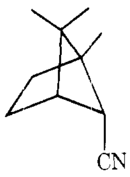

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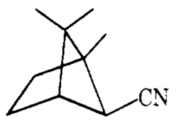

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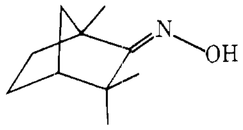

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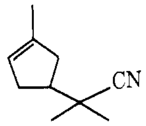
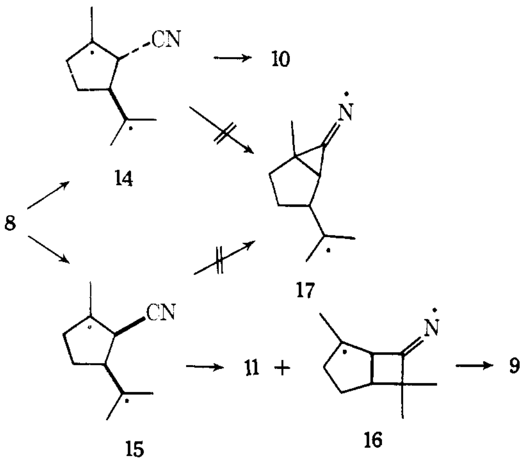


13

°C in refluxing chlorobenzene the propiophenone-sensitized irradiation of 8 furnished a volatile product consisting of 9 (60%), 10 (30%), and 11 (10%). All photolyses in which chlorobenzene was solvent were carried out with solid sodium bicarbonate added to the reaction mixture to prevent the possible accumulation of hydrogen chloride. In all experiments interconversion of the cis and trans isomers of geranonitrile (8) was rapid relative to other reactions, and a considerable amount of polymer was formed. The volatile products were isolated and purified by preparative vapor-phase chromatography, and 9 was tentatively identified on the basis of its spectroscopic properties[3] and the mechanistic considerations discussed below. This assignment was confirmed by comparison of the new photoproduct with an authentic sample of 9 prepared by the known acid-catalyzed Beckmann fragmentation of α-fenchone oxime (12).[4]

A stepwise mechanism for formation of 9, 10, and 11 from 8 is shown in Scheme II. This involves interaction of the double bonds of 8 to furnish biradicals 14 and 15, parallel to the suggested formation of 4 and 6 in Scheme I.[5] Closure of 15 to the bicyclic iminium species 16 and subsequent cleavage of the cyclobutane ring in the opposite sense could then furnish 9. Presumably this cyclization and rearrangement would not be possible in 14 because of the trans stereochemistry of the substituents. The postulated formation of 16 has reasonable precedent in intermediates discussed by other investigators for several 1,4 transfers of a cyano group in radical reactions.[6,7] In one of these earlier cases a labeling study has shown this transfer specifically to be an intramolecular rearrangement.[7] We are unaware, however, of any previous report of the *1,3* transfer of a cyano group in a free-radical process. If the mechanisms of Schemes I and II are valid, irradiation of 1 and 8 leads to analogous biradicals, but in the case of 1 the observed rearrangements entail a 1,2 migration of the formyl group, while in 8 the cyano group undergoes only a 1,3 shift.

Scheme II



One possible factor contributing to the observed specificity of rearrangement of the nitrile may be that a 1,2 shift in 14 or 15 would require an intermediate (see 17) with an sp^2-hybridized carbon atom in a strained three-membered ring. A similar intermediate in the rearrangement of 4 to 5, and of 6 to 7, would have only sp^3 carbons in the cyclopropane ring.

The present work then provides a second novel type of photochemical rearrangement that can compete with [2 + 2] cycloaddition at elevated temperature, and that can be rationalized through a biradical intermediate of the sort generally implicated[8] in such cycloadditions. We are continuing our search for additional examples of such processes.[9]

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(3) Spectroscopic data for **9** and **13** in CCl_4 follow. For **9**: IR 3048 (m), 2977 (s), 2940 (s), 2875 (s), 2850 (s), 2240 (m), 1655 (m), 1467 (s), 1451 (s), 1435 (s), 1382 (s), 1374 (m), 1367 (s), 977 (m) cm^{-1}; NMR (60 MHz) δ 5.24 (m, 1 H), 2.72 (br m, 1 h), 2.57–1.88 (m, 4 H), 1.78 (m, 3 H), 1.28 (s, 6 H). For **13**: IR 3045 (m), 2975 (s), 2930 (s), 2840 (s), 2235 (m), 1658 (w), 1468 (s), 1432 (s), 1380 (s), 1372 (m), 1362 (s), 1010 (m) cm^{-1}; NMR (60 MHz) δ 5.22 (m, 1 H), 2.30 (br s, 5 H), 1.72 (br s, 3 H), 1.33 (s, 6 H).

