g, 60% yield) was obtained from the reaction between 0.50 g (2 mmol) and 0.29 g (2.5 mmol) of methyl fluorosulfonate in 3 ml of methylene chloride under the same condition as the previous reaction: mp 149–152°; NMR ($CDCl_3$) $\delta$ 1.73 (s, 18 H), 1.42 (s, 9 H), 4.50 (s, 3 H), and 7.90 (s, 2 H).

The reaction between 0.20 g (1 mol) of 4,5-dimethylacridine and 0.23 g (2 mmol) of methyl fluorosulfonate in 3 ml of methylene chloride yielded 0.19 g (60% yield) of the corresponding *N*-methyl salt after the work-up: mp 165–167°; NMR ($Me_2SO$-$d_6$) $\delta$ 7.90 (m, 7 H), 2.90 (s, 6 H), and 4.60 (s, 3 H).

**Stabilities Studies.** A mixture of 0.30 g (1.8 mmol) of potassium iodide and 0.20 g (0.6 mmol) of 2,6-di-*tert*-butyl-*N*-methylpyridinium fluorosulfonate (**6**) or 0.17 g (0.5 mmol) of 2,6-di-*tert*-butyl-*N*-methylpyridinium iodide (**2**) was introduced into a piece of U-shaped tubing 15 cm long and plugged with glass wool at both ends. The glass tubing was heated to 300° in a silicone oil bath under a nitrogen atmosphere. After allowing the mixture to cool to room temperature, it was treated with chloroform. The solid recovered was found to be the original N-methylated salt, by NMR analysis. A mixture of 0.20 g (1 mmol) of *N*-methyl-2,6-lutidinium fluorosulfonate or 0.23 g (1 mmol) of *N*-methyl-2,6-lutidinium iodide and 0.50 g (3 mmol) of potassium iodide was heated under the same conditions described in the cases of **2** or **6**. Decomposition occurred at 170°. Only 2,6-lutidine was recovered; no *N*-methyl peak was observed in the NMR.

**Acknowledgment.** We thank Mr. H. Shimizu for the preliminary experimental work in this investigation.

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# New Synthetic Methods. 1,3-Alkylative Carbonyl Transposition

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**Abstract:** Reaction of carbonyl compounds with vinyllithium reagents followed by quenching with benzenesulfenyl chloride produces the allylic sulfoxide resulting from [2,3]-sigmatropic rearrangement. Sulfenylation of the corresponding anion results in a net isomerization of the allylic sulfoxide into a $\gamma$-hydroxy-$\alpha,\beta$-unsaturated thioether. Hydrolysis to the enone or enal accomplishes the equivalent of a directed aldol condensation. Application to carbonyl partners that are easily enolized and that are hindered is illustrated. Addition of organolithium reagents to enones, quenching with benzenesulfenyl chloride, sulfenylation, and hydrolysis effect a 1,3-carbonyl migration and concomitant carbon–carbon bond formation at the former carbonyl carbon. Application of these methods to a model system for fusidic acid and the synthesis of a volatile constituent of Greek tobacco is reported.

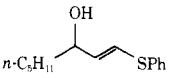
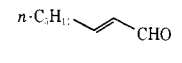
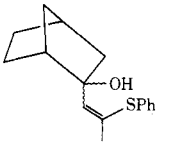
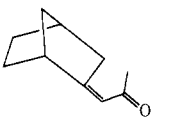
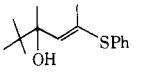
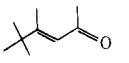
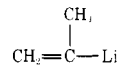
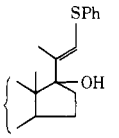
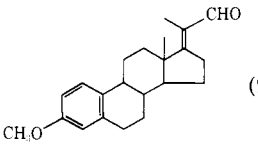
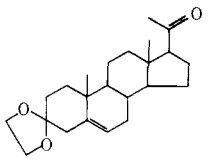
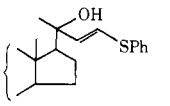
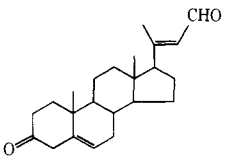
The aldol condensation continues to play a fundamental role in carbon–carbon bond forming reactions.[3] Despite its widespread utility, a decided limitation arises when nonidentical carbonyl partners are condensed as a result of the ambiguity in the direction of the cross condensation as well as the self-condensation of the partners. To overcome this restriction, various modifications to the mixed aldol reaction have appeared.

