= 6.8 Hz, Me_{19}), 0.77 (s, Me_{16}); mass spectrum, m/e 302 ($M^+ - H_2O$).

(4S*,7S*,14S*)-4,7,14-Trihydroxydolasta-1(15),8-diene (8). Reconcentration of the crude hexanes extract from Utila yielded impure crystalline **8**. Fractional recrystallization from benzene/hexanes gave fine needles: mp 163-166 °C; 371 mg (0.03%); $[\alpha]_D$ -112° ($CHCl_3$); ^1H NMR [(benzene-d_6 in Table I) $CDCl_3$] δ 0.72 (s, Me_{16}), 0.89 (d, J = 7 Hz, Me_{18}), 0.93 (d, J = 7 Hz, Me_{19}), 1.49 (s, Me_{20}); Mass spectrum, m/e 320 (M^+), 302 ($M^+ - H_2O$); exact mass m/e 302.211, calcd for $C_{20}H_{30}O_2$ 302.2244.

(4S*,6R*,14S*)-4,6-Diacetoxy-14-hydroxydolasta-1(15),8-diene (9). High-performance LC fraction 14 (6 mg) of the semipure oil from Dixon's Cove gave **9** as a yellow oil: $[\alpha]^{25}_D$ -144.6° (c 1.0, CH_3OH), ^1H and ^{13}C NMR data in Tables I and II; mass spectrum, m/e 404 (M^+), 338, 80 (base peak).

Dehydration of 5 to 4. Compound **5** stored in $CDCl_3$ at room temperature for several days quantitatively dehydrated to **4** as determined both by ^1H and ^{13}C NMR. The progress of this dehydration could easily be followed by monitoring the shift of (^1H NMR, benzene-d_6) multiplets of H_{17} (δ 1.82), H_6 (δ 3.14), and H_7 (δ 5.28) to H_{17} (δ 2.41), H_6 (δ 3.34), and H_7 (δ 5.34), respectively, and the appearance of H_{10} (δ 5.55).

Deacetylation of 4 to 6. A nitrogen-purged solution of compound **4** (1 mg) in 9.5 mL hexamethylphosphoric triamide (HMPT) and 0.5 mL distilled H_2O in a quartz tube was irridated with a low-pressure mercury lamp (λ = 2537 Å) for 5 h. Diethyl ether (20 mL) was added to the product mixture followed by washing with portions of H_2O (4 × 20 mL). Flash chromatography on silica gel (hexanes/diethyl ether), 95:5) gave **6** (<1 mg) whose ^1H NMR (360 MHz, benzene-d_6) was the same as that of the natural product isolated above (Table I).

Deacetylation of 5 to 10. Using the same procedure as described above, compound **5** (13 mg) in HMPT (1.9 mL) and water (0.1 mL) yielded, after silica gel flash chromatography (hexanes/diethyl ether, 1:1), pure **10** (3.4 mg) which showed the following: ^1H NMR (100 MHz, benzene-d_6) δ 5.36 (dd, J = 10, 4 Hz, H_7), 4.76 (s) and 4.58 (s), H_{15} and $H_{15'}$), 3.02 (dd, J = 14, 4 Hz, H_{6a}), 2.54 (dt, J = 10, 10, 4 Hz, H_{2a}), 1.16 (s, Me_{20}), 1.14 (d, J = 7 Hz, Me_{18}), 0.84 (s, Me_{16}), 0.82 (d, J = 7 Hz, Me_{19}).

Acetylation of 7 to 4. To compound **7** (13 mg) in 2 mL of dry pyridine was added 2 mL of freshly distilled acetic anhydride. This was stirred for 48 h at room temperature and diluted with 80 mL of benzene. It was washed with several portions of 1% HCl followed by $NaHCO_3$ solution (saturated). The organic layer was dried with $MgSO_4$, and the solvent was removed under vacuum. The residue was chromatographed by high-performance LC to give **4** whose ^1H NMR (360 MHz, benzene-d_6) matched that of an authentic sample.

Acetylation of 8 to 4. By employment of the above procedure, **8** (50 mg) yielded **4** whose ^1H NMR (360 MHz, benzene-d_6) matched that of an authentic sample.

Acknowledgment. We thank Professor William Fenical (UCSD-SIO) for a preprint of his manuscript and for copies of NMR spectra and Professor G. Pettit (ASU), who generously provided small samples of dolatriol and dolatriol-6-acetate. Support for this research was under a grant from the California Sea Grant Program, Department of Commerce, and a traineeship to B.L.M. We thank the University of California Research Expeditions Program for supporting our field work. We are also grateful to Professor David Ball (CSUC) for stimulating comments and to Mr. Jim Loo for his technical assistance with some of the spectroscopic work at UCSC. We thank Dr. Paul Silva (UCB) for assistance in algae identification. The 360-MHz NMR spectra were obtained at the Stanford Magnetic Resonance Laboratory supported by the National Science Foundation (Grant No. GR 23633) and the National Institutes of Health (Grant No. RR 00711).

Registry No. **3**, 75744-70-6; **4**, 79203-55-7; **5**, 80243-66-9; **6**, 80243-67-0; **7**, 80243-68-1; **8**, 80243-69-2; **9**, 80243-70-5; **10**, 80243-71-6; **11**, 80299-50-9.

Synthesis of (*E*)-1-Aryl-2-methyl-3-alkyl-2-propen-1-ones via Allylic Sulfoxide–Sulfenate Ester Rearrangements

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A synthon for vinyl anion **2** has been designed as the cornerstone for a versatile synthesis of (*E*)-1-aryl-2-methyl-3-alkyl-2-propen-1-ones (**1**). The choice of the allylic sulfoxide–sulfenate ester rearrangement as a synthesis conduit leads to formation of the desired *E* isomers stereoselectively. Attempted tetrahydropyran ring opening of enone **7c** was not successful.

As a prelude to a convergent organochemical preparation of members of the maytansine[1] family of antileukemic[2] ansa macrolides,[3] a general synthesis of (*E*)-1-aryl-2-methyl-3-alkyl-2-propen-1-ones (**1**) has been designed. The constraints of the synthesis plan mandated the intermediacy of an (*E*)-1-aryl-2-methyl-2-propen-1-one d_3 reagent,[4] i.e., the operational equivalent of the vinyl anion **2**.

