a solution of 6-(4-methoxy-2-nitroanilino)-5,8-dimethylisoquinoline (1.00 g, 3.10 mmol, 1.00 equiv), hydrazine hydrate (98%; 929 mg, 900 μL, 18.6 mmol, 6.00 equiv), and a catalytic amount of Raney nickel, all in 95% ethanol (10 mL), was heated to reflux on a steam bath for 1 h. At the end of this time, the solvent was removed at atmospheric pressure until the vapors were no longer alkaline. The resulting mixture was taken up in dichloromethane, filtered, washed with brine, dried, and evaporated to yield a brown solid (974 mg) which was used without further purification: ^{1}H NMR ($CDCl_3$) δ 2.42 (s, 3H), 2.54 (s, 3 H), 3.80 (broadened s, 5 H), 5.59 (br s, 1 H), 6.13–7.13 (m, 4 H), 7.98 (d, J = 6 Hz, 1 H), 8.37 (d, J = 6 Hz, 1 H), 9.12 (s, 1 H); IR (KBr) 3360, 3275, 3100, 1595, 1265, 1025, 820, 750 cm^{-1}.

5-Methoxy-1-(5,8-dimethylisoquinolin-6-yl)-1*H*-benzotriazole (9). By use of a modified procedure of Bisagni et al.[11] the crude 6-(2-amino-4-methoxyanilino)-5,8-dimethylisoquinoline (7, 974 mg) obtained above was dissolved in glacial acetic acid (5 mL) and water (0.5 mL) and diazotized with a solution of sodium nitrite (280 mg, 4.07 mmol, 1.10 equiv) in water (1 mL) while at 0 °C. The resulting solution was stirred for 2 h while warming to ambient temperature. At the end of this time, ice (25 g) was added, and the mixture was neutralized with concentrated aqueous ammonia and then extracted with dichloromethane. The combined extracts were washed with water followed by brine, dried, and evaporated to give a tan solid (885 mg, 94% yield) after chromatography on silica gel (eluting with 9:1 dichloromethane/fat extraction ether): mp 175–176 °C; ^{1}H NMR ($CDCl_3$) δ 2.39 (s, 3 H), 2.82 (s, 3 H), 3.92 (s, 3 H), 7.19 (s, 1 H), 7.20 (s, 1 H), 7.40 (s, 1 H), 7.49 (t, J = 2 Hz, 1 H), 7.92 (d, J = 6 Hz, 1 H), 8.74 (d, J = 6 Hz, 1 H), 9.59 (s, 1 H); IR (KBr) 3080, 2960, 1610, 1490, 1295, 1200, 1020, 865, 815, 800 cm^{-1}; high-resolution mass spectrum, calcd for $C_{18}H_{16}N_4O$ m/e 304.1324, found m/e 304.1292.

Ellipticine (1). A solution of 1-(5,8-dimethylisoquinolin-6-yl)-1*H*-benzotriazole (8; 20.0 mg, 72.9 μmol), acetone (1 mL), and methanol (14 mL) was injected via a motor-driven syringe at a rate of 0.382 mL/min into a 30-cm Vigreux column filled with quartz chips and heated to 500 °C under a flow of nitrogen (5 mL/s). The resulting yellow solution was evaporated to afford a yellow solid (14.8 mg) which was purified by preparative thin-layer chromatography on silica gel (eluting with 9:1 fat extraction ether/methanol) to yield ellipticine: 12.4 mg (69% yield); mp 308–311 °C dec (lit.[12] 309–313 °C); ^{1}H NMR (10% methanol-d_4 in $CDCl_3$) δ 2.73 (s, 3 H), 3.22 (s, 3 H), 7.38–7.73 (m, 6 H, $CHCl_3$ present), 7.90–8.16 (m, 2 H), 8.35–8.63 (m, 3 H), 9.73 (br s, 1 H).