One modification makes use of the regiospecific generation of lithium enolates and/or the addition of magnesium or zinc cations to trap the mixed aldol product as its chelate.[4,5] Chemically differentiating one aldol partner prior to reaction also serves to direct the condensation. Reaction of a silyl enol ether with a carbonyl group[6] or a ketal,[7] or of an enol acetate with a ketal[8] in the presence of titanium tetrachloride results in the desired cross-condensation. Similar results have been noted in the reactions of enol ethers and acetals or aldehydes with boron trifluoride or zinc chloride.[9]

Other methods, which are restricted to the synthesis of aldehydes, also rely on the prior discrimination of the partners. The nucleophilic member of the condensation has been masked as the corresponding dihydro-1,3-oxazine[10] and as the metalated Schiff's base.[11] Improvement in the dehydration portion of these sequences has been found by the use of diethyl 2-(cyclohexylamino)vinylphosphonate which leads directly to the $\alpha,\beta$-unsaturated imine.[12,13] The anion of diethyl carboxaldehydomethylphosphonate[14] and the Wittig reagent from $\beta$-ketophosphonium salts[15] condense well only with aldehydes.

A quite different approach involves a two-carbon homologation of carbonyl groups which relies upon the initial addition of an allylic Grignard reagent,[16] a vinyl Grignard reagent,[17] or an acetylide anion[18] followed by further modification to the directed aldol product. These procedures especially point out that the aldol condensation can be considered to be an intermolecular 1,3-carbonyl transposition.

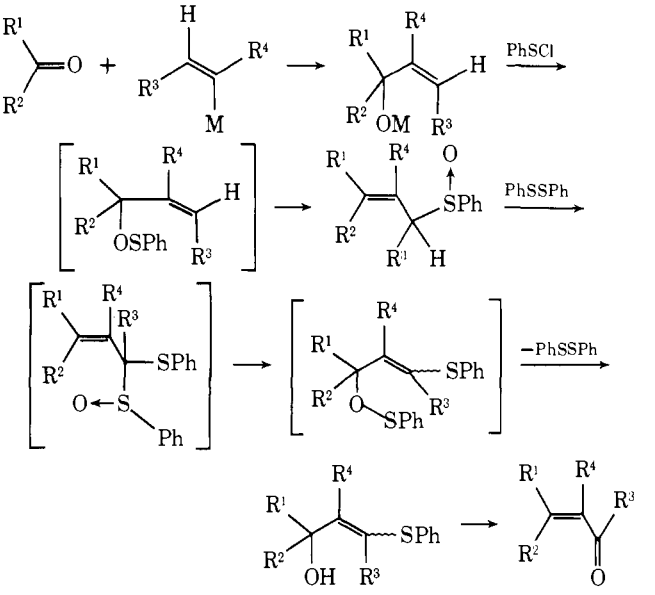
Table I. Intermolecular 1,3-Carbonyl Transposition[a]

| Entry | Carbonyl partner | Vinyl organometallic | Vinyl sulfide (%)[a] | Unsaturated carbonyl (%)[c] | Overall yield, %[b] |
|---|---|---|---|---|---|
| 1 | *n*-Hexanal | $CH_2$=CHMgBr |  (86) |  (93) | 80 |
| 2 | Norbornanone | $CH_3CH$=CHMgBr |  (57) |  (87) | 50 |
| 3 | Pinacolone | $CH_3CH$=CHMgBr |  (68) |  (71) | 48 |
| 4 | Estrone methyl ester |  |  (60) |  (92) | 55 |
| 5 |  | $CH_2$=CHMgBr |  (59) |  (75) | 44 |

[a] No attempt has been made to optimize yields. [b] This represents overall yield from starting carbonyl compound. [c] For discussion of stereochemistry, see text.