Table I. Overall Yields of Purified Ketones 7 from Allylic Sulfides 3

compd	% yield	compd	% yield
7a	41	7c	39
7b	50	7d	49

Results and Discussion

Appropriation of synthetic methodology pioneered by Evans and his co-workers[5] resulted in a suitable synthon

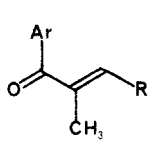
(1) (a) Kupchan, S. M.; Komoda, Y.; Braufman, A. R.; Sneden, A. T.; Court, W. A.; Thomas, G. J.; Hintz, H. P. J.; Smith, R. M; Karim, A.; Howie, G. A.; Verma, A. K.; Nagao, Y.; Daily, R. G., Jr.; Zimmerly, V. A.; Sumner, W. C., Jr. *J. Org. Chem.* **1977**, *42*, 2349. (b) Corey, E. J.; Weigel, L. O.; Chamberlin, A. R.; Hidetsura, C.; Hua, D. H. *J. Am. Chem. Soc.* **1980**, *102*, 6613. (c) Meyers, A. I.; Reider, P. J.; Campbell, A. L. *Ibid.* **1980**, *102*, 6597.

(2) Issell, B. F.; Crooke, S. T. *Cancer Treat. Rev.* **1978**, *5*, 199.

(3) Wehrli, W. *Top. Curr. Chem.* **1977**, *72*, 21.

(4) Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 239.

0022-3263/82/1947-0815$01.25/0



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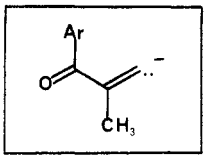
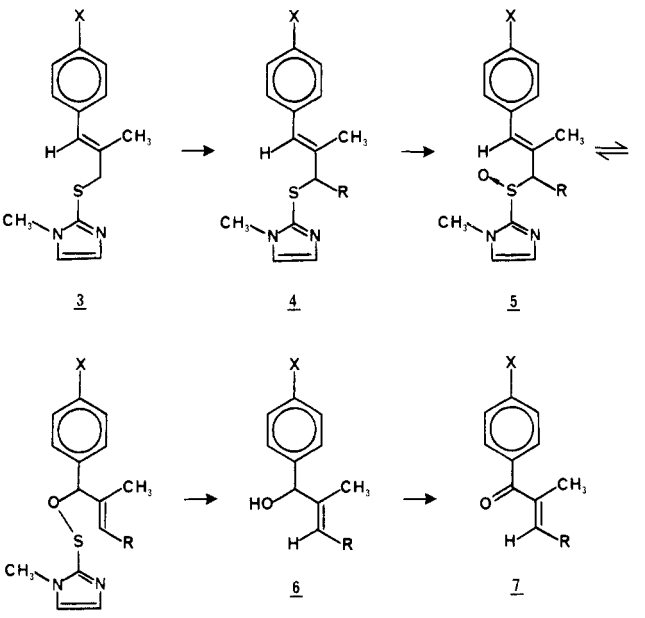


2

for anion **2**. Specifically, metalation (*n*-butyllithium) and alkylation (RI) of allylic sulfides **3**[6] provided sulfides **4** which were alkylated primarily α to sulfur,[7] due to the ability of the imidazole moiety to internally chelate lithium. Sulfides **4** were oxidized (*m*-chloroperoxybenzoic acid) to the corresponding allylic sulfoxides **5**, and advantage was taken of the well-known allylic sulfoxide–sulfenate ester equilibrium[8,9] to provide the desired allylic alcohols **6** via nucleophilic trapping (diethylamine) of the sulfenate ester.[5] Mild oxidation of alcohols **6** provided (*E*)-1-aryl-2-methyl-3-alkyl-2-propen-1-ones (**7**).[10,11] Some specific examples and overall yields are listed in Table I. The sequence of reactions outlined in Scheme I should be easily adaptable for the synthesis of a variety of phenyl ketones analogous to **7**.

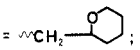
Scheme I



3 4 5

6 7

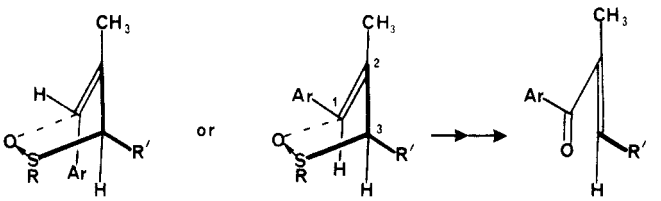
a. X = H, R = CH_3; b. X = Cl, R = CH_3;

c. X = H, R =  ; d. X = Cl, R =

Geometric Considerations

The sequence depicted in Scheme I is *E* specific, providing only one isomer of enones **7**. This can be discerned by ^{1}H NMR spectral comparison of **7a** to the known[12] *E* isomer and of **7b** to the known[12] *E* and *Z* isomers. Enones **7c** and **7d** are presumed to have the *E* geometry due to spectral similarities to **7a** and **7b** and to similar modes of preparation.

The *E* specificity of this enone synthesis is presumably dictated by the [2,3] sigmatropic rearrangement and is a hallmark of that process.[13] The allylic sulfoxide–sulfenate ester transformation appears to proceed through a cyclic five-membered transition state in which nonbonded interactions are minimized.[8] This usually requires pseudoequatorial positioning of substituents on the first and third carbons of the allyl system (see structure 8) to avoid energetically expensive 1,3-allyl interactions[14] and yields *E* alkenes[15] almost without exception.[16] In the present circumstance, ex post facto speculation leads to the pro-

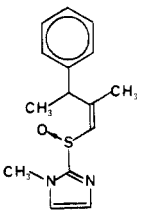


(Z)-8 or (E)-8 (E)-7

(5) Cf. Evans, D. A.; Andrews, G. C. *Acc. Chem. Res.* **1974**, *7*, 147.

(6) Allylic sulfides **3** were prepared from the appropriate α-methylcinnamaldehyde by conventional organochemical conversions (see Experimental Section).

(7) A specific search was made in the acid-soluble fractions of the workup (see Experimental Section) of allylic alcohols **6a** and **6c** for γ-alkylated products, which at that stage should be present as vinyl sulfoxides. In the former instance, an exiguous amount (~5%) of a product tentatively assigned structure a was isolated, but no γ-alkylated product could be found in the latter case (**6c**). Thus in spite of moderate overall yields for these syntheses, attrition of material cannot be ascribed to a lack of regioselectivity in the alkylation of sulfides **3**.



a

(8) Bickart, P.; Carson, F. W.; Jacobus, J.; Miller, E. G.; Mislow, K. *J. Am. Chem. Soc.* **1968**, *90*, 4869.

(9) For a beautiful application of this rearrangement for enzyme inactivation, see: Johnston, M.; Raines, R.; Walsh, C.; Firestone, R. *J. Am. Chem. Soc.* **1980**, *102*, 4241.

(10) The conformation depicted in Scheme I for enones **7** is arbitrarily chosen. For a discussion of actual conformations of such compounds, see: Thoai, N.; Chau, T.-M. *Can. J. Chem.* **1974**, *52*, 1331.

(11) The oxidation of alcohols **6** to ketones **7** appears to be the weak link in this synthetic sequence. Efforts to improve these yields are continuing.