9-Methoxyellipticine (2). A solution of 5-methoxy-1-(5,8-dimethylisoquinolin-6-yl)-1*H*-benzotriazole (9; 20.0 mg, 65.7 μmol), acetone (1 mL), and methanol (14 mL) was injected by means of a motor-driven syringe at a rate of 0.382 mL/min into a 30-cm Vigreux column filled with quartz chips and heated to 500 °C under a flow of nitrogen (5 mL/s). The resulting light brown solution was evaporated to yield a yellow-brown solid (20.1 mg). Purification by preparative thin-layer chromatography on silica gel (eluting with 9:1 fat extraction ether/methanol) gave an amber solid: 11.3 mg (62% yield); mp 291–295 °C dec (lit.[13] mp 293–295 °C); ^{1}H NMR (10% methanol-d_4 in $CDCl_3$) δ 2.70 (s, 3 H), 3.18 (s, 3 H), 3.73 (s, 3 H), 7.10–7.63 (m, 2 H), 7.63–8.07 (m, 2 H), 8.30–8.53 (m, 2 H), 9.53–9.70 (m, 1 H).

Acknowledgment. We thank the Cancer Research Coordinating Committee, University of California, and the Committee on Research, University of California, Davis, for partial support of this work.

Registry No. 1, 519-23-3; 2, 10371-86-5; 3, 76372-29-7; 4, 84537-53-1; 5, 84537-54-2; 7, 84537-55-3; 8, 84537-56-4; 9, 84537-57-5; 4-methoxy-2-nitroaniline, 96-96-8; *o*-nitroaniline, 88-74-4.

(10) Fletcher, T. L.; Namkung, M. J. *J. Org. Chem.* **1958**, *23*, 680.
(11) Rivalle, C.; Ducrocq, C.; Basagni, E. *J. Chem. Soc., Perkin Trans. 1* **1979**, 138.
(12) Kilminster, K. N.; Sainsbury, M. *J. Chem. Soc., Perkin Trans. 1* **1972**, 2264.
(13) Dalton, L. K.; Demerac, S.; Elmes, B. C.; Loder, J. W.; Swan, J. M.; Teitei, T. *Aust. J. Chem.* **1967**, *20*, 2715.

Epoxidation of Alkenes with Trichloroacetonitrile/Hydrogen Peroxide in a Neutral Biphasic Solvent System

Luis A. Arias, Stevie Adkins, Christopher J. Nagel, and Robert D. Bach*

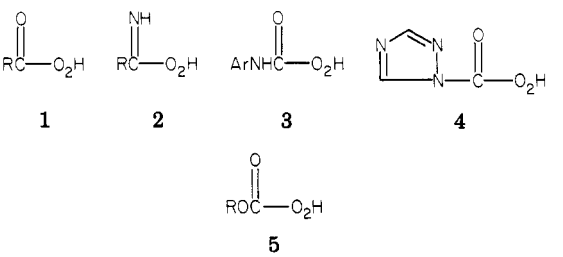
Department of Chemistry, Wayne State University, Detroit, Michigan 48202

Received July 1, 1982

An epoxide is a highly reactive functional group that can serve as a versatile synthetic intermediate. Epoxides are typically prepared from alkenes on a laboratory scale by the action of organic peroxides and metal catalysts[1] or by a variety of peroxy acids.[2] In general, the rate of epoxidation is enhanced by increased alkyl substitution on the double bond of the alkene which results in elevating the energy of the π bond (HOMO). Electron-withdrawing groups that have the capacity to lower the energy of the σ* level of the O–O bond (NLUMO) of the peracid will also facilitate oxygen transfer.

Trifluoroperacetic acid[3] is one of the most reactive peroxy acids, but it suffers the disadvantage of having to be prepared in situ by the action of trifluoroacetic anhydride and 90% hydrogen peroxide. The resulting solution is highly acidic and can have deleterious effects upon the yield of epoxide. Attempts to utilize a carboxylic acid–peracid exchange with H_2O_2 also requires a strong acid catalyst. Consequently, *m*-chloroperbenzoic acid (MCPBA)[4] is one of the most commonly used commercially available oxidants in the epoxidation of simple alkenes.

