ture. The crude, dried organomercury product **7** was directly subjected to a mercury-lithium exchange by treating with an excess of *n*-butyllithium. Hydrolysis of the resulting dark green solution yielded 40% of a solid **8** that proved to be *cis*-1,2-dihydrohexaphenylbenzene,[16] together with 16% of **6** and 8% of hexaphenylbenzene (**9**). The structure of **8** follows from the following: (a) heating **8** with *N*-bromosuccinimide in CCl_4 gave **9** in 86% yield; (b) its NMR (CCl_4), 4.42 (s, 2) and 6.8 (m, 30), whereas the *cis*[4]- and *trans*[17]-1,4-dihydrohexaphenylbenzenes display their benzylic protons at 4.67 ppm and the reported[18] *trans*-1,2-dihydrohexaphenylbenzene has its corresponding peak at 4.0 ppm; (c) its electronic spectrum has λ_{max}^{MeOH} 325 (10,300), whereas the known trans isomer has its long-wavelength peak at $\lambda_{max}^{CH_3CN}$ 312 (10,700); and (d) **8** melts almost completely at 150–152°, but then resolidifies and melts finally at 192–195° (trans mp 180–182°). The isolation of **8** and **6** as the principal hydrolysis products seems to be best interpreted as a disrotatory ring closure of the 1,6-dimercurio- or dilithiohexatriene resulting from **5**. The ring-closure product (e.g., the dilithio product **10**) would then be protonated, with or without allylic rearrangement, to yield **6** and **8**, respectively. In any case, the spectral *and* chemical data strongly support the conclusion that the fluorescent green boron derivative obtained by heating **4** must consist, in whole or in part, of molecules possessing the borepin structure **5**, rather than the 7-borabicyclo[4.1.0]heptadiene structure (**3**). The ultraviolet spectrum of **3** would be expected to resemble that of **8**, and hence the long-wavelength band of the green solid ($\lambda_{max}^{Et_2O}$ 412) would be unexplained. However, it may very well be that coordination complexes of **5** with Lewis bases, such as R_3N, OH^-, or Bu^- do actually assume the bicyclo structure shown in **3**, as may be the case for **11**. The observed λ_{max} for **11** is in better agreement with that of **8**, than with that reported for 1,6-diphenyl-1,3,5-hexatriene[19] ($\lambda_{max}^{C_6H_6}$ 358).

Although no definite information can be obtained on the coexistence of both valence isomers **3** and **5** for the heptaphenyl-substituted system, a study of the hexa-*p*-tolyl-substituted system has been rewarding. Thus, 1-phenyl-2,3,4,5-tetra-*p*-tolylborole was synthesized from the corresponding stannole and then was treated with di-*p*-tolylacetylene to form the Diels-Alder adduct analogous to **4**.[20] Heating the latter compound in toluene yielded the fluorescent green presumed 1-phenyl-2,3,4,5,6,7-hexa-*p*-tolylborepin (**12**): mp 276-281° dec; $\lambda_{max}^{Et_2O}$ (ϵ) 425 (5210), 345 (sh, 7810), 280 (sh, 23,100), and 249 (30,500). However, in toluene-d_8 at 25° **12** shows six distinct methyl signals of approximately equal intensity; raising the temperature to 57° causes two of these signals to coalesce. At temperatures above 113° in bromobenzene two more signals coalesce, leaving four methyl peaks. These results suggest that the borepin **12** is in equilibrium either with a nonplanar form or with its bicyclo valence isomer **13**, having a structure similar to **3**.

Whether planar borepins **5** and **12** are in equilibrium with nonplanar structures like **3**, as has been surmised for certain substituted tropenium salts,[14] is the focus of our continuing NMR and X-ray crystallographic investigations.[21]

Finally, it is noteworthy that the long-wavelength absorption of heptaphenylborepin at 412 nm bears a marked similarity to that of several heptaphenyltropylium salts, such as the bromide, fluoroborate, and perchlorate, which absorb at 405 nm in acetonitrile.[22] The other maxima of these salts at 250 (90,000) and 283 nm (17,000) also compare favorably with those of borepin **5** at 245 and 276 nm, respectively. The correspondence in electronic spectra supports the isoelectronic relationship between this borepin and its aromatic carbocyclic counterpart.