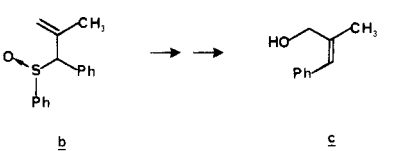
(12) (a) Dana, G.; Thuan, S. L. T.; Gharbi-Benarous, J. *Bull. Soc. Chim. Fr.* **1974**, 2089. (b) Lit.:[12a] ^{1}H NMR (CCl_4) for (*E*)-**7a** δ 1.90 (d, 3, J = 7 Hz, β-Me), 1.96 (d, 3, J = 0.5 Hz, α-Me), 6.36 (m, 1, olefinic H); for (*E*)-**7b** δ 1.88 (d, 3, J = 7 Hz, β-Me), 1.90 (d, 3, J = 0.5 Hz, α-Me), 6.3 (m, 1, olefinic H); for (*Z*)-**7b** δ 1.98 (d, 3, J = 6 Hz, β-Me), 2.05 (d, 3, J = 0.3 Hz, α-Me), 7.25 (m, 1, olefinic H). (c) Found: ^{1}H NMR (CCl_4) for (*E*)-**7a** δ 1.80 (d, 3, J = 7 Hz, β-Me), 1.84 (s, 3, α-Me), 6.29 (qm, J_1 = 7 Hz, olefinic H); for (*E*)-**7b** δ 1.80 (d, 3, J = 7 Hz, β-Me), 1.83 (s, 3, α-Me), 6.28 (qm, 1, J_1 = 7 Hz, olefinic H). (d) In spite of the puzzling discordance in methyl chemical shift data which is evident above, the diagnostic olefinic H chemical shifts are in agreement.

(13) Hoffman, R. W. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 563.

(14) For an unusual [2,3] sigmatropic (Wittig) rearrangement which exhibits a preference for a pseudoaxially substituted transition state, see: Still, W. C.; Mitra, A. *J. Am. Chem. Soc.* **1978**, *100*, 1927.

(15) Cf.: (a) Evans, D. A.; Andrews, G. C.; Fujimoto, T. T.; Wells, D. *Tetrahedron Lett.* **1973**, 1389. (b) For a recent application to maytansinoid synthesis, see: Ho, P.-T. *Can J. Chem.* **1980**, *58*, 861.

(16) A rearrangement in which sulfoxide b yields a 10:1 mixture of alkenes with *Z* isomer c predominating has been reported: Brownbridge, P.; Warren, S. *J. Chem. Soc., Perkin Trans. 1* **1976**, 2125. The bulky phenyl group apparently adopts a pseudoaxial position in the transition state to avoid steric interaction with the methyl substituent (see discussion in ref 14).



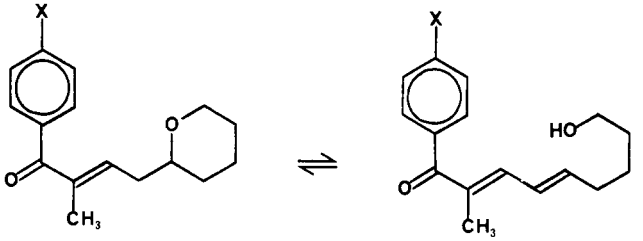
b c

posal of conformer (E)-8 of the E sulfoxides 5[17] as that which predominates and leads to the observed E products.

Diethylamine is a relatively sluggish thiophile (as contrasted with trimethylphosphite);[18] thus partial isomerization of E sulfoxides 5 to the Z isomers cannot be precluded. Current theory,[8,13] however, predicts the prevalence of E alcohols 6, irrespective of the geometry of the sulfoxide precursors (see putative major conformers (E)-8 and (Z)-8 above). This fortuitous circumstance does not necessarily obtain in the case of dissimilarly substituted allylic sulfoxides.

Ring Opening of Tetrahydropyranyl Ketones

Tetrahydropyranyl ketones **7c** and **7d** were prepared specifically to attempt ring opening to produce dienones **9**. This was in conjunction with model studies of may-



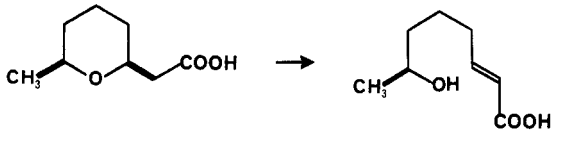
7c. X=H
7d. X=Cl

9

tansinoid synthesis and seemed feasible on the basis of recent accounts of similar processes.[19] Several different conditions (e.g., acid, base, protic, aprotic) failed to provide dienone **9**, yielding only starting materials or a mixture of byproducts.

Two particular examples are notable. Mukaiyama and Ishida[20] have used 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in dichloromethane to effect the conversion of β-methoxy aldehydes to polyenals, with molecular sieves present to scavenge the liberated methanol. When applied to ketone **7c** in which the liberated hydroxyl group remains a part of the parent molecule, these conditions return only starting material. Thus the tetrahydropyranyl ring either did not fragment or opened and then recyclized upon attempted isolation.

More appropos is the report[19e] that lithium diisopropylamide (LDA) brought about ring opening of the α-tetrahydropyranyl acid **10** to provide acyclic acid **11** in



10 11

high yield. When these conditions were applied to ketone **7c**, the isomeric β,γ-unsaturated ketone[21] was isolated and was easily converted back to the α,β-isomer by DBU in acetonitrile.

Experimental Section

Boiling points and melting points are uncorrected. Infrared spectra of neat liquids were recorded on a Pye-Unicam SP-1000 spectrophotometer. ^1H NMR spectra were run on $CDCl_3$ solutions with Me_4Si as an internal standard (δ 0) on either a Varian T-60 or an EM-360A 60-MHz spectrometer unless otherwise noted. Preparative TLC utilized Merck silica gel 60 GF_{254} as the adsorbent. Elemental analyses were performed by Galbraith Laboratories. Mass spectral data were provided by the Midwest Center for Mass Spectrometry at the University of Nebraska—Lincoln. Solutions of sodium bicarbonate, ammonium chloride, and potassium carbonate were aqueous and saturated. Tetrahydrofuran was distilled from lithium aluminum hydride immediately before use. Solutions were dried over anhydrous sodium sulfate.