Two research objectives in the area of oxirane chemistry that have recently received attention include the development of chiral metal catalysts for use in asymmetric epoxidation[5] and the utilization of hydrogen peroxide as the primary oxidant.[6] Since hydrogen peroxide is not sufficiently electrophilic to directly epoxidize a nonconjugated carbon–carbon double bond, its reactivity must be enhanced by placing the OOH moiety in conjugation with a multiple bond as exemplified in structures **1–5**.



1 **2** **3** **4**

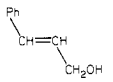
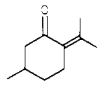
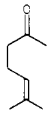
5

One of the earliest and most useful adaptations of this principle was accomplished by Payne.[7] He successfully activated the O–O bond by the in situ formation of a peroxyimidic acid (**2**) resulting from the base-catalyzed addition of H_2O_2 to a nitrile. Both aceto- and benzonitrile

(1) Sharpless, K. B.; Verhoeven, T. R. *Aldrichimia Acta* **1979**, *12*, 63.
(2) (a) House, H. O. "Modern Synthetic Reactions", 2nd ed.; W. A. Benjamin: Menlo Park, CA, 1972; p 292. (b) Swern, D. *Org. React.* **1953**, *7*, 378.
(3) Lewis, S. N. In "Oxidation"; Augustine, R. L., Ed.; Marcel Dekker: New York, 1969; Vol. 1, p 216.
(4) Fieser, M.; Fieser, L. F. "Reagents for Organic Synthesis"; Wiley-Interscience: New York, 1967; Vol. 1, p 135.
(5) (a) Katsuki, T.; Lee, A. W. M.; Ma, P.; Martin, V. S.; Masamune, S.; Sharpless, K. B.; Tuddenham, D.; Walker, F. J. *J. Org. Chem.* **1982**, *47*, 1373. (b) Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 5974.
(6) For a recent review see: Rebek, J., Jr. *Heterocycles* **1981**, *15*, 517.
(7) (a) Payne, G. B.; Deming, P. H.; Williams, P. H. *J. Org. Chem.* **1961**, *26*, 659. (b) Payne, G. B. *Tetrahedron Lett.* **1962**, *18*, 763.

0022-3263/83/1948-0888$01.50/0

Table I. Two-Phase Epoxidation of Alkenes with Peroxytrichloroacetimidic Acid[a]

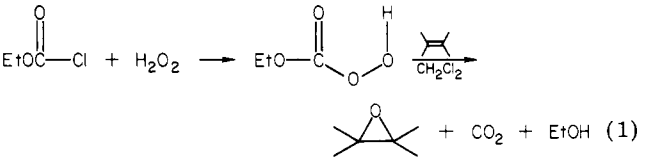
compd	equiv of reagents: Cl_3CCN	equiv of reagents: H_2O_2[b]	time, h	isolated yield of epoxide,[c] %
cyclohexene	2.5	2.5	3-6	60 (72)
1-methylcyclohexene	2.0	2.1	3	74 (82)
cis cyclooctene[d]	3.0	2.5	3-6	73 (88)
trans-cyclooctene	2.5	2.5	1.0	(90)
norbornene	2.0	1.9	6-10	68 (89)
1-nonene[e]	5.0	4.9	20-24	67 (71)
cis-stilbene	3.4	3.4	16	82
trans-stilbene	3.4	3.4	16	85
	3.0	2.6	24	57
	2.5	2.6	6	78 (89)
	2.0	1.5	3-6	80
	2.0	2.0	6-12	60 (78)

[a] All reactions were carried out at room temperature in CH_2Cl_2 at a pH of 6.8-7.0 in the aqueous phase. [b] Unless otherwise noted, commercial aqueous 30% H_2O_2 was utilized. [c] Values in parentheses were determined by gas chromatography. [d] When 1.05 and 1.2 equiv of reagents were used, the GC yield was over 84% after 16 h at 40 °C. [e] With 3 equiv of 90% H_2O_2 the reaction was complete in less than 20 h.

