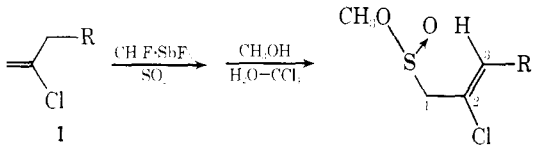
New Ene and Reverse Ene Reactions. Formation of Methyl Sulfinates in the Reaction of $CH_3F{\cdot}SbF_5$ in SO_2 and Loss of SO_2 from the Corresponding Sulfinic Acids

Sir:

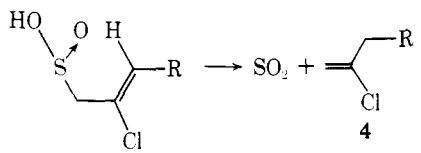
As mentioned in a recent review[1] the ene reaction has received less attention than the somewhat comparable Diels–Alder reaction. We now report two clean, rapid reactions, shown in Schemes I and II, which may be regarded as "ene" and reverse ene reactions, respectively. In the first reaction (Scheme I) we presume that vinyl halide **1** reacts

Scheme I



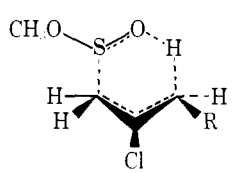
a. R = H; yield, 68%
b. R = $CH_2CH_2OCOCF_3$; yield, 83%

Scheme II



a. R = H; yield, 60% (GC analysis)
b. R = CH_2CH_2OH; yield, 60% (NMR analysis)

with the enophile, methylated, sulfur dioxide $[CH_3O\text{-}S{=}O]^+$ present in solutions of the strong methylating agent,[2] SbF_5–CH_3F in sulfur dioxide. Reaction via the six-electron, aromatic transition state, **5**, leads to a double bond shift. The methyl sulfinate **2**, probably remains protonated in the SO_2 solvent until the reaction mixture is added to a proton acceptor solvent (methanol). Alternatively, the reaction may proceed in discrete steps via a cationic intermediate.



A representative experimental procedure is the following. 4-Chloro-4-penten-1-yl trifluoroacetate, **1b** (20.3 g, 93 mmol) was dissolved in 20 ml of liquid SO_2 maintained at −65° in a 250-ml erlenmeyer flask. Antimony pentafluoride–methyl fluoride adduct in SO_2 (95 ml, 1 *M*) was added at −65° to the swirled solution. The mixture was poured immediately into 30 ml of CH_3OH and 3.32 g $NaHCO_3$, initially at −65°. The mixture was transferred to a 400-ml beaker and stirred magnetically as it was allowed to warm to room temperature. The acidic solution was brought to approximately pH 7 by addition of 50 ml of saturated $NaHCO_3$ and extracted with two 50-ml portions of CCl_4. Distillation of the washed (3 × 50 ml saturated NaCl) and dried ($MgSO_4$) extract through a short glass column gave 15.92 g, 57.6%: bp 118°, 0.25 Torr; ^1H NMR, CCl_4, δ 3.7 (s, CH_3O), 3.6 (m, CH_2SO_2R), 4.4 (t, $CH_2O_2CCF_3$), 5.85 (t, =CH–); ^{13}C NMR, $CDCl_3$, internal TMS, 28.17 (CH_2), 54.73 (CH_3O), 65.86 ($CH_2O_2CCF_3$), 67.52 (CH_2SO_2R), ca. 111, (q, CF_3), 126.25 (=CHR), 127.52 (=CClR), ca. 152 (q, C=O). Anal. Calcd for $C_8H_{10}F_4O_4S$: C, 32.61; H, 3.42. Found: C, 32.79; H, 3.48.