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(13) This compound melted at 233–236°. Anal. Calcd for $C_{48}H_{35}B$: C, 92.61; H, 5.66. Found: C, 92.58; H, 5.75. Both **4** and **5** gave strong parent peaks with the proper $^{10}B/^{11}B$ ratios in their mass spectra at 70 eV.

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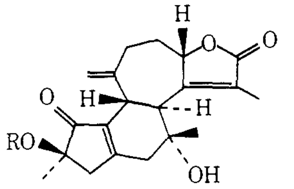
The Structure of Crotofolin A, a Diterpene with a New Skeleton

Sir:

The identification of the cocarcinogenic principles of *Croton tiglium* L. (Euphorbiaceae) as esters of the diterpene phorbol has stimulated considerable interest in the chemistry of this genus.[1,2] Although various diterpenes have been isolated from *Croton* these are of the commoner skeletal types such as labdane (or rearranged labdane),[3,4] pimarane,[4] and tigliane.[1,5] We now report the isolation and structural elucidation of a novel diterpene, crotofolin A (**1**), which possesses a new carbon skeleton,[6] for which we propose the name crotofolane.

Crotofolin A, $C_{20}H_{24}O_5$ (M^+ 344.1703), was isolated from a benzene extract of *C. corylifolious* L.[7] as colorless crystals, mp 277-279°, $[\alpha]^{25}D$ −20.0 (ethanol), and λ_{max} (ethanol) 227 (ϵ 23,800) nm, and had ir (Nujol) absorption bands attributed to the following functional groups: hydroxyl (3465 cm^{-1}), α,β-unsaturated γ-lactone (1740 cm^{-1}), α,β-unsaturated cyclopentenone (1705 and 1650 cm^{-1}) and an exo-cyclic methylene (900 cm^{-1}). The NMR spectrum (DMSO-d_6) of **1** showed the presence of two methyl groups located on fully substituted carbon atoms bearing oxygen functions (δ 1.09 and 1.30), one vinylic methyl group (δ 1.92), and a terminal methylene group (δ 4.50 and 4.84). In addition, a broad doublet of doublets centered at δ 5.15 (1 H, J = 10 and 2 Hz) is assigned to an allylic proton situated on a carbon bearing an oxygen function and adjacent to a pair of nonequivalent protons. The presence of two D_2O exchangeable protons (δ 4.56 and 4.58) indicates that crotofolin A is a diol.



1, R = H
2, R = CH_3CO

Treatment of crotofolin A with acetic anhydride in pyridine (25° for 18 hr) yielded a crystalline monoacetate: mp 240-243° (M^+ 386); λ_{max} (ethanol) 225 (ϵ 18,835) nm; ν (KBr) 3560, 1760, 1730, 1715, 1650, and 900 cm^{-1}; δ ($CDCl_3$) 1.18 (3 H, s), 1.40 (3 H, s), 1.90 (3 H, s), 2.05 (3 H, s), 2.30 (1 H, exchangeable with D_2O), 4.50 (1 H, s) 4.87 (1 H, s), and 5.14 (1 H, broad d, J = 10 Hz). The acetate is tentatively assigned structure **2**.

Determination of the structure and relative configuration of crotofolin A was effected through a single-crystal, X-ray analysis. Crystals of **1**, grown from methanol, formed in the orthorhombic space group $P2_12_12_1$ with a = 16.649 (3), b = 15.700 (3), and c = 6.640 (1) Å and one molecule per asymmetric unit. A total of 1404 unique reflections with $2\theta \leq 114°$ was measured on a fully automated four-circle diffractometer using graphite monochromated Cu Kα (1.5418 Å) radiation. After Lorentz, polarization, and background corrections 1256 reflections (89%) were judged to be observed ($F_o^2 > 3\sigma(F_o^2)$). Periodically monitored standard reflections showed no decline in intensity. The fractional coordinates, important bond distances and angles will appear in the microfilm edition; see paragraph at end of paper regarding supplementary material.