were employed as coreactants in the epoxidation of a variety of alkenes in methanol solvent. More recently, Rebek[8] has developed a number of reactive oxidizing reagents resembling **3** and **4** and related α-substituted hydroperoxides[9] that form oxiranes under very mild conditions. Another novel oxidizing agent based upon the addition of hydrogen peroxide to hexafluoroacetone has been reported by Ganem.[10,11]

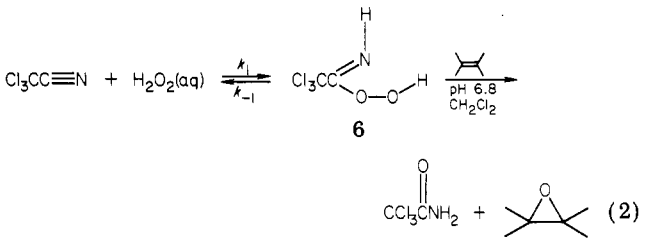
Our initial interest in the epoxidation reaction was stimulated by an observation by Coates[12] that *O*-benzylmonoperoxycarbonic acid was capable of epoxidizing an alkene and was intermediate in reactivity between peroxybenzoic acid and MCPBA. We found that an *O*-alkylperoxycarbonic acid could be readily generated in situ and reported[13a] a general epoxidation procedure based upon this reaction (eq 1).

Our dual objective in the present study was to develop a highly reactive epoxidizing reagent based upon 30% H_2O_2 that could compete with MCPBA on both a cost and reactivity basis. Safety and cost considerations often



(1)

discourage the use of MCPBA for large-scale syntheses. We recently demonstrated[13b] that the acetonitrile–hydrogen peroxide system reported by Payne[7] could be adapted to achieve alkene epoxidation on a molar scale.[14] This is a relatively safe and inexpensive procedure that avoids the handling of an organic peroxide. The intermediate peroxyimidic acids (**2**) in these reactions are highly reactive and have, to our knowledge, not yet been isolated. However, recent theoretical studies based upon ab initio calculations suggest that the structural and electronic features of peroxyformic[15a] and peroxyformimidic acids[15b] are quite similar. This observation prompted us to examine the effect of electron-withdrawing substituents on the reactivity of peroxyimidic acids in the epoxidation reaction. By analogy to the observed trends with peroxy acids (**1**), the trichloromethyl substituent should exhibit enhanced reactivity. As anticipated, the electron-deficient nitrile, trichloroacetonitrile, affords a highly efficient oxygen transfer reagent upon addition of H_2O_2 (eq 2).



(2)

Our procedure utilizes a biphasic solvent system that takes advantage of the fact that the rate of epoxidation is usually maximized in nonpolar solvents like methylene chloride.[16] In a typical experiment, 2–3 mmol of alkene and 4–6 mmol of trichloroacetonitrile in 30 mL of CH_2Cl_2 was cooled to 0 °C, and 4–6 mmol of H_2O_2 was added dropwise. The pH of the 30% aqueous H_2O_2 was adjusted to 6.8–7.0 prior to addition with the appropriate amount of K_2HPO_4. The reaction mixture was allowed to come to room temperature and then stirred for 3–24 h. For highly reactive alkenes or large-scale reactions, additional cooling may be required. The procedure is readily adaptable to large-scale synthesis of epoxides.[17,18]

The results summarized in Table I suggest that this oxidizing reagent exhibits the same reactivity trends as MCPBA. The rate of epoxidation is faster for more highly substituted and strained alkenes. The trichloroperoxyimidic acid (**6**) is sufficiently reactive to effect epoxidation of 1-nonene. A useful measure of the relative reactivity

(8) (a) Rebek, J., Jr.; Wolf, S.; Mossman, A. *J. Org. Chem.* **1978**, *43*, 180. (b) Rebek, J., Jr.; McCready, R.; Wolf, S.; Mossman, A. *Ibid.* **1979**, *44*, 1485.