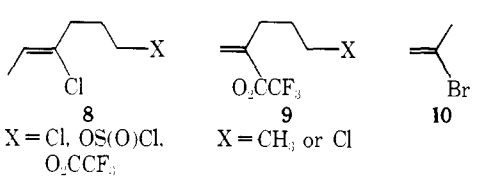
Identification of **2a** and **2b** is based on elemental analysis[3] of distilled products, plus ^{13}C and ^1H NMR spectroscopy including comparison with spectra of a sample of methyl butanesulfinate, kindly furnished by Professor I. B. Douglass. (See our ref 4 for references to studies of sulfinate esters by Professor Douglass and others.) The asymmetric sulfur should lead to magnetic nonequivalence of the S–CH_2 hydrogens in **2.** Under a variety of conditions, including the presence of shift reagents the CH_2 region is not resolved or is obscured by the CH_3O resonance at ~δ 3.7. In benzene solvent, however, with decoupling of vinyl hydrogens the 100-MHz spectrum of **2a** shows two ^1H peaks in the S–CH_2 region, attributable to the larger peaks of an AB quartet arising from nonequivalence and geminal coupling of the methylene hydrogens.

The double bond geometry of sulfinate **2b** was tentatively assigned from the following considerations. The ^{13}C chemical shift of C-1 in **2b** (67.52 ppm from TMS) should be similar to values which we measure (shown in parentheses) for the corresponding carbon in the vinyl halides **6** or **7**, after a correction is made for the effect of the sulfinate group. The correction term was estimated as the difference (42.33) between the chemical shift of the CH_3 group of hexane (14.16) and the CH_2–S carbon in methyl butanesulfinate, $CH_3OS(O)CH_2(CH_2)_2CH_3$ (56.49). The predicted values are 68.37 (based on **6**) and 62.70 (based on **7**), compared to

67.52, suggesting that **2b** has the carbons trans, as in **6.** (Chemical shifts were measured for 10% solutions in $CDCl_3$ on a CFT-20 spectrometer with 16K core.) The stereoselectivity (>90%, based on the ^{13}C NMR spectrum of **2b**) is tentatively attributed to interactions of groups which are cis on the double bonds in a product-like transition state. In the isomer having the carbon trans, R is cis to Cl and H is cis to CH_2. The interaction between R and Cl is thought to be preferred to the interaction between R and CH_2, which is present in the other isomer.

In addition to the examples given in Scheme I, the compounds shown in Scheme III appear to undergo the methyl-

Scheme III



sulfinylation reaction, based on ^1H NMR spectroscopy of the SO_2 solutions and CCl_4 extracts. In the case of the compounds **8** the vinyl hydrogen quartet of the NMR spectrum (δ, CCl_4, internal TMS, 5.65) changes to a vinyl triplet (δ, CCl_4, 5.70) upon reaction, providing striking evidence for the double bond shift. This evidence prompted us to postulate the reaction of Scheme I. The compatibility of halogen, trifluoroacetate, and chlorosulfite groups with the reaction conditions is noteworthy, as is the speed of the reactions. Only one enophile, hexafluorothioacetone, has previously

been observed to react rapidly to Dry Ice temperature (−78°).[5] We are investigating the conversion of the methyl sulfinylation products of **9** (for NMR data, see footnote 6) to β-ketosulfinates. Mixtures containing some methyl sulfinates were obtained upon reaction of **1**, R = CH_2CH_2CN, or 1-hexene[7] with $CH_3F{\cdot}SbF_5$ in SO_2.

The reverse ene reaction Scheme II, occurred upon basic hydrolysis of sulfinates **2a** and **2b**, followed by acidification and extraction with CCl_4. The extracts gave clean NMR spectra identical with those of solutions quantitatively prepared from distilled samples of vinyl halides. Yields, given in Scheme II, were based on NMR and GC analyses of the extracts and the corresponding standard solutions.

Currently there is considerable interest in the use of sulfoxide and sulfone activating groups in synthetic procedures, including alkylations.[8] Conditions required for removal of the sulfur activating group limit the scope of such procedures, however. We are exploring the possibility that comparable synthetic procedures may be based on the introduction and removal of sulfinate ester groups via the reactions of Schemes I and II.