(A) Synthesis of Allylic Sulfides 3. 2-Methyl-3-phenyl-2-propen-1-ol. Sodium borohydride (50.0 g, 1.3 mol) was added in portions to a stirred solution of 100.0 g (0.7 mol) of 2-methyl-3-phenyl-2-propenal (α-methylcinnamaldehyde; Aldrich) in 1 L of methanol which was cooled to 2 °C. The addition rate was such that the internal temperature remained below 10 °C (2.5 h). After removal of the methanol (rotary evaporator), the residue was diluted with 600 mL of ether, washed with seven 150-mL portions of water and 200 mL of brine, and dried. Removal of solvent left 95.9 g of crude alcohol. Distillation afforded the pure product (92%) as a colorless liquid: bp 92–93 °C (1.5 torr) [lit.[22] bp 85–88 °C (0.6 torr)]; IR 3100–3600 (OH) cm^{-1}; ^1H NMR δ 1.77 (s, 3 H, Me), 3.53 (s, 1 H, OH), 4.05 (s, 2 H, CH_2), 6.46 (br s, 1 H, olefinic H), 7.16 (s, 5 H, Ph)[22] (in some spectra a 1-Hz coupling was observed between the olefinic H and Me).

(3-Chloro-2-methyl-1-propenyl)benzene. This procedure is adapted from that of Rorig,[24a] and Cignarella.[22] Concentrated HCl[24b] (152 mL) was added to 89.61 g (0.61 mol) of 2-methyl-3-phenyl-2-propen-1-ol and the mixture stirred for 1 h. The mixture was diluted with 500 mL of ether and shaken, and the layers were separated. The organic phase was washed thrice with water and dried. Solvent removal left 97.20 g of crude chloride. Distillation provided 87.88 g (87%) of the pure product as a pale yellow liquid: bp 114–118 °C (12 torr) [lit.[22] bp 75 °C (1 torr)]; IR 1600 (w), 1446 (m), 1265 (m) cm^{-1}; ^1H NMR δ 1.87 (d, 3 H, J = 1 Hz, Me), 4.05 (s, 2 H, CH_2), 6.50 (br s, 1 H, olefinic H), 7.22 (s, 5 H, Ph).

1-Methyl-2-[(2-methyl-3-phenyl-2-propenyl)thio]-1*H*-imidazole (3a). This procedure is adapted from analogous ones by Evans and Andrews.[5,18b] 2-Mercapto-1-methylimidazole (6.930 g, 0.061 mol; Aldrich) was added to a stirring solution of sodium methoxide (from 1.395 g, 0.061 mol, of sodium) in 40 mL of methanol which was chilled in an ice/salt bath and protected from moisture by a $CaCl_2$ drying tube. After 5 min, 10.111 g (0.061 mol) of (3-chloro-2-methyl-1-propenyl)benzene was added in one

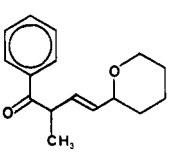
(17) The E geometry of sulfide **3b** is demonstrable by a straightforward nuclear Overhauser experiment, which shows an 18% peak height enhancement of the ^1H NMR signal for the vinyl hydrogen upon irradiation of the methylene and a 4% enhancement upon methyl irradiation (the sample was not degassed, and these NOE data are not necessarily maximal). For an NOE experiment on a similar compound, see ref 16. Sulfide **3a** is presumed to be E, owing to its spectral similarities to **3b** and their similar modes of preparation.

(18) (a) Evans, D. A.; Andrews, G. C. *J. Am. Chem. Soc.* **1972**, *94*, 3672. (b) Andrews, G. C. Ph.D. Dissertation, University of California at Los Angeles, 1974.

(19) Inter alia note the following. (a) α-Tetrahydropyranyl amide: Tulshian, D. B.; Fraser-Reid, B., personal communication. (b) α-Tetrahydropyranyl nitrile: Franck, R. W.; John, T. V. *J. Org. Chem.* **1980**, *45*, 1170. (c) α-Tetrahydropyranyl ketone: Kozikowski, A. P.; Schmiesing, R. J.; Sorgi, K. L. *J. Am. Chem. Soc.* **1980**, *102*, 6577. α-Tetrahydropyranyl acids: (d) Bartlett, P. A.; Adams, J. L. *Ibid.* **1980**, *102*, 337. (e) Seebach, D.; Pohmakotr, M. *Helv. Chim. Acta* **1979**, *62*, 843.

(20) Mukaiyama, T.; Ishida, A. *Chem. Lett.* **1975**, 1167, 1201.

(21) Salient features of the ^1H NMR spectrum (100 MHz) of β,γ-enone d: δ 1.20 (d, 3, J = 7 Hz, Me), 3.96 (q, 1, J = 7 Hz, MeCH), 5.32 (dd, 1, J_1 = 16 Hz, J_2 = 5 Hz, olefinic H), 5.57 (ddd, 1, J_1 = 16 Hz, J_2 = 6 Hz, J_3 = 2 Hz, olefinic H).



d

(22) Cignarella, G.; Occelli, E.; Testa, E. *J. Med. Chem.* **1965**, *8*, 326.

(23) Brownbridge, P.; Warren, S. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1131.

(24) (a) Rorig, K.; Johnston, J. D.; Hamilton, R. W.; Telinski, T. J. "Organic Syntheses"; Wiley: New York, 1963; Collect. Vol. IV, p 576. (b) For a milder, alternative preparation of allylic chlorides from allylic alcohols, see: Collington, E. W.; Meyers, A. I. *J. Org. Chem.* **1971**, *36*, 3044.

portion, and the mixture was stirred and allowed to come to room temperature overnight (~14 h). The milky yellow solution was diluted with 250 mL of water and extracted thrice with 100-mL portions of ether. The combined ether extracts were washed with 10% NaOH, water, brine, and dried. Evaporation of the solvent left 14.310 g (97%) of allylic sulfide **3a** as a yellow liquid. Due to its acceptable degree of purity and its heat lability,[25] this product was routinely used in the next reaction without purification. An analytical sample was prepared by preparative TLC [R_f 0.45–0.80 (ether)]: IR 1648 (w, C=C) cm^{-1}; ^1H NMR δ 1.97 (d, 3 H, J = 1 Hz, olefinic Me), 3.52 (s, 3 H, NMe), 3.70 (s, 2 H, CH_2), 6.08 (br s, 1 H, olefinic H), 6.87 (d, 1 H, J = 1 Hz, imidazole H), 7.08 (d, 1 H, J = 1 Hz, imidazole H), 7.17 (m, 5 H, Ph); mass spectrum, m/e 244 (M^+, base) 229, 211, 153, 131, 116, 91, 72; exact mass m/e 244.1043 (calcd for $C_{14}H_{16}N_2S$, 244.1034).