Normalized structure factors were computed and phase angles assigned to 150 E's larger than 1.48 by a multiple solution, weighted tangent formula approach.[8] The phased, three-dimensional E-synthesis revealed 22 of the 25 nonhydrogen atoms with a subsequent F-synthesis revealing the rest of the atoms. Full-matrix least-squares refinements using anisotropic temperature factors for the non-hydrogen atoms and isotropic temperature factors for the hydrogen atoms smoothly converged to an unweighted crystallographic residual of 0.035. A computer generated drawing of the final X-ray model is shown in Figure 1.[9]

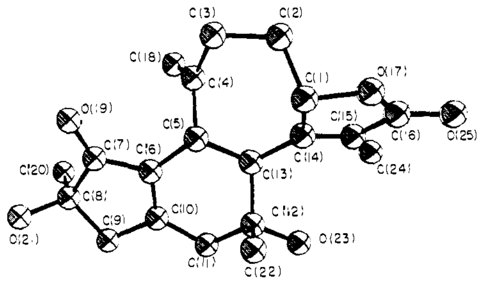
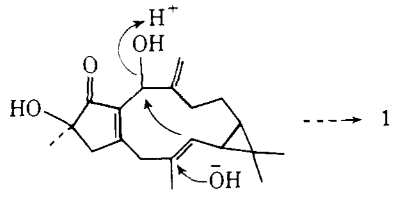


Figure 1. A computer generated perspective view (relative stereochemistry) of crotofolin A (**1**).

As can be seen from Figure 1 a cyclopentenone ring is fused to a cyclohexene ring, with a double bond shared by both rings. The cyclohexene ring is trans fused to a seven-membered ring which possesses an exo-cyclic methylene. The molecule is completed by a butenolide moiety fused to the seven-membered ring. The crystalline structure contains two intermolecular hydrogen bonds—one between O(19) and O(23) with distances of O(19)-O(23), 2.848; O(19)-H(23), 2.05; O(23)-H(23), 0.88 Å, and the angle O(19)-H(23)-O(23) of 151°. Another hydrogen bond exists between O(21) and O(25) with distances of O(21)-O(25), 2.942; O(25)-H(21), 2.20; O(21)-H(21), 0.75 Å, and the angle O(21)-H(21)-O(25) of 170°.

The biogenesis of the crotofolane skeleton probably occurs via a transannular closure of a bicyclic precursor such as **3**. Compounds embodying the salient skeletal features depicted in **3** have recently been isolated[10] from the Euphorbiaceae.



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Supplementary Material Available. A listing of fractional coordinates, bond distances, and angles will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JACS-75-4437.

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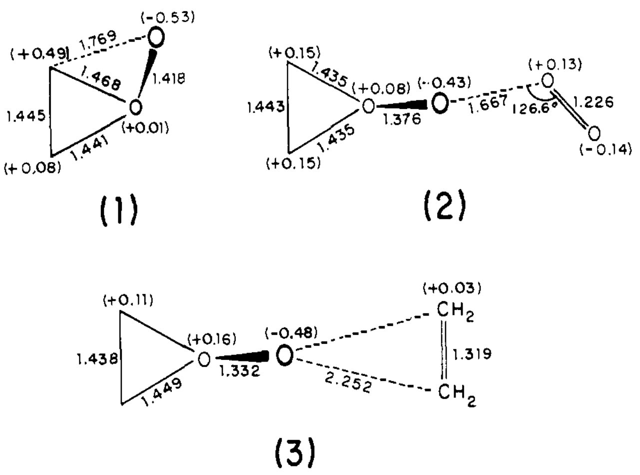


Figure 1. Calculated transition states for reactions 1-3. Bond lengths are given in Å, formal charges (in brackets) in electrons.

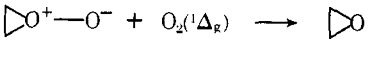
A Possible Mechanism for the Formation of Oxiranes in Reactions of Singlet Molecular Oxygen with Olefins

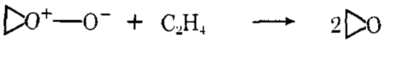
Sir:

Singlet ($^1\Delta_g$) molecular oxygen normally reacts with olefins to form either allylic hydroperoxides (ene reaction) or dioxetanes (1,2-cycloaddition). While both concerted pericyclic mechanisms and two-step processes involving intermediate peroxiranes have been suggested for these reactions,[1] most authors have tended to favor the former in view of failure[2] to detect peroxirane intermediates.

