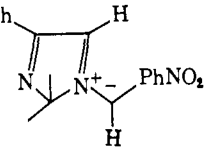
possibility of a triplet diradical was excluded by failure to detect an epr signal at 77°K from the colored intermediate. Two possible ylides, **6a** and **6b**, may be derived from **5**. From the structure of **9**, it seems reasonable to assign the cis structure **6a** to the ylide observed.[10] Consequently, the photoinduced ring opening appears to involve a conrotatory motion which is allowed from the ground state[11] in contrast to a disrotation described by Huisgen and coworkers for a simpler aziridine–azomethine ylide system.[8a] Experiments are under way to investigate the possibility of a "hot" ground-state reaction analogous to the one suggested by Ullman and Henderson for the indenone–pyrylium oxide system.[12,13]



6a



6b

Acknowledgment. We are indebted to Professor H. W. Heine for stimulating discussions and a generous supply of the aziridine.

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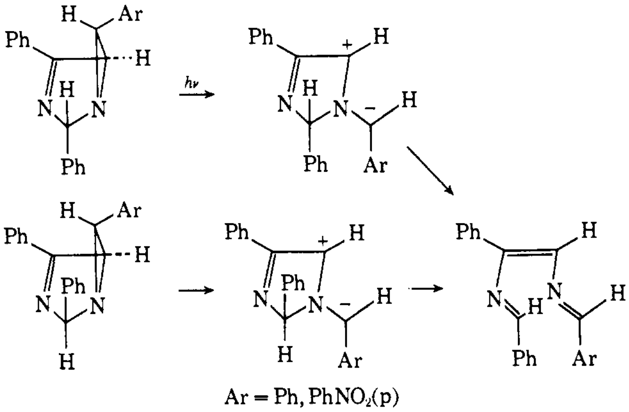
(10) It can be seen that **6** and **6a** are only two of several resonance structures contributing to the ground state of the ylide.

(11) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(12) E. F. Ullman and W. A. Henderson, *J. Amer. Chem. Soc.*, **86**, 5050 (1966).

(13) We have also examined isomeric aziridines of type **1** and **2** whose ylides would be expected to be mirror images of each other. In agreement with the proposed mechanism, irradiation in ethanol glass at 77°K was found to produce spectroscopically identical colored intermediates which on warming to room temperature gave the same enediimine. Irradiation of **5** in 2-methyltetrahydrofuran glass at 77°K gave a blue intermediate, which, upon warming, was converted to **6**. The nature of this intermediate and its relation to the solid-state photochromism of **5** and related compounds will be discussed in a future report.



Ar = Ph, $PhNO_2$(p)

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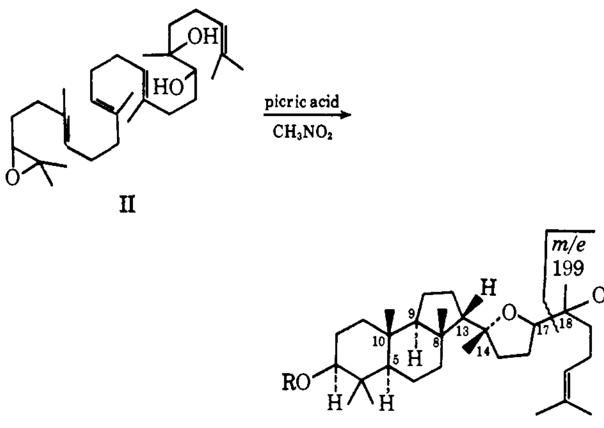
Received August 31, 1970

d,l-Malabaricanediol. The First Cyclic Natural Product Derived from Squalene in a Nonenzymic Process

Sir:

Recently Chawla and Dev reported the isolation of the unique triterpene malabaricanediol (I).[1] The unusual perhydrocyclopenta[*a*]napthalene skeleton of I, although previously unknown among natural triterpenoids, had been observed in nonenzymic cyclizations of squalene 2,3-oxide by van Tamelen and coworkers at Stanford.[2] We now report that acid-catalyzed cyclization of the epoxydiol II produces *d,l*-malabaracanediol (I) in 7% yield. This is the first natural compound ever derived from nonenzymatic cyclization of a squalene derivative and the yield is remarkable if one considers that the molecule has nine asymmetric centers, six of which must be formed stereospecifically during the course of the cyclization. Picric acid was used for the first time as a cyclization catalyst and was found to have dramatic advantages over all previously employed acidic agents.



I, R = R' = H
III, R = R' = TMS
V, R = Ac; R' = H

The required epoxydiol II was prepared from the intact squalene molecule. The synthetic sequence involves some novel new chemistry and chromatographic separations of squalene derivatives and is described elsewhere.[3] The diol function in II derives from trans hydration of a corresponding epoxide and thus has the erythro configuration. Assuming that the two sites of asymmetry in II have formed independently of one another, then there are equal amounts of the four possible stereoisomers, and only 50% of the material (*i.e.*, one pair of enantiomers) can lead to racemic I. The 7% yield was calculated using this correction.