3-(4-Chlorophenyl)-2-methyl-2-propenal. This procedure was adapted from one by Kraft.[26] Freshly distilled propanal (10.859 g, 0.187 mol) was added dropwise to a stirring solution of 1.2 g (0.02 mol) of potassium hydroxide and 25.003 g (0.178 mol) of 4-chlorobenzaldehyde (Aldrich) in a mixture of 1.2 mL of water and 150 mL of 95% ethanol which was cooled in an ice/salt bath. The rate of addition was such that the internal temperature remained at 2 °C (1.5 h). The mixture was stirred and allowed to come to room temperature overnight (17 h). HCl (0.1 M, 105 mL) was added, and the mixture was chilled in an ice bath for 1 h. The precipitate was collected by filtration, washed with cold water, and dissolved in 100 mL of chloroform (attempted air-drying was not successful). The chloroform solution was washed with water and dried. Evaporation of solvent left a liquid which changed to a low-melting semisolid: mp 30–39 °C; 68% yield. A suitable crystallization solvent was not found. Distillation attempts were thwarted due to solidification of the distillate in the still head. The boiling point is approximately 110 °C (0.8 torr) [lit.[27] bp 120–125 °C (0.8 torr)]. The unpurified aldehyde was routinely used immediately in the next reaction: IR 1688 (s), 1626 (m) cm^{-1}; ^1H NMR δ 1.95 (d, 3 H, J = 1 Hz, Me), 7.10 (br q, 1 H, J = 1 Hz, olefinic H), 7.35 (s, 4 H, ClPh), 9.11 (s, 1 H, CHO); semicarbazone, mp 113–115 °C (95% ethanol).

3-(4-Chlorophenyl)-2-methyl-2-propen-1-ol. This reaction was carried out essentially as described above for 2-methyl-3-phenyl-2-propen-1-ol with 7.922 g (0.0209 mol) of sodium borohydride and 19.583 g (0.108 mol) of 3-(4-chlorophenyl)-2-methyl-2-propenal in 165 mL of absolute methanol to provide 17.384 g (88%) of the desired alcohol as a pale yellow solid, mp 48–54.5 °C. A suitable crystallization solvent was not found. Distillation can be inefficiently carried out (52% recovery) to provide the alcohol as a clear liquid [bp 120–142 °C (1.3–1.4 torr)] which slowly solidified. On one occasion during methanol evaporation, a small amount of crystalline product separated, was collected, and was dried to give white, crystalline flakes: mp 63–64.7 °C; IR (KBr) 3300 (s), 1580 (w), cm^{-1}; ^1H NMR δ 1.71 (s, 3 H, Me), 2.94 (br s, 1 H, OH), 3.93 (s, 2 H, CH_2), 6.18 (br s, 1 H, olefinic H), 6.98 (m, 4 H, ClPh).

Anal. Calcd for $C_{10}H_{11}OCl$: C, 65.76; H, 6.07; Cl, 19.41. Found: C, 65.57; H, 6.00; Cl, 19.18.

1-Chloro-4-(3-chloro-2-methyl-1-propenyl)benzene. Unpurified 3-(4-chlorophenyl)-2-methyl-2-propen-1-ol (17.384 g, 0.095 mol) was powdered and added in small portions (~0.5 g) over 0.5 h to 25 mL of concentrated HCl[24b] which was stirred and cooled in an ice bath. After an additional 1 h, the mixture was diluted with 260 mL of ether, washed with water, sodium bicarbonate solution, and brine, and dried. Removal of solvent gave 17.759 g of a dark yellow liquid. Microdistillation provided the desired chloride as a pale yellow liquid: 73% yield; bp 78–87 °C (0.1 torr). Product purified in this way was routinely used in the next reaction. The analytical sample was prepared by preparative TLC (R_f 0.60–0.91; ether): IR 1900 (w), 1591 (w), cm^{-1}; ^1H NMR δ 1.82 (d, 3 H, J = 1 Hz, Me), 3.97 (s, 2 H, CH_2), 6.26 (br s, 1 H, olefinic H), 6.99 (m, 4 H, ClPh); mass spectrum, m/e 202 (M^+), 200, 165 (base), 139, 130, 129, 115; exact mass m/e 202.0131 (calcd for $C_{10}H_{10}{}^{35}Cl^{37}Cl$, 202.1260).

(*E*)-2-[[3-(4-Chlorophenyl)-2-methyl-2-propenyl]thio]-1-methyl-1*H*-imidazole (3b). This reaction was carried out essentially as described above for the analogous compound **3a** by using 3.671 g (0.0320 mol) of 2-mercapto-1-methylimidazole (Aldrich), 0.743 g (0.0323 mol) of sodium in 25 mL of methanol, and 6.465 g (0.0322 mol) of 1-chloro-4-(3-chloro-2-methyl-1-propenyl)benzene to provide 8.593 g (96%) of crude allylic sulfide **3b** as a golden liquid. This was dissolved in a *minimum* amount of 1:1 ether/petroleum ether, chilled, and seeded to provide 6.605 g (74%) of the pure product **3b** as white, flaky crystals: mp 50.9–52.1 °C; IR (KBr) 1495 (m), 1445 (m), 1290 (m), 950 (m) cm^{-1}; ^1H NMR (270 MHz) δ 1.88 (d, 3 H, J = 1.5 Hz, Me), 3.46 (s, 3 H, NMe), 3.59 (d, 2 H, J = 0.9 Hz, CH_2), 5.92 (br s, 1 H, olefinic H), 6.84 (d, 1 H, J = 1.3 Hz, imidazole H), 6.95 (dm, 2 H, J = 8.5 Hz, 2 H of ClPh), 7.02 (d, 1 H, J = 1.3 Hz, imidazole H), 7.15 (dm, 2 H, J = 8.5 Hz, 2 H of ClPh).

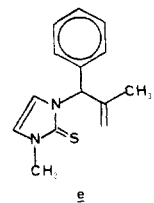
Anal. Calcd for $C_{14}H_{15}ClN_2S$: C, 60.31; H, 5.42; Cl, 12.72; N, 10.05. Found: C, 60.36; H, 5.51; Cl, 12.84; N, 9.99.

(B) Alkylation of Allylic Sulfides. 2-[(1,2-Dimethyl-3-phenyl-2-propenyl)thio]-1-methyl-1*H*-imidazole (4a). This procedure is adapted from analogous ones by Evans and Andrews.[18b] *n*-Butyllithium (10.7 mL of a 2.3 M solution in hexane, 0.0246 mol; Alfa) was added under nitrogen to 10 mL of dry tetrahydrofuran (THF) which was stirred and chilled in a dry ice/acetone bath. A solution of 5.770 g (0.024 mol) of unpurified allylic sulfide **3a** in 5 mL of THF was added dropwise over 5 min. After 10 min, a solution of 4.075 g (0.029 mol) of methyl iodide in 5 mL of THF was added, and the mixture was stirred for an additional 20 min. After being quenched with 5 mL of ammonium chloride solution, the mixture was allowed to warm to ambient temperature over 0.75 h, diluted with 500 mL of ether, washed with water and brine, and dried. Evaporation of the solvent left 6.160 g (101%) of the crude product **5a** as a golden liquid which was routinely used directly in the next reaction. The analytical sample was prepared by preparative TLC (R_f 0.29–0.64; 85:15 ether/petroleum ether): 92% yield; IR 1645 (w), 1600 (w) cm^{-1}; ^1H NMR δ 1.27 (d, 3 H, J = 7 Hz, Me), 1.74 (d, 3 H, J = 1 Hz, olefinic Me), 3.26 (s, 3 H, NMe), 3.83 (q, 1 H, J = 7 Hz, methine), 5.68 (br s, 1 H, olefinic H), 6.53 (d, 1 H, J = 1 Hz, imidazole H), 6.72 (d, 1 H, J = 1 Hz, imidazole H), 6.67–7.07 (br m, 5 H, Ph); mass spectrum, m/e 258 (M^+), 244, 225, 167, 153, 145 (base), 129, 114, 105, 91; exact mass m/e 258.1189 (calcd for $C_{15}H_{18}N_2S$, 258.3881).