(9) (a) Rebek, J., Jr.; McCready, R. *Tetrahedron Lett.* **1979**, 1001. (b) Rebek, J., Jr.; McCready, R. *Ibid.* **1980**, 2491. (c) Rebek, J., Jr.; McCready, R. *J. Am. Chem. Soc.* **1980**, *102*, 5602. (d) Rebek, J., Jr.; McCready, R.; Wolak, R. *J. Chem. Soc., Chem. Commun.* **1980**, 705.

(10) Heggs, R. P.; Ganem, B. *J. Am. Chem. Soc.* **1979**, *101*, 2484.

(11) For additional reagents utilizing H_2O_2 as the oxidant see: (a) Krishnan, S.; Kuhn, D.; Hamilton, G. *Tetrahedron Lett.* **1977**, 1369. (b) Mitsunobu, O.; Tomari, H.; Morimoto, H.; Sato, T.; Sudo, M. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 3607.

(12) Coates, R. M.; Williams, J. W. *J. Org. Chem.* **1974**, *39*, 3054.

(13) (a) Bach, R. D.; Klein, M. W.; Ryntz, R. A.; Holubka, J. W. *J. Org. Chem.* **1979**, *44*, 2569. (b) Bach, R. D.; Knight, J. W. *Org. Synth.* **1981**, *60*, 63.

(14) We reacted 4.4 mol of *cis*-cyclooctene with 522 g (4.6 mol) of commercial 30% H_2O_2 at 25–35 °C and recovered 335 g (60–61%) of *cis*-cyclooctene oxide when acetonitrile was used as the coreactant.[13b]

(15) (a) Bach, R. D.; Willis, C. L.; Lang, T. J. *Tetrahedron* **1979**, *35*, 1239. (b) Lang, T. J.; Wolber, G. J.; Bach, R. D. *J. Am. Chem. Soc.* **1981**, *103*, 3275.

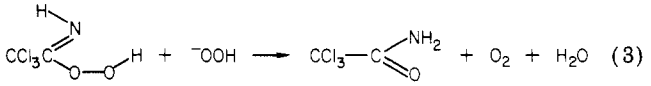
(16) The oxidizing agents derived from H_2O_2 and carbonylditriazole and related compounds containing a nitrogen that can hydrogen bond to the hydrogen of the peroxy group are insensitive to solvent basicity.[8b] This trend is in marked contrast to peroxy acids where disruption of hydrogen bonding results in a rate decrease.

(17) Slightly improved yields were realized if the organic phase was separated, pentane was added to facilitate precipitation of the trichloroacetamide, and the mixture was then cooled in a freezer prior to filtration.

(18) For example, 50. g (0.45 mol) of *cis*-cyclooctene on treatment with 1.5 equiv of CCl_3CN and 3 equiv of H_2O_2 (pH 6.8) afforded 48.0 g (84%) of *cis*-cyclooctene oxide. On a 2 molar scale the yield of epoxide was 76%.

of an oxygen-transfer reagent is its ability to epoxidize a weakly nucleophilic terminal alkene. Our data also demonstrate that **6** has chemoselectivity of practical value to the synthetic chemist. The deactivated double bonds of α,β-unsaturated carbonyls are epoxidized, although 2-cyclohexenone failed to react under our typical reaction conditions. No products derived from a Baeyer–Villiger oxidation were in evidence. The carbon–carbon double bond in 6-methyl-5-hepten-2-one was also selectively epoxidized. Another unique characteristic of this oxidant is its capacity to epoxidize 1-cyclopenteneacetonitrile without disturbing the nitrile functional group. The reaction is also stereospecific as evidenced by the formation of only cis epoxide from *cis*-stilbene and the trans epoxide from *trans*-cinnamyl alcohol, *trans*-stilbene, and *trans*-cyclooctene.