Polyene epoxide cyclizations have to date been accomplished only with strong acid catalysts.[4] These strong acids ($SnCl_4$, BF_3 etherate, etc.) readily attack olefins and other functional groups as well as epoxides. In spite of numerous attempts at cyclization of diol epoxide II with these harsh catalysts, no trace of the desired natural product I was detected. Malabaricanediol I was found to cyclize further under the conditions employed. Clearly what was needed here was a protonic acid (Lewis acids can irreversibly tie up the diol) strong enough to protonate epoxides, but not double bonds. Weaker acids, however, are better nucleophiles and could interfere with cyclization. Picric acid, being of reasonable acidity and hopefully

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(1) A. Chawla and S. Dev, *Tetrahedron Lett.*, 4837 (1967).

(2) E. E. van Tamelen, J. Willet, M. Schwartz, and R. Nadeau, *J. Amer. Chem. Soc.*, **88**, 5937 (1966).

(3) K. B. Sharpless, *Chem. Commum.*, in press.

(4) E. E. van Tamelen, *Accounts Chem. Res.*, **1**, 111 (1968); W. S. Johnson, *ibid.*, **1**, 1 (1968).

too hindered to act as a nucleophile, seemed an ideal candidate. Trial experiments with 1 equiv of picric acid (11% water) in anhydrous nitromethane revealed that whereas malabaricanediol and squalene were stable for at least 1 week, squalene oxide was completely cyclized after 20 hr. Furthermore, the distribution of cyclization products was quite different from that previously observed with stannic chloride in benzene.[5] This is probably the first example of a purely kinetically controlled product mixture from a polyene cyclization. Picric acid is thus the superior catalyst for epoxide opening and may also prove of value for cyclizations initiated by other functional groups.

A solution of 95 mg of epoxydiol II and 88 mg of picric acid in 20 ml of dry nitromethane was allowed to stand 22 hr at room temperature. The crude product (95 mg) was subjected to preparative tlc on silver nitrate impregnated silica gel (17% ethyl acetate–hexane). This afforded 15 mg of an oil with the mobility of authentic malabaricanediol (I). A portion of this oil was exposed to silylation conditions sufficient to effect bistrimethylsilylation of the authentic diol I.[6] Tlc revealed complete silylation (R_f identical with III) and glc analysis[7] revealed four principal components (Table I).

Table I

Component	% of mixture	Retention time relative to III
A	22	0.00
B	48	1.26
C	16	2.17
D	14	2.33

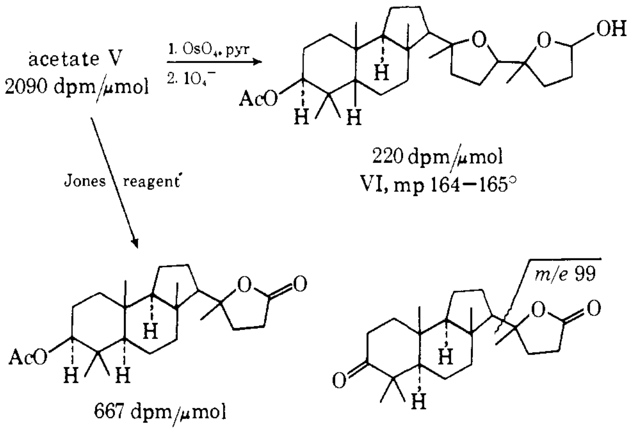
Compounds A, B, C, and D were collected from glc for ir and mass spectral comparison with authentic III. All four substances gave very similar mass spectra with important ions appearing at *m/e* 604 (M^+), 520, 432, 319, 315, 283, 229, 199 (base), and 69. The spectrum of A was identical with that of the authentic bis-TMS ether III. The base peak in all cases was *m/e* 199, which high-resolution data showed to be $C_{11}H_{23}OSi$—the result of the highly favorable side-chain fragmentation.

The ir spectra of III and of A as neat liquids were identical, while the spectra of B, C, and D, although quite similar to the other two, showed significant differences in the C–O stretching region (1000–1200 cm^{-1}). These data suggested that A was *d,l*-III and B, C, and D were diastereomers of the same carbon skeleton.

Glc pure samples of A, B, and a C + D mixture (these two compounds were not well resolved) were hydrolyzed to the corresponding diols (A′, B′, and C′ + D′). Following Dev's procedure,[1] Jones oxidations of diols A′ and B′ both gave the octanorlactone E; oxidation of the C′ + D′ diol mixture also gave a single octanorlactone (F), but it was distinct from lactone E by glc (F/E = 1.33, 3% OV-17 at 210°). The mass spectrum of lactone E was identical with that of authentic lactone IV;[8] the base peak (*m/e* 99) results from cleavage of the γ-lactone substituent. The spectrum of F showed only minor differences in peak intensities from that of lactone E.