2-[[3-(4-Chlorophenyl)-1,2-dimethyl-2-propenyl]thio]-1-methyl-1*H*-imidazole (4b). This reaction was carried out essentially as described for the preparation of compound **4a** to provide crude product **4b** as a golden liquid (103%) which was routinely used directly in the next reaction. The analytical sample[28] was prepared by preparative TLC (R_f 0.13–0.44; chloroform): 75% yield; IR 1645 (w), 1598 (w) cm^{-1}; ^1H NMR δ 1.41 (d, 3 H, J = 7 Hz, Me), 1.86 (d, 3 H, J = 1 Hz, olefinic Me), 3.48 (s, 3 H, NMe), 4.04 (q, 1 H, J = 7 Hz, methine), 5.87 (br s, 1 H, olefinic H), 6.73–7.31 (m, 6 H, ClPh and both imidazole H); mass spectrum, m/e 292 (M^+), 259, 181, 179 (base), 167, 153, 144, 128, 114; exact mass m/e 292.0799 (calcd for $C_{15}H_{17}{}^{35}ClN_2{}^{32}S$, 292.2571).

1-Methyl-2-[[2-methyl-3-phenyl-1-[(tetrahydro-2*H*-pyran-2-yl)methyl]-2-propenyl]thio]-1*H*-imidazole (4c). This reaction was carried out essentially as described for the preparation of compound **4a**, with the following exceptions: tetrahydro-2-

(25) Distillation of allylic sulfide **3a** caused its partial transmogrification into an isomeric alkene, tentatively identified as e (via a [3,3] sigmatropic rearrangement). Evans and Andrews[18b] have observed the analogous rearrangement of similar compounds.



e

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(28) An unidentified (isomeric?) impurity persisted in this sample (~30%).

(iodomethyl)pyran[29] was used instead of methyl iodide, and after the 20-min reaction period at -78 °C the mixture was allowed to warm to room temperature over 1 h before being quenched. The crude product **4c** was obtained as a light brown, viscous oil (102%) which was routinely used directly in the next reaction. The analytical sample (as a diastereomeric pair) was prepared by preparative TLC (R_f 0.13–0.56; 3:1 ether/petroleum ether): 79% yield; IR 1655 (w), 1609 (w) cm^{-1}; ^1H NMR δ 1.1–2.03 (m, 8 H, 4 CH_2) 1.86 (d, 3 H, J = 1 Hz, olefinic Me), 3.03–4.13 (m, 3 H, CH_2OCH), 3.43,3.46 (each s, 6 H, NMe from 2 diastereomers), 5.80, 5.94 (each br s, 2 H, olefinic H from 2 diastereomers), 6.80–7.28 (m, 7 H, Ph and 2 imidazole H); mass spectrum, m/e 342 (M^+), 309, 251, 228, 153, 143, 129, 114, 91, 85 (base); exact mass m/e 342.1769 (calcd for $C_{20}H_{26}N_2O^{32}S$, 342.5064).

2-[[3-(4-Chlorophenyl)-2-methyl-1-[(tetrahydro-2*H*-pyran-2-yl)methyl]-2-propenyl]thio]-1-methyl-1*H*-imidazole (4d). This reaction was carried out essentially as described for the preparation of compound **4c** to yield crude product **4d** (113%) as a viscous, golden oil which was routinely used directly in the next reaction. The analytical sample (as a diastereomeric pair) was prepared by preparative TLC (R_f 0.33–0.59; ether): 74% yield; IR 1650 (w), 1595 (w), 1585 (w) cm^{-1}; ^1H NMR (100 MHz) 0.93–1.95 (m, 8 H, 4 CH_2), 1.79 (d, 3 H, J = 1 Hz, olefinic Me), 2.91–3.51 (m, 2 H, OCH_2), 3.39, 3.41 (each s, 6 H, NMe from 2 diastereomers), 3.70–3.92 (m, 1 H, OCH), 5.68, 5.82 (each br s, 2 H, olefinic H from 2 diastereomers), 6.51–7.19 (m, 6 H, ClPh and 2 imidazole H); mass spectrum, m/e 376 (M^+), 278, 262, 251, 165, 153, 128, 114, 85 (base); exact mass m/e 376.1374 (calcd for $C_{20}H_{25}{}^{35}ClN_2O^{32}S$, 376.3760).

(C) Allylic Sulfoxide–Sulfenate Ester Rearrangement. Preparation of Allylic Alcohols from Alkylated Sulfides. α-(1-Methyl-1-propenyl)benzenemethanol (6a). This procedure is adapted from a similar one of Evans and Andrews.[18b] A solution of 1.842 g of 80–90% *m*-chloroperoxybenzoic acid (Aldrich) in 25 mL of dichloromethane was added dropwise over 20 min to a stirring solution of 2.118 g (8.209 mmol) of unpurified allylic sulfide **4a** in 25 mL of dichloromethane which was chilled in an ice/salt bath. The mixture was stirred 10 min at 0 °C under a drying tube, and then a mixture of 9.6 mL of diethylamine and 30 mL of methanol was added dropwise over 20 min. After an additional 10 min, the ice bath was removed and stirring continued for 23 h. The mixture was diluted with 300 mL of ether, washed with water, 10% HCl,[7] potassium carbonate solution, and brine, and dried. Evaporation of solvent afforded 1.032 g (78%) of the desired alcohol **6a** as a pale yellow liquid: IR 3440 (s), 1730 (m?), 1625 (m) cm^{-1}; ^1H NMR δ 1.39 (d, 3 H, J = 1 Hz, Me α to OH carbon), 1.55 (d, 3 H, J = 7 Hz, Me β to OH carbon), 2.77 (br s, 1 H, OH), 5.00 (br s, 1 H, methine), 5.59 (qm, 1 H, J = 7 Hz, olefinic H), 7.03–7.37 (m, 5 H, Ph). This spectrally pure product was used without purification in the next reaction due to its thermal and chromatographic lability.