The intramolecular 1,3-carbonyl transposition of $\alpha,\beta$-unsaturated systems has considerable synthetic value. On treatment with hydrazine, an $\alpha,\beta$-epoxy carbonyl system rearranges to the inverted allylic alcohol.[19] The exchange of functionality can also be accomplished by the acid catalyzed allylic rearrangement of tertiary vinyl carbinols to the primary allylic acetates.[20] Allylic interconversions of an oxygen with an amine oxide,[21] sulfoxide,[22] and selenoxide[23] are available via 2,3-sigmatropic rearrangements. Most recently, a sequence involving an isoxazole constructed from an $\alpha,\beta$-unsaturated ketone has been developed.[24] We wish to report a single process that results either in an intermolecular 1,3-carbonyl transposition as an equivalent of a directed aldol condensation or in an alkylative intramolecular enone transposition which combines the direct sulfenylation of anions with the 2,3-sigmatropic rearrangement of allylic sulfoxides.[25,26]

Scheme I. Intermolecular 1,3-Carbonyl Transposition

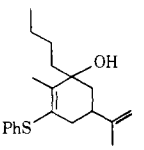
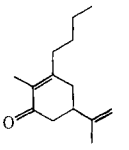
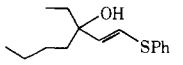
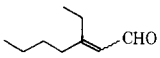
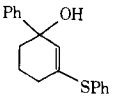
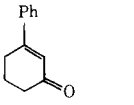
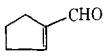
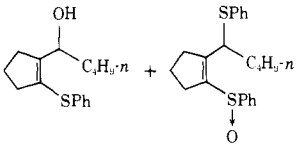
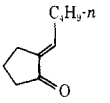


## Results

Scheme I and Table I illustrate the sequence for the intermolecular process. Typically, an allylic alcohol, generated by the addition of a vinyl organometallic to the carbonyl group, is treated with benzenesulfenyl chloride[27] to produce the allylic sulfoxide via a [2,3]-sigmatropic rearrangement. Addition of the allylic sulfoxide to 2 equiv of lithium diethylamide (preferable base) or lithium diisopropylamide in THF at −78° generates the anion which is inversely quenched by addition to 1 equiv of diphenyl disulfide in THF at 0°. The initial product of sulfenylation suffers in situ rearrangement and desulfenylation to yield the hydroxy enol thioether directly. Thus, there is no net consumption of diphenyl disulfide. The overall effect of this sulfenylation reaction is a novel isomerization of the allylic sulfoxide into the $\gamma$-hydroxy-$\alpha,\beta$-unsaturated thioether. Hydrolysis of the vinyl sulfide with 1–3 equiv of mercuric chloride[28] liberates the $\alpha,\beta$-unsaturated carbonyl compound in overall yields of 44–80%.

For the examples shown in entries 1 and 5, Table I, the hydroxy vinyl sulfide possesses only the *E* geometry as determined by the vinyl coupling constants in the NMR spectrum (see Experimental Section). In the latter case, two singlets at $\delta$ 1.25 and 1.36 for the methyl group at C-20 and a pair of doublets at $\delta$ 6.41 and 6.33 ($J$ = 16 Hz) for the vinyl proton at C-23 indicate an approximately 55:45 ratio of diastereomers at C-20. In both cases, however, the $\alpha,\beta$-unsaturated aldehyde[28] has the *E* geometry (entry 1, >99% *E*; entry 5, 95:5 *E*:*Z*). In the pinacolone example (Table I, entry 3), the NMR spectrum of the vinyl sulfide shows the presence of a single isomer, tentatively assigned the *E* geometry on comparison of the chemical shift of the vinyl proton to the other related compounds. Stereohomogeneity of the hydrolysis product[29] of this vinyl sulfide is indicated by