Recently, however, the photosensitized oxidation of 2,2′-biadamantylidene in pinacolone has been reported[3] to yield not only the corresponding dioxetane but also the oxirane and *tert*-butyl acetate. The formation of the latter two compounds was attributed to the trapping of a peroxirane intermediate in a Baeyer-Villiger type reaction with the solvent. Subsequently, the photooxidations of 7,7′-binorbornylidene[4] and of norbornene[5] have likewise been shown to lead to the corresponding dioxetane and oxirane. In these cases, however, the products were obtained in a variety of solvents, including benzene[4] and acetonitrile[5], which are clearly incapable of Baeyer-Villiger type reactions. It was established in each case[4,5] that the oxirane was a genuine photooxidation product but no mechanism for its formation was suggested.

In order to derive a mechanism for these reactions[3-5] we have carried out MINDO/3[6] calculations for an analogous case, the reaction of ethylene with singlet molecular oxygen. An earlier MINDO/3 study[7] had led us to the conclusion that reactions of singlet oxygen with olefins always involve the initial formation of peroxirane intermediates (or, in the case of $-E$ substituted olefines, zwitterionic intermediates) which occupy shallow minima on the potential surface. We therefore decided to investigate the following reactions using theoretical techniques described previously[7]


(1)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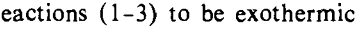
(3)

The closed-shell ground-state MINDO/3 calculations predict these reactions (1–3) to be exothermic by 49.4, 36.2, and 98.1 kcal/mol, with calculated activation energies of 34.1, 29.2, and 8.6 kcal/mol, respectively. The fully optimized structures for the three transition states are shown in Figure 1. The transition state for reaction 3 shows C_s symmetry and can be regarded as a weak π-complex between peroxirane and ethylene, similar to the C_s transition state found for the addition of singlet molecular oxygen to ethylene to form peroxirane.[7]

The calculated values for the heats of formation and activation energies are naturally subject to the errors of the MINDO/3 method which usually are less than 5 kcal/mol.[6] In our present case, however, we have to consider that oxirane is given too stable by MINDO/3, by 13.9 kcal/mol, and we expect a similar situation for peroxirane for which no experimental data are available. The calculated activation energies for eq 1 and 2 must therefore be too large, probably by similar amounts.[8] That for eq 3 should be little affected since the transition state closely resembles the reactants in structure (see Figure 1). All these reactions must in any case be exothermic. Several conclusions then follow.

For sterically nonhindered olefins, the reduction (eq 3) of an intermediate peroxirane by the olefin is predicted to be more facile than the reduction (eq 2) by singlet oxygen or the rearrangement (eq 1) to the dioxetane. The reaction between ethylene and singlet molecular oxygen (which has not yet been observed experimentally) should therefore yield oxirane as the main product, via mechanism 3, and not dioxetane or its cleavage product formaldehyde, as might have been assumed.

In the case of 2,2′-biadamantylidene,[3] 7,7′-binorbornylidene,[4] and norbornene,[5] the formation of the oxirane via route 3 is expected to be very unfavorable since the reduction of the peroxirane by the olefin is sterically inhibited. This is supported by the observation in the 7,7′-binorbornylidene system[4] that the ratio of oxirane to dioxetane in the product increased fourfold when the concentration of the olefin was reduced by a factor of 20. Our calculations indicate that in this situation the dioxetane and oxirane should be formed with similar ease via route 1 and 2, and concomitant formation of the two compounds is indeed observed.[3-5]

We therefore suggest that the formation of oxirane in these reactions involves the reduction of an intermediate peroxirane by singlet molecular oxygen. Detection of the ozone thus formed may be difficult since ozone reacts with olefins such as 7,7′-binorbornylidene to give oxiranes.[4] The most obvious test of the proposed mechanism would be provided by studies of the product ratio as a function of the