We propose a bimolecular mechanism involving nucleophilic attack of the alkene HOMO on the antibonding orbital of the O–O bond.[15b] The equilibrium constant for formation of **6** is quite low (i.e., $k_{-1} \gg k_1$). The rate expression consistent with this suggestion is rate = $K_{eq}k_2$-$[CCl_3CN][H_2O_2]$[alkene]. Consequently, the rate of reaction may be increased by increasing the ratio of coreactants to alkene. An increase in pH favors formation of **6**, but a competing reaction with the anion of H_2O_2 reduces the concentration of active oxygen by a direct nucleophilic displacement on the peroxide bond (eq 3).[19] The reaction times may be reduced by carrying out the reaction at reflux (~40 °).



The reaction may also be accomplished in methanol as the solvent, where the relative rates of epoxidation with benzonitrile and trichloroacetonitrile are comparable. However, under our biphasic conditions employing CH_2Cl_2 solvent, benzonitrile did not afford a detectable amount of epoxide. We made similar observations earlier where we noted that methanol solvent was required when acetonitrile was employed as the coreactant.[13b] We attribute these observations to a lack of solubility of the peroxyimidic acids (1; R = CH_3, Ph) in a nonpolar solvent.

We conclude that the trichloroacetonitrile–H_2O_2 system provides the versatility, specificity, ease of preparation, and mild reaction conditions required of an epoxidizing agent. This reagent should provide a practical substitute for MCPBA in many instances.

Experimental Section

6-Methyl-5,6-epoxyheptan-2-one. To a stirring solution of trichloroacetonitrile (8.5 g, 0.059 mol) and 6-methyl-5-hepten-2-one (3.72 g, 0.0294 mol) in 40 mL of methylene chloride was added dropwise 5.0 mL of 30% H_2O_2 (0.044 mol). The H_2O_2 was adjusted to pH 6.8 by the addition of 2.25 g of K_2HPO_4 prior to addition. The biphasic mixture was magnetically stirred at room temperature while the depletion of alkene was monitored by GLC (6-ft column, 10% UCW on Chromosorb W, 130 °C). After 3 h, 25 mL of pentane was added, and the precipitated trichloroacetamide was removed by filtration through a fritted disk and washed with pentane. The filtrates were washed with water (20 mL), cold 3% Na_2SO_3 solution (25 mL), and brine (25 mL) and dried ($MgSO_4$). The solvents were removed by aspiration, and the yellow residue was fractionally distilled to afford 3.35 g (80%) of epoxide, bp 42–42.5 °C (20 mm).

Acknowledgment. We gratefully acknowledge support from the National Science Foundation (Grant No. CHE-81-06520) and the National Institutes of Health (Grant No. ES00761-09).

Registry No. Cl_3CCN, 545-06-2; H_2O_2, 7722-84-1; cyclohexene, 110-83-8; cyclohexene oxide, 286-20-4; 1-methylcyclohexene, 591-49-1; 1-methylcyclohexene oxide, 1713-33-3; *cis*-cyclooctene, 931-87-3; *cis*-cyclooctene oxide, 4925-71-7; *trans*-cyclooctene, 931-89-5; *trans*-cyclooctene oxide, 57378-33-3; norbornene, 498-66-8; norbornene epoxide, 278-74-0; 1-nonene, 124-11-8; 1-nonene oxide, 28114-20-7; *cis*-stilbene, 645-49-8; *cis*-stilbene oxide, 1689-71-0; *trans*-stilbene, 103-30-0; *trans*-stilbene oxide, 1439-07-2; *trans*-cinnamyl alcohol, 4407-36-7; *trans*-cinnamyl alcohol epoxide, 40641-81-4; 2-isopropylidene-5-methylcyclohexanone, 15932-80-6; 2-isopropylidene-5-methylcyclohexanone epoxide, 17677-87-1; 6-methyl-5-hepten-2-one, 110-93-0; 6-methyl-5,6-epoxyheptan-2-one, 16262-93-4; 1-cyclopenteneacetonitrile, 22734-04-9; 1-cyclopenteneacetonitrile epoxide, 84694-14-4; peroxytrichloroacetimidic acid, 84694-15-5.