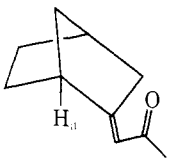
Table II. Intramolecular 1,3-Alkylative Carbonyl Transposition[a]

| Entry | Enone | Organometallic | Vinyl sulfide (%)[b] | | Unsaturated carbonyl (%)[b] | | Overall yield (%)[c] |
|---|---|---|---|---|---|---|---|
| 1 | Carvone | $n$-$C_4H_9Li$ |  | (68) |  | (92) | 63 |
| 2 | Ethyl vinyl ketone | $n$-$C_4H_9Li$ |  | (51) |  | (65) | 33 |
| 3 |  | PhLi |  | (77) |  | (92) | 71 |
| 4 |  | $n$-$C_4H_9Li$ |  1 + 1,3 | (85) |  | (68–71) | 59 |

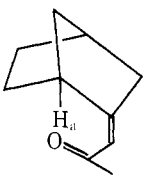
[a] Optimization of yields has not been performed. [b] For a discussion of stereochemistry, where applicable, see text. [c] This represents overall yield from starting enone.

the presence of only four clean absorptions in the NMR spectrum (see Experimental Section). The low-field absorption for the vinyl methyl group in this spectrum suggests the geometry at the double bond to be *E*.

The hydroxy vinyl sulfide from norbornanone appears to be a 1:5:13:13 mixture of all four stereoisomers as determined by the relative intensities of the four broad singlets for the vinyl proton at $\delta$ 6.23, 6.14, 5.98, and 5.92. The vinyl methyl group curiously appears as one sharp singlet at $\delta$ 2.04. Hydrolysis gave a 1:4 mixture of enones. The major isomer was assigned the stereochemistry depicted in **1a** and



**1a**

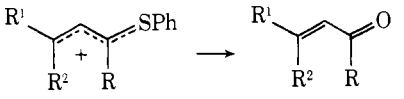


**1b**

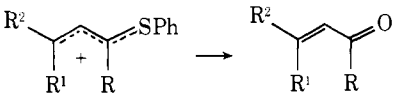
the minor isomer that in **1b**, based upon the fact that the bridgehead hydrogen, $H_a$, in the major isomer appears at $\delta$ 2.79 and in the minor isomer at $\delta$ 3.95. $Eu^{3+}$-induced shifts confirm this assignment. In the major isomer, addition of 10% $Eu(dpm)_3$ shifted the $CH_2CO$ from $\delta$ 2.48 to 3.71, while only shifting $H_a$ from $\delta$ 2.79 to 3.22.

In the estrone example (Table I, entry 4), a single hydroxy vinyl sulfide tentatively assigned the depicted stereochemistry was obtained after sulfenylation. The stereohomogeneity is indicated by the sharp singlets at $\delta$ 0.97, 1.95, and 6.04 for the angular and vinyl methyl groups and the vinyl proton, respectively. Nevertheless, hydrolysis led to a 1:1.2 *E*:*Z* mixture. The major isomer could be assigned the *E* stereochemistry based upon the higher field position ($\delta$ 1.00) of its angular methyl group in the proton NMR spectrum compared with that ($\delta$ 1.11) for the minor isomer.

The above results indicate that the stereochemistry of the final product is not determined by the stereochemistry of the hydroxy vinyl sulfide. The olefinic geometry can be rationalized by considering the relative stabilities of the presumed intermediates of hydrolysis, **2a** and **2b**.



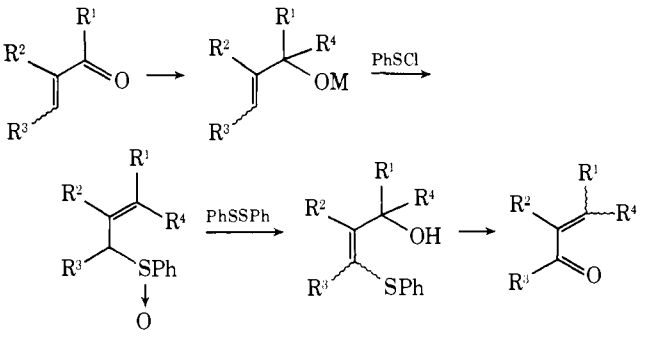
**2a**



**2b**

The availability of allylic alcohols by the organometallic addition or hydride reduction of enone systems allows the above method to be utilized as an intramolecular 1,3-carbonyl transposition. Scheme II and Table II summarize the

