aqueous solution of NH_4Cl. The reaction mixture was extracted with ether (3 × 60 mL). The combined ethereal extracts were dried over $MgSO_4$, filtered, and concentrated in vacuo to give a pale yellow residue, which was subjected to column chromatography.

Registry No. **1a**, 6317-10-8; **1b**, 76312-48-6; **1c**, 84811-68-7; **1d**, 7049-31-2; **7a** [R = CH_3], 15733-08-1; **7a** [R = C_2H_5], 38793-64-5; **7a** [R = $CH_3(CH_2)_3$], 35088-70-1; **7a** [R = $C_6H_5CH_2$], 6622-09-9; **7b** [R = CH_3], 84811-69-8; **7b** [R = C_2H_5], 84811-70-1; **7b** [R = $CH_3(CH_2)_2$], 84811-71-2; **7b** [R= $(CH_3)_2CH$], 84811-72-3; **7b** [R = $CH_3(CH_2)_3$], 84811-73-4; **9c** [R = CH_3], 84811-74-5; **9c** [R = C_2H_5], 84811-75-6; **9c** [R = $CH_3(CH_2)_2$], 84811-76-7; **9c** [R = $CH_3(CH_2)_3$], 84811-77-8; **9d** [R = CH_3], 84811-78-9; **9d** [R = C_2H_5], 84811-79-0; **9d** [R = $CH_3(CH_2)_3$], 84811-80-3; **10d** [R = CH_3], 84811-81-4; **10d** [R = C_2H_5], 84811-82-5; **10d** [R = $CH_3(CH_2)_3$], 84811-83-6; **11** [R = $C_6H_5CH_2$], 1822-76-0; CH_3I, 74-88-4; C_2H_5I, 75-03-6; $CH_3(CH_2)_3I$, 542-69-8; $C_6H_5CH_2Br$, 100-39-0; $CH_3(CH_2)_2Br$, 106-94-5; $(CH_3)_2CHBr$, 75-26-3; $CH_3(CH_2)_3Br$, 109-65-9; $CH_3(CH_2)_2I$, 107-08-4.

Addition of Phthalimidonitrene to 1,4-Dihydronaphthalene 1,4-*endo*-Oxide. An Attempted Synthesis of *N*-Phthalimidonaphth[2,3-*b*]azirine

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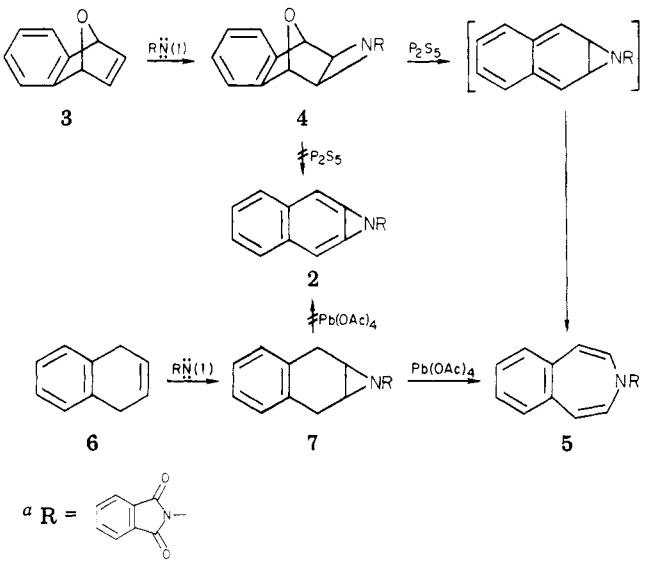
Phthalimidonitrene (1) generated by the oxidation of *N*-aminophthalimide with lead tetraacetate undergoes facile cycloaddition with a variety of substrates.[1] The reaction of 1 with acetylene has been shown to yield 2*H*-azirine which was assumed to arise by the rearrangement of the initially formed 1*H*-azirine.[2] This unique rearrangement has been attributed to the unfavorable electronic delocalization due to antiaromaticity existing in 1*H*-azirine. Such a rearrangement will be energeticaly expensive in naphth[2,3-*b*]azirine **2**. The ideal route to **2** would involve the addition of phthalimidonitrene either to 1,4-dihydronaphthalene 1,4-*endo*-oxide followed by treatment with P_2S_5 or to 1,4-dihydronaphthalene followed by oxidation with lead tetraacetate (or DDQ).