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(5) For the original proposals of such biradical intermediates in the formation of **10**, **11**, and the photoproducts from citral at room temperature, see ref 2 and also R. C. Cookson, J. Hudec, S. A. Knight, and B. R. D. Whitear, *Tetrahedron*, **19**, 1995 (1963), and G. Büchi and H. Wüest, *J. Am. Chem. Soc.*, **87**, 1589 (1965).

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(8) For references to mechanistic studies of [2 + 2] photocycloaddition see R. O. Loutfy and P. de Mayo, *J. Am. Chem. Soc.*, **99**, 3559 (1977).

(9) This investigation was supported by the National Science Foundation through Grant CHE74-21436. We thank Dr. W. I. Taylor, International Flavors and Fragrances, Inc., for a generous gift of geranonitrile.

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Received May 15, 1978

Poitediol, a New Nonisoprenoid Sesquiterpene Diol from the Marine Alga *Laurencia poitei*

Summary: A new sesquiterpenoid diol, poitediol (1), has been isolated from ethanol extracts of the red seaweed *Laurencia poitei* (Lamouroux) Howe. The structure of poitediol, as determined by X-ray crystallography, is composed of an unprecedented and nonisoprenoid bicyclo[6.3.0]undecane skeleton.

Sir: Red seaweeds of the genus *Laurencia* are known to produce regular terpenoids which contain halogens.[1] Brominated compounds are more commonly observed, but many chlorinated examples are known. Structurally these compounds appear to be the products of a bromonium ion induced cyclization of acyclic precursors.[2] We wish to report here the structure of an unusual *Laurencia* metabolite, poitediol (1), which contains neither the expected halogen substituents nor regular sesquiterpenoid structure characteristic of metabolites from this source. Recent investigations indicate that halogen solvolysis and concomitant rearrangement may be the

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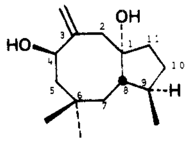

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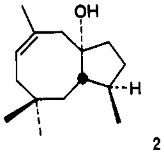

2

mechanistic pathway for the production of these nonisoprenoid metabolites.[3]

Standard column chromatography of the $CHCl_3$–ethanol extract of *L. poitei* (Lamouroux) Howe,[4] followed by extensive LC on μ-Porasil, gave poitediol (1) and dactylol (2), in addition to several other nonhalogenated sesquiterpenoids. Details of isolation and purification are included as Supplementary Material. Dactylol (2) has been recently isolated from the digestive glands of the herbivorous marine opisthobranch mollusc *Aplysia dactylomela*.[5] In view of the isolation of dactylol from this seaweed source, it seems likely that Aplysia concentrates this metabolite while grazing on *L. Poitei* or a related *Laurencia* species.

Poitediol (1), $[\alpha]_D$ −62.6° (*c* 4.3, $CHCl_3$), isolated finally as a very low melting solid, mp ~40 °C, showed only an $M^+ - H_2O$ fragment in its mass spectrum, but could be assigned the molecular composition $C_{15}H_{26}O_2$ by elemental analysis. Acetylation (Ac_2O/py at 25 °C) gave a monoacetate which still contained hydroxyl absorptions (3450 cm^{-1}) in its infrared spectrum, indicating that 1 is a diol composed of one secondary and one tertiary hydroxyl function. The ^1H NMR spectrum of 1 ($CDCl_3$) showed bands at δ 5.18 (d, J = 2 Hz) and 5.05 (d, J = 2 Hz) which were attributed to an *exo*-methylene constellation. A four-line pattern at δ 4.21 (J = 12, 4 Hz), which shifted to δ 5.50 in the corresponding acetate, was assignable as the secondary alcohol methine proton. Another feature of the spectrum was a two-proton singlet at δ 2.32, which was observed as an AB double doublet in the spectrum of the acetate. Three methyl bands were also observed, two of which were singlets at δ 0.94 and 0.86 and one of which was an overlapping doublet at δ 0.95. The region δ 1.2–2.1 showed complex bands which integrated for ten additional protons.