The above correlations revealed that although A′ and B′ are diastereomeric at carbons 17 and 18, they are otherwise identical. Compounds C′ and D′ are also diastereomeric in the same sense. Thus A′, B′, C′, and D′ all have the gross structure of malabaracanediol (I), and the yield of this structural type from II is 16%.

A radioactive tracer experiment confirmed the stereochemical assignments for A and B. A 2-mg portion of the 15 mg of crude malabaricane-type cyclization products was acetylated with [^{3}H]acetic anhydride in pyridine. The labeled acetates were combined with 200 mg of the authentic acetate V.[9] Acetate V was then transformed to the lactol VI and the octanorlactone VII as indicated.[10] Recrystallization of each substance to constant specific activity revealed that the glc determined ratio of A:B (0.46) was in good agreement with the tracer determined ratio of A:B (0.49).



220 dpm/μmol
VI, mp 164–165°

667 dpm/μmol
VII, mp 198–198.5°

IV, E, F

Sobti and Dev have correlated malabaricol with ambreinolide, establishing the absolute configurations at carbons 5, 8, 9, and 10 as indicated in I.[11] This synthesis further establishes that the relative configurations at carbons 17 and 18 are those derived from formal trans hydroxylation of the double bond. On the basis of other evidence,[5] the configuration at carbons 13 and 14 is probably as indicated in structure I. Diols C′ and D′ are thought to have the same structure as A′ and B′ through the first three rings, but the β configuration of the C-13 substituent.

The success of this biogentic-type synthesis suggests that the epoxydiol II may well be the natural precursor of the malabaracane family, and that malabaricanediol is the product of a relatively primitive cyclase which functions by exploiting a primary mode of its substrates' inherent reactivity.

Acknowledgments. I am especially indebted to Dr. Hans-J. Förster of Professor Klaus Biemann's group for obtaining all the mass spectral data. Professor

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(5) K. B. Sharpless, Ph.D. Dissertation, Stanford University, 1968.

(6) "TRI-SIL-TBT" (Pierce Chemical Co.) in a closed vessel at 80° for 24 hr.

(7) Performed at 200° on 6 ft × 1/8 in. column packed with 5% DEGS on HP Chromosorb W (100–200 mesh).

(8) Lactone IV is a degradation product of malabaricol and was donated by Professor S. Dev; it is identical on glc with lactone E.

(9) Prepared from authentic malabaricol supplied by Professor S. Dev. This acetate could not be obtained crystalline.

(10) Correct elemental analyses and nmr and ir spectral data were obtained for all new derivatives of malabaricol.

(11) R. R. Sobti and S. Dev, *Tetrahedron Lett.*, 2215 (1968).

Biemann's facility is supported by National Institutes of Health Grant No. RR00317 from the Division of Research Resources. Through the kindness of Professor S. Dev, I received generous samples of malabaricol and lactone IV as well as valuable synthetic details. I am also grateful to the Perkin-Elmer Corporation for use of a 900 gas chromatograph for collection of samples and for the micro ir spectra which they ran on their 180 instrument. I thank a Du Pont Fundamental Research Grant for providing financial support.

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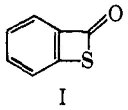
Received July 20, 1970

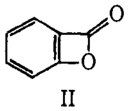
2-Thiobenzpropiolactone[1]

Sir:

We wish to record a facile synthesis of the highly reactive compound, 2-thiobenzpropiolactone (I). This substance is the thio analog of the unknown benzpropiolactone (II) which has been considered as a possible



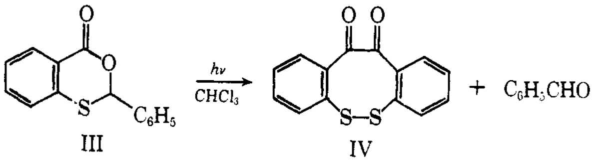
I



II

intermediate in the decomposition of *o*-diazoniumcarboxylate to benzyne.