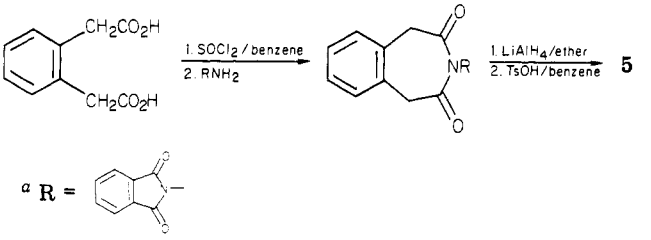
Phthalimidonitrene adds smoothly to 1,4-dihydronaphthalene 1,4-*endo*-oxide[3] (**3**) to give the adduct **4**. Its IR spectrum showed the presence of phthalimido carbonyls (1745, 1720 cm^{-1}) and C–O–C stretching (1150 cm^{-1}). The structure was further supported by the presence of a molecular ion peak at *m/e* 304 ($M^{+\cdot}$) in the mass spectrum. The exo stereochemistry is assigned on the basis of the NMR spectrum which contained singlets at δ 3.3 (H_2, H_3) and 6.7 (H_1, H_4). Dreiding models indicate a dihedral angle close to 90° for the exo adduct, while the endo adduct should show appreciable coupling. Similar exo specificity has been observed in the addition of dibromocarbene to **3**.[4]

The adduct was treated with P_2S_5[5] in anticipation of formation of naphth[2,3-*b*]azirine **2**. The reaction mixture

Scheme I[a]



Scheme II[a]



when subjected to column chromatography on neutral alumina gave a stable compound (40%) which showed no upshield shift in the NMR for the aromatic protons. The mass spectrum showed the molecular ion peak at *m/e* 288. Structure **2** could be ruled out on the basis of these data. The product was found to be different from the known *N*-phthalimido-β-naphthylamine.[6] The UV absorption at λ_{max} (EtOH) 225 nm (ϵ 24170) 290 (1036), and 340 (186.7) is characteristic of a benzazepine ring system[7] and hence enabled the assignment of the azepine structure **5** to the compound.

Another attempted approach to *N*-phthalimidonaphth[2,3-*b*]azirine involves the cycloaddition of 1 to 1,4-dihydronaphthalene (**6**), which gave an adduct in 70% yield. On the basis of the spectral data, structure **7** has been proposed for the adduct. The aziridine **7** when subjected to dehydrogenation with either lead tetraacetate or dichlorodicyano-*p*-benzoquinone (DDQ) gave *N*-phthalimido-3-benzazepine (**5**). The reaction sequence is represented in Scheme I.

N-Phthalimido-3-benzazepine was independently synthesized by the route shown in Scheme II to confirm the structure **5**. The product obtained from *o*-phenylenediacetyl chloride and *N*-aminophthalimide, without purification, was treated with $LiAlH_4$ and dehydrated to give **5** in 20% overall yield.

Experimental Section

All melting points are uncorrected. Infrared (IR) spectra were recorded on a Beckman IR-20 spectrometer, and nuclear magnetic resonance (NMR) spectra were obtained by using a Perkin-Elmer

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R-32 (90 MHz) spectrometer. Chemical shifts are reported in δ units downfield from internal Me_4Si, and the J values are given in hertz.

Recommended General Procedure for Nitrene Reaction. *N*-Aminophthalimide (0.01 mol) was stirred with dry dichloromethane (15 mL/g), and the olefin (0.011 mol) was added. Lead tetraacetate (0.012 mol) was then added to the stirred suspension at 5–10 °C during 10 min. After being stirred for a further 15 min, the reaction mixture was filtered, and the residue was washed with dichloromethane. The combined filtrate was then washed sequentially with water and with a saturated solution of sodium bicarbonate to remove any traces of acetic acid. The dichloromethane layer was then dried (Na_2SO_4) and evaporated to dryness. The residue was examined by TLC, and the subsequent purification was effected as mentioned for each aziridine.

Reaction of Phthalimidonitrene with 1,4-Dihydronaphthalene 1,4-*endo*-Oxide. Addition of phthalimidonitrene from *N*-aminophthalimide (1.63 g) and lead tetraacetate (5.33 g) to the *endo*-oxide (1.58 g) gave the aziridine **4**: 2.90 g (92%); mp 183 °C; IR (KBr) ν_{max} 1780, 1745, 1150 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.3 (2 H, S), 5.7 (2 H, S), 7.2–7.7 (8 H, m); mass spectrum, m/e 304 ($M^{+\cdot}$). Anal. Calcd for $C_{18}H_{12}N_2O_3$: C, 70.8; H, 4.0. Found: C, 70.3; H, 4.1.

Reaction of Phthalimidonitrene with 1,4-Dihydronaphthalene. Addition of phthalimidonitrene from *N*-aminophthalimide (1.63 g) and lead tetraacetate (5.33 g) to 1,4-dihydronaphthalene (1.43 g) gave the aziridine **7**: 2.03 g (70%); mp 180 °C (ethyl acetate–petroleum ether); IR (KBr) ν_{max} 3010, 1750, 1720, 1610 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.0 (2 H, J = 9, t), 3.1 (4 H, J = 10 Hz, d), 7.2–7.7 (8 H, m); mass spectrum, m/e 290 ($M^{+\cdot}$). Anal. Calcd for $C_{18}H_{14}N_2O_2$: C, 74.48; H, 4.8. Found: C, 74.01; H, 4.5.