The structure of poitediol was rigorously established by X-ray crystallography. Crystals of poitediol belong to the chiral, monoclinic space group $P2_1$ with a = 9.412 (6), b = 17.489 (8), c = 9.721 (3) Å, and β = 114.69 (4)°. A calculated and measured density of 1.09 g/cm^3 (Z = 4) indicated that *two* molecules of $C_{15}H_{26}O_2$ formed the asymmetric unit. All diffraction maxima with $2\theta \leq 114.1°$ were collected on a fully automated four-circle diffractometer using graphite-monochromated Cu Kα (1.54178 Å) radiation. Data were corrected for Lorentz, polarization, and background effects and only 1290 (63%) of the 2046 reflections surveyed were judged observed ($F_o^2 \geq 3\sigma(F_o^2)$).

The angular dependence of the reflections was eliminated as they were converted to normalized structure factors.[6] Some difficulty was experienced in finding a reasonable set of phases. Presumably this difficulty had its genesis in the poor diffracting power of the crystal, which severely limited the high angle data. A magic integer approach[7] was employed successfully. A total of 100 starting sets, each composed of 54 normalized structure factors, was expanded into phases for the 250 largest normalized structure factors. A weighted E synthesis of the best set showed 21 chemically reasonable atoms. The remaining nonhydrogen atoms were located on the subsequent F_o synthesis.[8] Full-matrix least-squares refinements with anisotropic temperature factors for carbon and oxygen and isotropic hydrogens have converged to a final, unweighted crystallographic residual of 0.05 for the observed reflections.

Figure 1 is a computer-generated perspective drawing of one of the two crystallographically independent molecules of poitediol. The two conformations were identical within experimental error and the metrical details in the following discussion are averages. Poitediol is an unusual sesquiterpene with a trans-fused bicyclo[6.3.0]undecane. The five-membered ring is in the envelope conformation with C(8) as the flap (0.615 Å removed from the plane of atoms C(1), C(11), C(10), and C(9)). The eight-membered ring does not assume any simple conformation. This may be a result of the hydrogen bonding observed in the crystal and characterized by the following short intermolecular contacts: O(17)–O(17′) (2.905 Å), O(17)–O(16′) (2.960 Å), and O(16)–O(16′) (3.010 Å). The torsional angles can be found in the Supplementary Material along with other crystallographic details. The X-ray experiment defines only the relative configuration of the molecule, which is 1S*,4R*,8S*,9R*. Molecular distances and angles are generally in agreement with accepted values.[9]

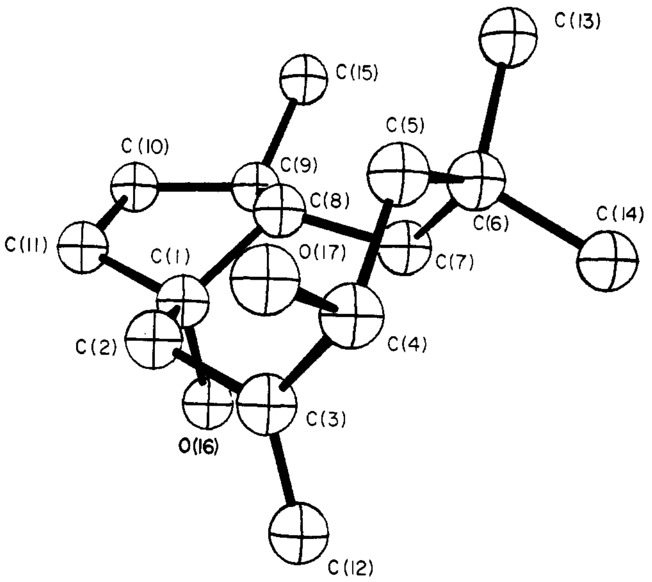

Figure 1. A computer-generated perspective drawing of one molecule from the crystal structure of poitediol.

Acknowledgments. We (W.F. and G.R.S.) are grateful for financial support of this research from the National Science Foundation, Oceanography Section, under Grant No. OCE 75-03824. In addition, we wish to acknowledge our use of the NMR instrumentation of the Department of Chemistry, University of California, San Diego, which is supported by NIH Grant No. RR-408.