(19) Wiberg, K. B. *J. Am. Chem. Soc.* **1953**, *75*, 3961.

(24*S*)-24*H*-Isocalysterol: A New Steroidal Cyclopropene from the Marine Sponge *Calyx niceaensis*[1]

Toshihiro Itoh, Donato Sica,[2] and Carl Djerassi*

Department of Chemistry, Stanford University, Stanford, California 94305

Received July 13, 1982

Calysterol [23,28-cyclostigmasta-5,23(24)-dien-3β-ol, **N1**],[3,4] the principal sterol component of the sponge *Calyx niceaensis*, possesses one of the most intriguing functionalities, a cyclopropene ring, among the great variety of unusual side-chain substituents of marine sterols.[5] Recently we determined the absolute configuration (28*R*) of calysterol and isolated a novel steroidal cyclopropene, (23*R*)-23*H*-isocalysterol [(23*R*)-23,28-cyclostigmasta-5,24(28)-dien-3β-ol, **N2**] from *C. niceaensis*.[4] Our continuing study of the sterols of this sponge has now led to the isolation and characterization of a third steroidal cyclopropene, (24*S*)-24*H*-isocalysterol [(24*S*)-23,28-cyclostigmasta-5,23(28)-dien-3β-ol, **N3**] which forms the subject of this paper; in addition we have isolated two members of the rare class of Δ^{23}-unsaturated sterols, viz., (23*E*)- (**N4**) and (23*Z*)-stigmasta-5,23-dien-3β-ol (**N5**).

Reverse-phase HPLC of the sterol mixture of *C. niceaensis* yielded **N3** [M^+, m/z 410 ($C_{29}H_{46}O$); mp 111–113 °C; $[\alpha]^{20}_D$ −26° (*c* 0.007, CCl_4)]. The 360-MHz ^1H NMR spectrum (C_6D_6) showed the following side-chain signals: δ 1.020 (3 H, d, J = 6.8 Hz), 1.033 (3 H, d, J = 6.8 Hz), 1.092 (3 H, d, J = 6.6 Hz), 1.547 (1 H, d, J = 4.1 Hz), 1.70 (1 H, m), 1.975 (3 H, t, J = 1.4 Hz), 2.316 (1 H, ddd, J = 1.2, 7.9, 16.2 Hz), 2.473 (1 H, ddd, J = 1.9, 3.2, 16.2 Hz), besides signals arising from the usual Δ^5-3β-hydroxy sterol nucleus[6] [δ 0.659 (3 H, s, C-18), 0.931 (3 H, s, C-19), 3.38 (1 H, m, C-3α), 5.34 (1 H, m, C-6)]. Irradiation at δ 1.020,

(1) Minor and Trace Sterols in Marine Invertebrates. 36. For part 35 in this series, see: Itoh, T.; Sica, D.; Djerassi, C. *J. Chem. Soc. Perkin Trans. 1*, in press.

(2) Istituto di Chimica Organica dell'Università di Napoli, Naples, Italy.

(3) Fattorusso, E.; Magno, S.; Mayol, L.; Santacroce, C.; Sica, D. *Tetrahedron* **1975**, *31*, 1715.

(4) Li, L. N.; Li, H.-T.; Lang, R. W.; Itoh, T.; Sica, D.; Djerassi, C. *J. Am. Chem. Soc.* **1982**, *104*, 6717.

(5) Djerassi, C. *Pure Appl. Chem.* **1981**, *53*, 873 and references cited therein.

(6) Rubinstein, I.; Goad, L. J.; Clague, A. D. H.; Mulheirn, L. J. *Phytochemistry* **1976**, *15*, 195.

0022-3263/83/1948-0890$01.50/0