Irradiation of 2-phenyl-3,1-benzoxathian-4-one (III) at room temperature in chloroform has been reported to give IV and benzaldehyde.[2] These authors considered two biradicals and a thione ketene as possible intermediates in the formation of IV.[2] Our experiments show that this reaction in fact proceeds *via* I and gives V rather than IV.[3] Irradiation of III at 77 °K in an in-



frared cell[6] causes disappearance of III and produces bands characteristic of benzaldehyde (see ν_{CO} 1699 cm^{-1}, Figure 1) and a new species with ν_{CO} at 1803 cm^{-1} and other bands at 1570, 1430, 820, 670, and 630 cm^{-1}. No bands characteristic of V are observed at 77 °K. The absence of the intense band at 900 cm^{-1} is particularly clear evidence that V is not formed during the irradiation of III at 77 °K. Warming the irradiated sample to −40° gives rise to characteristic bands of V with concurrent disappearance of the 1803-cm^{-1} species. The 1803-cm^{-1} species is thus the thermal precursor of V. When the irradiation of III is carried out in the presence of methanol at 77 °K, the 1803-cm^{-1} species is observed. Warming of the irradiated sample in this case gives rise to bands characteristic of methyl *o*-mercaptobenzoate

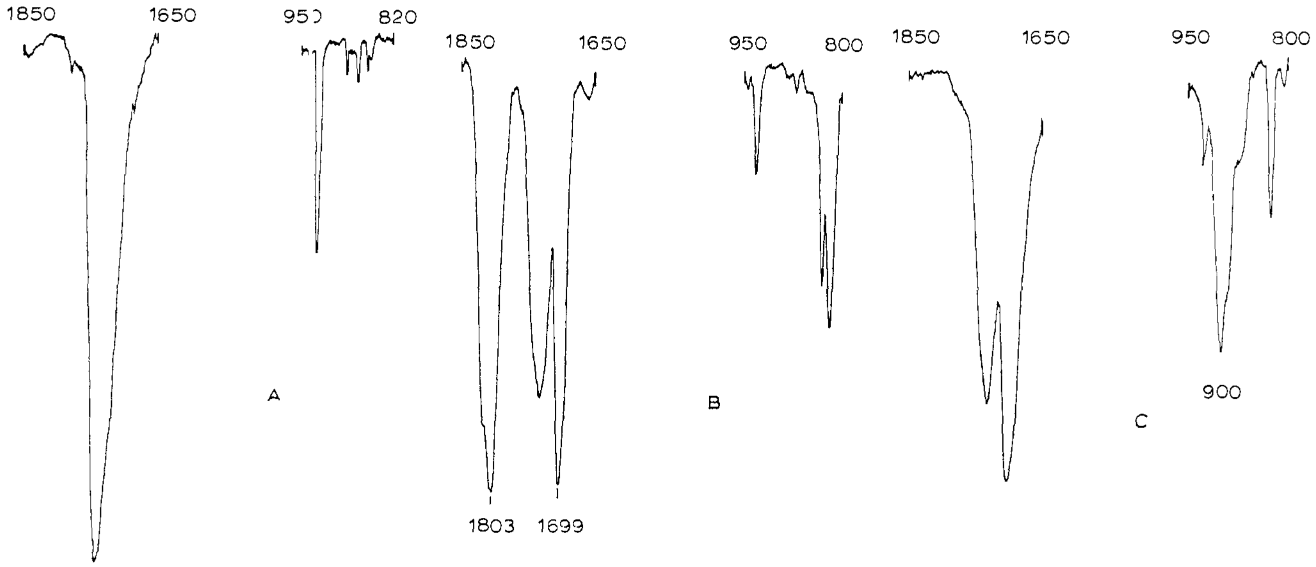


Figure 1. A. Infrared spectrum of 2-phenyl-3,1-benzoxathian-4-one at 77°K before irradiation. B. Infrared spectrum of same sample after irradiation at 77°K through Pyrex; note bands at 1803 and 1699 cm^{-1} characteristic of I and benzaldehyde. C. Infrared spectrum at 77°K of the same sample after warming to room temperature; note appearance of the band at 900 cm^{-1} characteristic of V.

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(1) Photochemical Transformations. LXI.

(2) A. O. Pedersen, S.-O. Lawesson, P. D. Klemmensen, and J. Kolc, *Tetrahedron*, **26**, 1157 (1970).

(3) The evidence presented for structure IV was nonidentity of IV with authentic V in melting point and tlc retention and reduction in low yield to benzil.[2] The absence of ultraviolet maxima above 240 nm in the product and the difficulty in rationalizing formation of structure IV led us to question this assignment. In our hands, the photoproduct from III and authentic V[4] are identical in melting point and infrared absorption after the trimer has been separated from authentic V. The reduction of V to benzil probably occurs *via* a transannular reduction analogous to that observed by Metlesics and Sternbach[5] in the zinc–acetic acid reduction of dibenzocine derivatives. The identity of the photoproduct from III and authentic V has been confirmed by Dr. J. C. Clardy by comparison of X-ray powder patterns.

(4) W. Baker, A. S. El-Nawawy, and W. D. Ollis, *J. Chem. Soc.*, 3163 (1952).

(5) W. Metlesics and L. H. Sternbach, *J. Amer. Chem. Soc.*, **88**, 1077 (1966).

(6) O. L. Chapman and J. D. Lassila, *ibid.*, **90**, 2449 (1968).