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References and Notes

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(2) G. A. Olah, J. R. DeMember, and R. H. Schlosberg, *J. Am. Chem. Soc.*, **91**, 2112 (1969).
(3) For **2a**: Anal. Calcd for $C_4H_7ClO_2S$: C, 31.07; H, 4.56; Cl, 22.92; S, 20.73. Found: C, 31.24; H, 4.63; Cl, 22.74; S, 20.82. For **2a**, δ, ^1H NMR, CCl_4, internal TMS, 3.65 (d, CH_2S) 3.75 (s, CH_3O), 5.45 (s, $=CH_2$); ^{13}C NMR, neat, internal TMS, 58.6 (CH_3O), 68.2 (CH_2S), 121.8 ($=CH_2$), 131.6 ($=CCl$).
(4) (a) I. B. Douglass, *J. Org. Chem.*, **39**, 563 (1974); (b) *ibid.*, **30**, 633 (1965); (c) I. B. Douglass and D. A. Koop, *ibid.*, **27**, 1983 (1962); (d) I. B. Douglass, *ibid.*, **24**, 2004 (1959); (e) A. Meuwsen and H. Gebhardt, *Ber. Dtsch. Chem. Ges. B*, **70**, 792 (1937); (f) A. Meuwsen and H. Gebhardt, *ibid.*, **69**, 937 (1936); (g) P. Carre' and D. Liberman, *C. R. Acad. Sci*, **200**, 2086 (1935).
(5) W. J. Middleton, E. G. Howard, and W. M. Sharkey, *J. Am. Chem. Soc.*, **83**, 2589 (1961).
(6) NMR data for the methylsulfination product of **9**, X = CH_3, is as follows: ^1H, CCl_4, internal TMS, δ, 0.93 (t, CH_3), 1.45 (m, CH_2), 2.05, (q, CH_2), 3.62 (s, CH_2S), 3.72 (s, CH_3O), 5.65 (t, $=CH$); ^{13}C, $CDCl_3$, ppm from internal TMS, 13.57 (CH_3), 21.85 (CH_2), 27.91 (CH_2), 54.67 (OCH_3), 61.15 (CH_2S), 127.06 ($=CH$).
(7) It is reported that slow addition of alkenes to excess $CH_3F{\cdot}SbF_5$ in SO_2 gives carbon alkylation: G. A. Olah, J. R. DeMember, R. H. Schlosberg and Y. Halpern, *J. Am. Chem. Soc.*, **94**, 156 (1972).
(8) (a) P. A. Grieco and C. S. Pogonowski, *J. Org. Chem.*, **39**, 732 (1974); (b) P. A. Grieco, *J. Chem. Soc., Chem. Commun.*, 702 (1972); (c) B. M. Trost and T. N. Salzmann, *J. Am. Chem. Soc.*, **95**, 6843 (1973); (d) D. A. Evans, G. C. Andrews, T. T. Fujimoto, and D. Wells, *Tetrahedron Lett.*, 1385 (1973).

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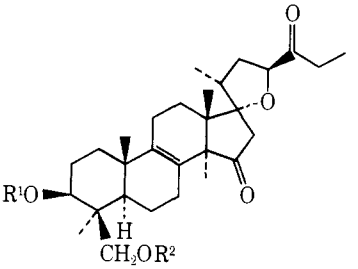
Eucosterol, a Novel Spirocyclic Nortriterpene Isolated from Bulbs of *Eucomis* Species

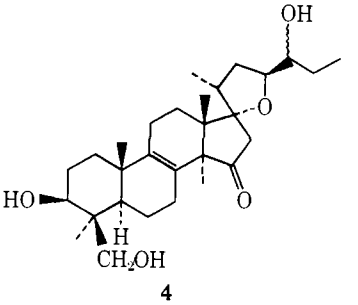
Sir:

During the past years a new class of natural products, the homoisoflavanones, has been discovered in the bulbs of several species of *Eucomis* (Liliaceae).[1-4] We now have isolated a hitherto unknown substance, which we name eucosterol (**1**), from the neutral extracts of the bulbs of *Eucomis autumnalis* (Mill.) Chitt., *Eucomis punctata* l'Hérit., and of a botanically undefined *Eucomis* species (ca. 60 mg per kilogram of undried bulbs). Eucosterol (**1**) proved to be a nortriterpene possessing a furanoid spirocyclic system as novel structural element. It crystallized as colorless needles from acetone, mp 221–223°; $[\alpha]^{25}D$ +20.4 ± 2° (chloroform). The molecular formula, $C_{29}H_{44}O_5$, was deduced from high resolution mass spectrometry.[5]

The positive Liebermann–Burchard test[6,7] and the formation of a 2,4-dinitrophenylhydrazone suggested the presence of a steroid or triterpene containing a double bond, a carbonyl, and hydroxyl groups. These results were supported by the ir spectrum (KBr) which exhibited absorptions at 1710 and 1728 cm^{-1} (C=O); 3290 and 3350 cm^{-1} (OH), and the uv spectrum with maxima at 290 (log ε 1.72) and 196 nm (log ε 3.77) (ethanol). The latter absorption suggested the presence of a tri- or tetrasubstituted double bond[8] and a cyclopentanone system. The 100-MHz ^1H NMR spectrum ($CDCl_3$) of **1** indicated the presence of four tertiary methyl groups (singlets at 0.96, 0.98, 1.28, and 1.41 ppm) of one secondary methyl group (doublet at 1.15 ppm, J = 7 Hz) and of an ethyl group attached to a carbonyl function (triplet at 1.09 ppm and quartet at 2.51 ppm, J = 7 Hz). The elimination of $C_3H_5O^+$ in the mass spectrum confirmed the latter assignment. The presence of one primary and one secondary hydroxyl group was detected in the ^1H NMR spectrum in $(D_3C)_2SO$ (multiplet at 4.08 ppm and doublet at 4.98 ppm, respectively). Accordingly, acetylation of **1** yielded a diacetate **2**, $C_{33}H_{48}O_7$, mp 168–170°; M^+ at m/e 556). Treatment of **1** with $CuSO_4$ in acetone[9]



1, $R^1 = R^2 = H$
2, $R^1 = R^2 = Ac$
3, $R^1 = R^2 = C(CH_3)_2$
6, $R^1 = H$; $R^2 = p\text{-}BrC_6H_4SO_2$–



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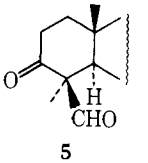

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yielded the *O*-isopropylidene derivative **3**, $C_{32}H_{48}O_5$, mp 203–204°, M^+ at m/e 512. This result, together with the findings that eucosterol (**1**) is not oxidized by KIO_4, indicated a 1,3-relationship of the two hydroxyl groups. Catalytic hydrogenation of **1** with PtO_2 in glacial acetic acid gave dihydroeucosterol **4**, $C_{29}H_{46}O_5$, mp 245–246°, $[\alpha]^{27}D$ +37 ± 2° (chloroform), M^+ at m/e 474. The ir spectrum showed only one carbonyl group at 1731 cm^{-1}. Upon treatment of **1** with CrO_3 in H_2SO_4–acetone, the keto aldehyde **5** ($C_{29}H_{40}O_5$, mp 205–213, $[\alpha]^{26}D$ +1.8 ± 2° (chloroform), M^+ at m/e 468) was formed. In the ir it exhibited several absorption bands between 1700 and 1735 cm^{-1}. The signal at 9.3 ppm (singlet) in the 100-MHz ^1H NMR spectrum is assigned to the aldehyde group.

Treatment of eucosterol **1** with *p*-bromobenzenesulfonyl chloride in pyridine at 25° yielded the *p*-bromobenzene-