Scheme II. Intramolecular 1,3-Carbonyl Transposition



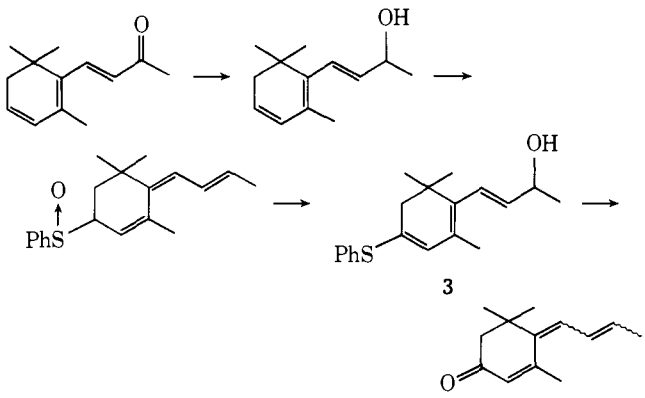
examples. In each case, the initial organometallic adduct was quenched with freshly prepared benzenesulfenyl chloride to produce the allylic sulfoxide directly. Sulfenylation and hydrolysis was performed as described earlier. 3-Ethyl-2-heptenal (Table II, entry 2) is produced as a nearly 1:1 isomeric mixture as determined by NMR spectroscopy and VPC. On the other hand, 2-pentylidenecyclopentanone[30] (Table II, entry 4) appears to be stereohomogeneous as shown by the presence of only one vinyl proton absorption. The cyclopentene-1-carboxaldehyde series was the only case in which the allyl anion sulfenylated both $\alpha$ and $\gamma$ with respect to the sulfoxide group. As expected, the product of $\alpha$-sulfenylation undergoes normal rearrangement and desul-

fenylation, but the product of γ-sulfenylation is isolated unchanged. While this ambident behavior becomes a problem in other applications of these substrates,[22b-d] this sequence is unaffected since both products hydrolyze to the same enone. However, for hydrolysis it is necessary to reduce the sulfoxide to the sulfide, which can be conveniently accomplished with stannous chloride and acetyl chloride in acetonitrile.[31]

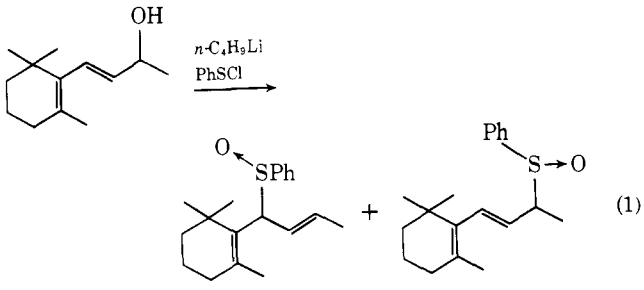
While the intermediates along the way have normally been isolated, a one pot transformation of the carbonyl compound into the hydroxy enol thioether has been performed in the case of ethyl vinyl ketone (Table II, entry 2). By comparison with the other examples, yields seem to be improved by purifying the sulfoxide immediately prior to sulfenylation.

An interesting application of this method is the conversion of 3,4-dehydro-β-ionone[32] to megastigma-4,6,8-trien-3-one, a key flavoring compound from Burley tobacco condensate as well as Greek and Turkish tobaccos (see Scheme III).[33,34] Initial studies were carried out with β-ionol.[35] Sul-

Scheme III. Synthesis of Megastigma, 4,6,8-trien-3-one




fenate-sulfoxide rearrangement (eq 1) led mainly to un-

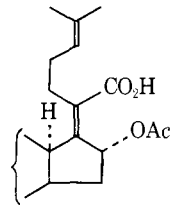



(1)

rearranged β-ionyl phenyl sulfoxide.[36] *On the other hand, 3,4-dehydro-β-ionol, available from 3,4-dehydro-β-ionone by reduction with diisobutylaluminum hydride, undergoes [2,7]-sigmatropic rearrangement!* While the course of this reaction remains unknown, a reasonable possibility is a series of three [2,3]-sigmatropic rearrangements. Sulfenylation results in an equally facile net [2,7] rearrangement to give **3** in 25% overall yield. The *E* stereochemistry is assigned on the basis of the 16 Hz coupling constant between the vinyl protons. While **3** is stereohomogeneous, hydrolysis produces a geometric mixture whose spectral properties agree with the published data.[34]