4-Chloro-α-(1-methyl-1-propenyl)benzenemethanol (6b). This preparation was carried out essentially as described for compound **6a** to yield the alcohol **6b** (68%) as a pale yellow liquid: IR 3440 (s), 1910 (w), 1735 (m?), 1628 (w) cm^{-1}; ^1H NMR δ 1.39 (d, 3 H, J < 1 Hz, Me α to OH carbon), 1.57 (d, 3 H, J = 6 Hz, Me β to OH carbon), 2.13 (br s, 1 H, OH), 4.98 (br s, 1 H, methine), 5.57 (qm, 1 H, J = 6 Hz, olefinic H), 7.17 (s, 4 H, ClPh). This product appeared quite pure by ^1H NMR and, owing to its thermal and chromatographic lability, was used without purification in the next reaction.

α-[1-Methyl-3-(tetrahydro-2*H*-pyran-2-yl)-1-propenyl]benzenemethanol (6c). This preparation was carried out essentially as described for compound **6a** to provide the alcohol **6c** (77%) as a golden liquid:[7] IR 3430 (s), 1728 (w?), 1625 (w) cm^{-1}; ^1H NMR δ 0.72–1.88 (m, 6 H, $CH_2CH_2CH_2$), 1.40 (br s, 3 H, Me), 2.17 (dd, 2 H, J_1 = J_2 = 7 Hz, allylic CH_2), 2.85–3.62 (m, 3 H, OCH_2, OH), 3.62–4.07 (m, 1 H, OCH), 5.03 (br s, 1 H, methine), 5.62 (br t, 1 H, J = 7 Hz, olefinic H), 7.02–7.43 (m, 5 H, Ph). This product appeared to be quite pure by ^1H NMR, and owing to its thermal and chromatographic lability, it was used without purification in the next reaction.

4-Chloro-α-[1-methyl-3-(tetrahydro-2*H*-pyran-2-yl)-1-propenyl]benzenemethanol (6d). This preparation was carried out essentially as described for compound **6a** to give alcohol **6d** (82%) as a golden liquid: IR 3450 (s), 1910 (w), 1735 (m?), 1600 (w) cm^{-1}; ^1H NMR δ 0.60–1.95 (m, 6 H, $CH_2CH_2CH_2$), 1.40 (br s, 3 H, Me), 2.14 (dd, 2 H, J_1 = 8 Hz, J_2 = 6.5 Hz, allylic CH_2), 2.99–3.65 (m, 3 H, OCH_2OH), 3.65–4.10 (m, 1 H, OCH), 5.00 (br s, 1 H, methine), 5.59 (br t, 1 H, J = 6.5 Hz, olefinic H), 7.18 (s, 4 H, ClPh). This product appeared to be sufficiently pure by ^1H NMR for use directly in the next reaction.

(D) Oxidation of Allylic Alcohols to α,β-Unsaturated Ketones. (E)-2-Methyl-1-phenyl-2-buten-1-one (7a). A solution of 201 mg (1.241 mmol) of unpurified alcohol **6a** in 3 mL of benzene was added to a stirred suspension of 2.1 g of activated manganese dioxide[30] in 25 mL of benzene. The mixture was stirred at room temperature for 1.5 h, filtered, and concentrated in vacuo to afford 172 mg of crude product. Preparative TLC (R_f 0.25–0.47; 95:5 petroleum ether/ether) provided the pure ketone **7a** (52%) as a pale yellow liquid; IR 1731 (s), 1646 (s) cm^{-1}; ^1H NMR[12] δ 1.79 (d, 3 H, J = 6.5 Hz, β-Me), 1.82 (br s, 3 H, α-Me), 6.12 (qm, 1 H, J = 6.5 Hz, olefinic H), 7.03–7.53 (m, 5 H, Ph); 2,4-dinitrophenylhydrazone, mp 156–158 °C (from 95% ethanol).

Anal. Calcd for $C_{17}H_{16}N_4O_4$: C, 60.00; H, 4.74; N, 16.46. Found: C, 59.92; H, 4.72; N, 16.36.

(E)-1-(4-Chlorophenyl)-2-methyl-2-buten-1-one (7b). This reaction was carried out as described for compound **7a**. Preparative TLC (R_f 0.34–0.60; 9:1 petroleum ether/ether) gave the pure ketone **7b** (74%) as a pale yellow liquid: IR 1925 (w), 1734 (m), 1652 (s), 1592 (s) cm^{-1}; ^1H NMR[12] δ 1.75 (d, 3 H, J = 7 Hz, β-Me), 1.86 (s, 3 H, α-Me), 6.27 (qm, 1 H, J = 7 Hz, olefinic H), 7.23, 7.49 (AB, 2 H each, J = 8 Hz, ClPh); 2,4-dinitrophenylhydrazone, mp 177.5–178.5 °C (from 95% ethanol).

Anal. Calcd for $C_{17}H_{15}ClN_4O_4$: C, 54.48; H, 4.03; Cl, 9.46; N, 14.95. Found: C, 54.47; H, 4.01; Cl, 9.59; N, 14.92.

(E)-2-Methyl-1-phenyl-4-(tetrahydro-2*H*-pyran-2-yl)-2-buten-1-one (7c). A mixture of 414 mg (1.683 mmol) of unpurified allylic alcohol **6c** and 636 mg (1.691 mmol) of pyridinium dichromate[31] in 6 mL of dichloromethane was stirred at the ambient temperature for 4.5 h, diluted with 25 mL of ether, and filtered over a short silica gel column (Merck silica gel 60, 70–230 mesh) to provide 377 mg of crude ketone **7c** as a yellow liquid. Preparative TLC (R_f 0.32–0.55; 3:1 petroleum ether/ether) gave the pure ketone **7c** (50%) as a colorless liquid: IR 1648 (s), 1598 (m), 1578 (w) cm^{-1}; ^1H NMR δ 1.14–2.01 (m, 6 H, $CH_2CH_2CH_2$), 1.89 (d, 3 H, $J \approx 1$ Hz, Me), 2.36 (dd, 2 H, J_1 = 7 Hz, J_2 = 7 Hz, allylic CH_2), 3.06–3.54 (m, 2 H, OCH, and axial H of OCH_2), 3.62–4.00 (dm, 1 H, J_1 = 11 Hz, equatorial H of OCH_2), 6.27 (tq, 1 H, J_1 = 7 Hz, $J_2 \approx 1$ Hz, olefinic H), 7.11–7.70 (m, 5 H, Ph); 2,4-dinitrophenylhydrazone, mp 145–146 °C (from 95% ethanol).

Anal. Calcd for $C_{22}H_{24}N_4O_5$: C, 62.25; H, 5.70; N, 13.20. Found: C, 62.12; H, 5.85; N, 13.23.