Reaction of Aziridine 4 with P_2S_5. A solution of the aziridine **4** (0.50 g) in carbon disulfide (250 mL) was stirred with phosphorous pentasulfide (4.00 g) at room temperature for 2 h. The filtered solution was evaporated to dryness, and the residue was taken up in benzene and purified by chromatography over basic alumina. Crystallization from ethyl acetate–petroleum ether afforded *N*-phthalimido-3-benzazepine: 0.18 g (40%); mp 63 °C; UV (EtOH) λ_{max} 225 nm (ϵ 24170), 290 (1036), 340 (186.6); IR ($CHCl_3$) ν_{max} 1600 cm^{-1}; ^1H NMR (CCl_4) δ 7.1–7.6 (m); mass spectrum, m/e 286 ($M^{+\cdot}$). Anal. Calcd for $C_{18}H_{12}N_2O_2$: C, 75.0; H, 4.2. Found: C, 74.6; H, 3.9.

Oxidation of Aziridine 7. To a solution of the aziridine **7** (8.7 g) in dry chloroform (50 mL) was added lead tetraacetate (13.3 g) in small portions at 45 °C. The precipitated lead diacetate was removed by filtration. The residue was washed with water, dried (Na_2SO_4), and evaporated to give a dark-colored oily product which was purified with a column of basic alumina. Elution by ethyl acetate–benzene (1:9) gave *N*-phthalimido-3-benzazepine: 2.3 g (30%); mp 63 °C. The oxidation when carried out with dichlorodicyano-*p*-benzoquinone under similar conditions gave the same azepine **5** in 20% yield.

Synthesis of *N*-Phthalimido-3-benzazepine. The acid chloride prepared from *o*-phenylenediacetic acid (3.86 g) was refluxed for 5 h with *N*-aminophthalimide (3.24 g) in dry benzene (80 mL) with a few drops of pyridine. Benzene was removed, and the residue was extracted with ether (100 mL). The ether layer was washed with water and was concentrated (20 mL), and lithium aluminium hydride (1.55 g) was added to it. The workup gave an oil: IR ν_{max} 3480, 3450, 1780, 1740, 1610 cm^{-1}.

The oily product was refluxed in dry benzene with catalytic amounts of *p*-toluenesulfonic acid for 2 h. Benzene was then removed, and the product was chromatographed on an alumina column. Elution with benzene gave the required azepine: 0.75 g (20%); mp 64 °C.

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Registry No. **1**, 24965-33-1; **3**, 573-57-9; **4**, 84648-94-2; **5**, 84648-95-3; **6**, 612-17-9; **7**, 84648-96-4; *N*-aminophthalimide, 1875-48-5.

Synthesis of Costatolide, a Halogenated Monoterpenoid from the Red Alga *Plocamium costatum*

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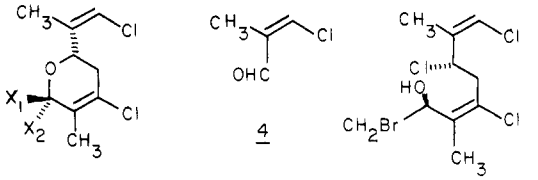
Marine red algae are the source of numerous halogenated products. Excellent reviews of the progress in isolation and structure determination of these compounds are available.[1] Many of these marine metabolites present interesting synthetic targets since the patterns of halogenation which they exhibit are particularly intriguing. Correlation of the structures of many marine natural products reveals that a number of simple building blocks (i.e., four-, five-, and six-carbon pieces) with well-defined patterns of halogenation are found in several different compounds. Recently, we have focused our efforts on the numerous unique, polyhalogenated monoterpenes isolated from various species of red algae belonging to the genus *Plocamium*. We outline below some initial results in this area culminating in the synthesis of the natural product costatolide (**1**).

The structures of the three marine natural products costatolide (**1**),[2a] costatone (**2**),[2a,b] and costatol (**3**)[2b] are given below. The structures and the absolute configura-



4

1 $X_1, X_2 = O$

2 $X_1 = OH$, $X_2 = CHBr_2$

3

tions of compounds **2** and **3** have been confirmed by X-ray diffraction analysis.[2] The key structural feature in all of these compounds is the terminal (*Z*)-chloro olefin. This is depicted in the structures as the uppermost carbon atoms. It appeared to us that a suitable precursor of the (*Z*)-chloro olefin in all of these compounds would be the four carbon unit (*Z*)-3-chloro-2-methylpropenal (**4**). Compound **4** has not been previously characterized in the literature, and thus we sought a convenient preparation of this material.[3,4]

Our preparative route to aldehyde **4** proceeds from 2-methyl-1,2,3-trichloropropane (**5**, Scheme I). Compound **5** is easily obtained by chlorination of methallyl chloride.[5]

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(3) An obvious method for the preparation of β-halo α,β-unsaturated carbonyl compounds utilizes the Vilsmeier–Haack–Arnold acylation. Cf.: Jutz, C. In "Advances in Organic Chemistry: Methods and Results"; Boehme, H., Viehe, H. G., Eds.; Wiley: New York, 1976; Vol IX, pp 225–342.

(4) The reaction of propionaldehyde with the phosphorus oxychloride–dimethyformamide adduct is described; cf.: Arnold, A.; Zemlicka, J. *Collect. Czech. Chem. Commun.* **1959**, *24*, 2385. The major isomer (>97%) formed in this reaction corresponds to (*E*)-3-chloro-2-methylpropenal (**8**; see Scheme I).

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