Supplementary Material Available: Experimental details on extraction of *Laurencia poitei*, isolation and characterization of poitediol, crystallographic information, and Tables I–III giving fractional coordinates and temperature factors, bond distances, and bond angles (10 pages). Ordering information is given on any current masthead page.

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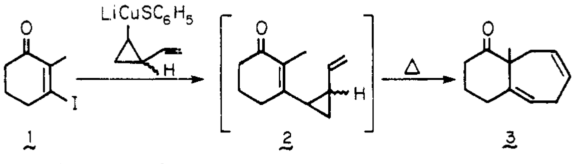
Received February 20, 1978

Stereoselective Preparation of Lithium Phenylthio[2,2-dimethyl-*cis*-(and -*trans*-)-3-vinylcyclopropyl]cuprates and Their Reaction with β-Iodocyclohexenones. Cope Rearrangement of 3-(2,2-Dimethyl-3-vinylcyclopropyl)-2-cyclohexen-1-ones

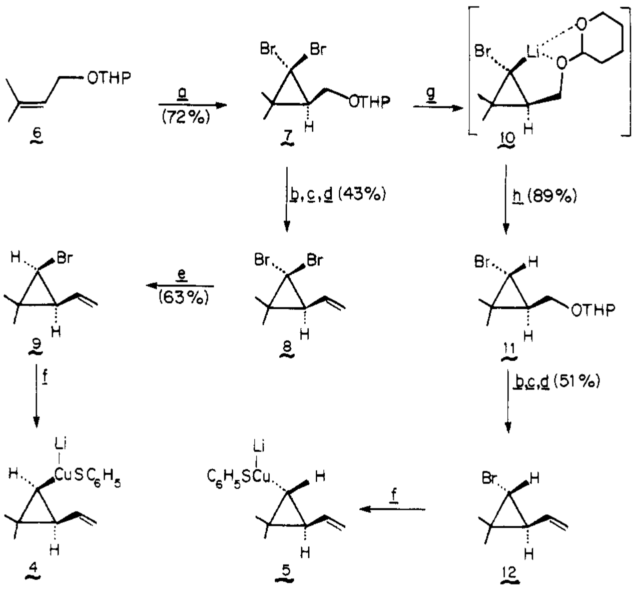
Summary: Lithium phenylthio[2,2-dimethyl-*cis*-(and -*trans*-)-3-vinylcyclopropyl]cuprates were prepared in a highly stereoselective fashion and were allowed to react with 3-iodo-2-cyclohexen-1-one and 3-iodo-2-methyl-2-cyclohexen-1-one. The Cope rearrangement of the resultant products [β-(2,2-dimethyl-3-vinylcyclopropyl)cyclohexenones] was investigated.

Sir: Reports concerning the results of recent studies in this[1] and other[2,3] laboratories have indicated that the Cope rearrangement of β-(2-vinylcyclopropyl)-α,β-unsaturated ketones could be a reaction of considerable synthetic utility. Our work[1] involved the preparation of the required substrates by reaction of β-iodo enones with suitable cyclopropylcuprate reagents. For example, treatment of 3-iodo-2-methyl-2-cyclohexen-1-one (**1**) with lithium phenylthio(2-vinylcyclopropyl)cuprate (mixture of epimers), followed by thermal rearrangement of the initially formed products **2**, afforded the bicyclic dienone **3** (82%).