(E)-1-(4-Chlorophenyl)-2-methyl-4-(tetrahydro-2*H*-pyran-2-yl)-2-buten-1-one (7d). This procedure was suggested by one of Meyers and Brinkmeyer.[32] A mixture of 162 mg (0.714 mmol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ; Aldrich) and 190 mg (0.677 mmol) of unpurified allylic alcohol **6d** in 7 mL of THF was stirred under nitrogen at room temperature for 72 h and then filtered over a short alumina column (Baker grade I, neutral alumina) with elution of 225 mL of ethyl acetate. Evaporation of the solvent left 186 mg of crude product. Preparative TLC (R_f 0.24–0.40; 3:1 ether/petroleum ether) gave the pure ketone **7d** (60%) as a pale yellow liquid: IR 1650 (s), 1590 (m) cm^{-1}; ^1H NMR (100 MHz) δ 0.68–1.97 (m, 6 H, $CH_2CH_2CH_2$), 1.85 (d, 3 H, J = 2 Hz, Me), 2.35 (dd, 2 H, J_1 = 10 Hz, allylic CH_2), 3.01–3.43 (m, 2 H, OCH, and axial H of OCH_2), 3.80 (dm, 1 H, J_1 = 11 Hz, equatorial H of OCH_2), 6.23 (tq, 1 H, J_1 = 10 Hz, J_2 = 2 Hz, olefinic H), 7.30, 7.51 (AB, 2 H each, J = 12 Hz, ClPh); 2,4-dinitrophenylhydrazone, mp 180–182 °C (from 95% ethanol).

Anal. Calcd for $C_{22}H_{23}ClN_4O_5$: C, 57.58; H, 5.05; Cl, 7.73; N, 12.21. Found: C, 57.47; H, 5.06; Cl, 7.70; N, 12.13.

Acknowledgment. The financial support of this work

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Registry No. 3a, 80317-38-0; **3b**, 80317-39-1; **4a**, 80317-40-4; **4b**, 80317-41-5; (*R**,*R**)-**4c**, 80317-42-6; (*R**,*S**)-**4c**, 80317-43-7; (*R**,*R**)-**4d**, 80317-44-8; (*R**,*S**)-**4d**, 80317-45-9; **6a**, 80317-46-0; **6b**, 80317-47-1; **6c**, 80317-48-2; **6d**, 80317-49-3; **7a**, 20047-50-1; **7a** 2,4-DNP derivative, 80317-50-6; **7b**, 56790-89-7; **7b** 2,4-DNP derivative, 80317-51-7; **7c**, 80317-52-8; **7c** 2,4-DNP derivative, 80317-53-9; **7d**, 80317-54-0; **7d** 2,4-DNP derivative, 80317-55-1; 2-methyl-3-phenyl-2-propen-1-ol, 1504-55-8; 2-methyl-3-phenyl-2-propenal, 101-39-3; (3-chloro-2-methyl-1-propenyl)benzene, 1507-88-6; 2-mercapto-1-methylimidazole, 60-56-0; 3-(4-chlorophenyl)-2-methyl-2-propenal, 24654-54-4; propanal, 123-38-6; 4-chlorobenzaldehyde, 104-88-1; 3-(4-chlorophenyl)-2-methyl-2-propen-1-ol, 80317-56-2; 1-chloro-4-(3-chloro-2-methyl-1-propenyl)benzene, 80317-57-3; methyl iodide, 74-88-4; tetrahydro-2-(iodomethyl)pyran, 43216-12-2.

Dibenzoxanthene Derivatives and Related Products from β-Naphthol and Aldehydes or Acetals

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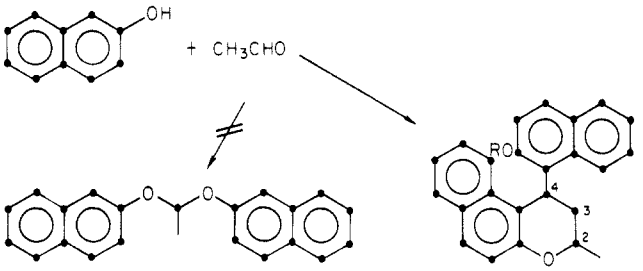
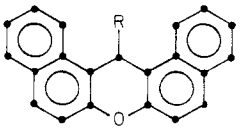
We have investigated several reactions of β-naphthol with aldehydes or aldehyde equivalents. Many of these reactions give novel structures. For example, reaction with paraldehyde does not yield the dinaphthyl acetal as previously reported but instead a compound which we show by spectroscopic methods to be 2-methyl-4-(2-hydroxy-1-naphthyl)benzo[*d*]chroman. Further, reaction with methyl dimethoxyacetate gives a furanone derivative and with malondialdehyde yields a dinaphthodioxabicyclo[3.3.1] derivative. The unusual reactions limit the utility of this reaction sequence for the preparation of xanthene derivatives.

Results

Claisen[1] reported that β-naphthol and paraldehyde react to form a compound, mp 200–201 °C, to which he attributed the structure **1**, the dinaphthyl acetal of acetaldehyde. Under similar conditions, we isolated a material, mp 198–200 °C, which we show has instead structure **2a**, 2-methyl-4-(2-hydroxy-1-naphthyl)benzo[*d*]chroman.



1 **2a**, R = H; **2b**, R = Ac



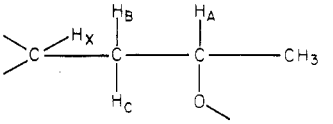
3a, R = CH_3
3b, R = $CH_2CH(OH)CH_3$

The mass spectrum and elemental analysis of **2a** are consistent with the structure shown. In the ^{13}C NMR spectrum, 19 of 20 possible aromatic resonances are observed, ruling out any structure with a plane of symmetry. Additional resonances indicated the presence of four aliphatic carbon atoms. On the basis of the off-resonance decoupled spectrum, these signals included one methyl (δ 22.3, q), one methylene (32.6, t), and two methine carbons, one bearing oxygen (25.3, d and 67.2, d).

Table I. ^1H NMR Data for Compound 2a (Me_2SO-d_6 Solvent)

	chemical shifts (δ)	coupling constant (Hz)
CH_3	1.50	J_{CH_3A} = 7.0
H_A	3.68	J_{AB} = 5.0
H_B	2.84	J_{AC} = 1.5
H_C	1.88	J_{BC} = 14.4
H_X	6.37	J_{BX} = 12.3
OH	8.65	J_{CX} = 2.1

^1H NMR studies, facilitated by decoupling experiments, support the following connectivity:



Chemical shifts and coupling constants are shown in Table I.

Structure **3b** was also considered to be consistent with these data. For structure **3b**, the magnetic nonequivalence of the naphthyl rings would be attributed to the chiral center in the hydroxypropyl side chain. Further, we have observed the formation of the symmetrical compound **3a**

(1) Claisen, L. *Justus Liebigs Ann. Chem.* **1887**, *237*, 271.

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