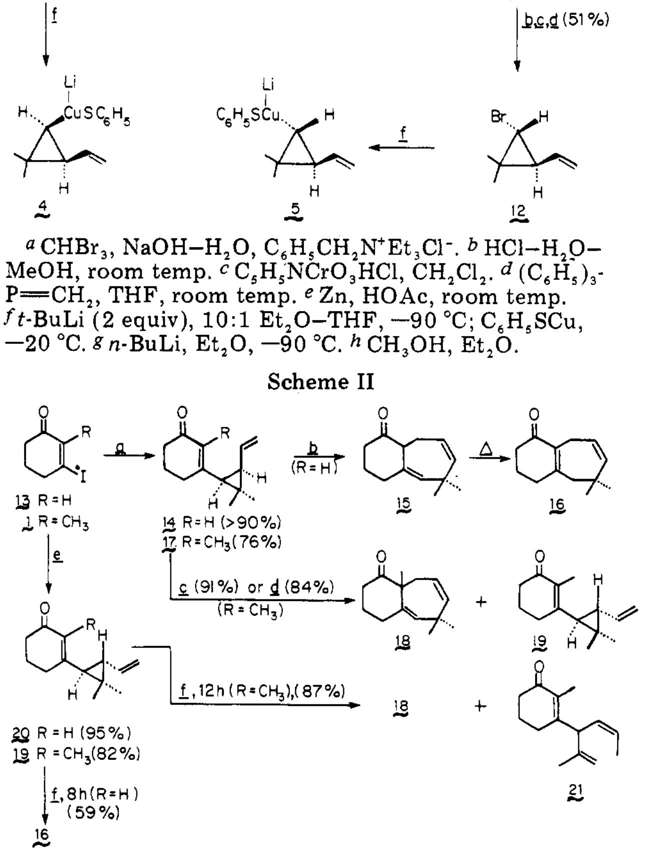
In order to study the effect of structural variations on the Cope rearrangement step, and to produce rearrangement products which could serve as suitable synthetic precursors in projected natural product syntheses, we have extended this type of work to include the use of highly functionalized cyclopropylcuprate reagents. We report herein (a) the *stereoselective* preparation of lithium phenylthio[2,2-dimethyl-*cis*-(and -*trans*-)-3-vinylcyclopropyl]cuprates (**4** and **5**, respectively), (b) the reaction of these reagents with the β-iodo enones **1** and **13** to give the corresponding β-(2,2-dimethyl-3-vinylcyclopropyl)cyclohexenones, and (c) the thermal rearrangement of the latter compounds. In connection with the last item, we have found that the Cope rearrangement of 2-methyl-3-(2,2-dimethyl-*cis*-3-vinylcyclopropyl)-2-cyclohexen-1-one (**17**) is a remarkably sluggish reaction, particularly when compared with the facile rearrangement of structurally very similar compounds (e.g., **2**, **14**).

Scheme I



[a] CHBr$_3$, NaOH–H$_2$O, C$_6$H$_5$CH$_2$N$^+$Et$_3$Cl$^-$. [b] HCl–H$_2$O–MeOH, room temp. [c] C$_5$H$_5$NCrO$_3$HCl, CH$_2$Cl$_2$. [d] (C$_6$H$_5$)$_3$P=CH$_2$, THF, room temp. [e] Zn, HOAc, room temp. [f] *t*-BuLi (2 equiv), 10:1 Et$_2$O–THF, −90 °C; C$_6$H$_5$SCu, −20 °C. [g] *n*-BuLi, Et$_2$O, −90 °C. [h] CH$_3$OH, Et$_2$O.

Scheme II



[a] **4** (1.5 equiv), Et$_2$O–THF, room temp. [b] See text. [c] Refluxing *o*-dichlorobenzene, 3 h. [d] Refluxing *o*-xylene, 48 h. [e] **5** (1.5 equiv), Et$_2$O–THF, room temp. [f] *o*-Dichlorobenzene, sealed tube, 220 °C.

The starting material for the synthesis of the two cuprate reagents **4** and **5** was the tetrahydropyranyl ether of 3-methyl-2-buten-1-ol (**6**)[4] and the reactions involved are summarized in Scheme I. Of particular note in these syntheses was the high stereoselectivity associated with each of the transformations **8** → **9**[5] and **7** → **11**.[6] In the former conversion, it was presumably steric factors which were primarily responsible for the preferential reductive removal of the less hindered bromine atom (cis to CH$_3$ and H, trans to CH$_3$ and CH=CH$_2$). On the other hand, the exchange reaction (step g) employed in the conversion of **7** into **11** was expected to involve the bromine atom which was cis to the CH$_2$OTHP moiety. Protonation of the stabilized intermediate (cf. **10**) thus formed would afford **11**.

The ^{1}H NMR spectra of the two epimeric compounds **9** and **12** fully corroborated the stereochemical assignments. In **9** the proton adjacent to the bromine atom appeared as a doublet (δ 3.02) with a coupling constant of 8 Hz, while the corresponding proton in **12** gave rise to a doublet (δ 2.78) with J =

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