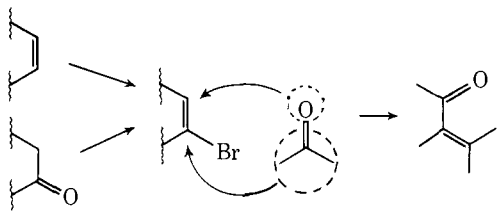
## Discussion

The intermolecular version of this carbonyl transposition sequence can be considered as a novel approach to cross aldol condensation. We have achieved the equivalent of such a condensation in which acetaldehyde, propionaldehyde, and acetone would have served as the active methylene partner. The utilization of organolithiums rather than enolates or their equivalents has an advantage in terms of the higher reactivity of the former and the irreversibility of their addition. Thus, hindered ketone partners (Table I, entries 3 and 4) react well. The estrone example suggests this approach may be suitable for adding the side chain of fusidic acid (**4**) onto a steroid nucleus.



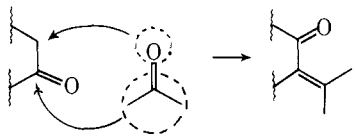

**4**

This approach also complements the existing methods. It employs a different substrate, a vinyl bromide, as the "active methylene partner". Since the availability of the latter from olefins and ketones is well documented,[37,38] it serves as an elaboration of such systems (eq 2). The latter is par-

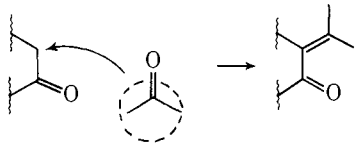



(2)

ticularly intriguing since it involves a novel reorientation (see eq 3) of the active methylene partner relative to the aldol condensation (see eq 4).

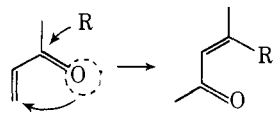



(3)




(4)

Conceptually, the intramolecular version achieves a net inversion of an α,β-unsaturated carbonyl system with the ability to form a new carbon-carbon or carbon-hydrogen bond at the former carbonyl group (eq 5).




(5)

## Experimental Section

Melting points were taken on a Thomas-Hoover melting point apparatus and are corrected. Infrared spectra were determined on a Perkin-Elmer 267 spectrophotometer, and ultraviolet spectra were recorded on Cary Model 11 and Model 15 spectrophotometers. NMR spectra were determined on a MHL-100 spectrometer fitted with a variable-temperature probe. Chemical shifts are given in parts per million relative to $Me_4Si$ as an internal standard. Mass spectra were taken on a MS-902 mass spectrometer at an ionizing current of 40 mA and ionizing voltage of 70 V. VPC analyses were performed on an Aerograph Model 90P instrument.

Tetrahydrofuran was dried by distillation from sodium benzophenone ketyl. Diethyl and diisopropylamines were freshly distilled from calcium hydride.

All TLC and PLC operations were performed utilizing silica gel PF-254. Dry column chromatography used W. R. Grace silica gel grade 62 (60–200 mesh) with 0.5% by weight of Du Pont 609 phosphor.

**Hexanal Series. A. Preparation of 3-Hydroxy-1-octene.** Utilizing the standard procedure of Normant,[39] vinylmagnesium bromide was prepared from 27.8 g (0.26 mol) of vinyl bromide and 5.84 g (0.24 g-atom) of magnesium in 90 ml of dry THF. In this way, 28.0 g (100%) of colorless oil, bp 30° (0.15 mm) [lit.[40] bp 81–82° (20 mm)] was obtained.

**B. Preparation of 1-(*E*)-2-Octenyl Phenyl Sulfoxide.** Utilizing the procedure of Grieco et al.,[22c] the lithium alkoxide of 3-hydroxy-1-octene, prepared from 670 mg (5.23 mmol) of alcohol in 15 ml of dry THF and 3.35 ml of 1.50 *M* (5.23 mmol) *n*-butyllithium in hexane, was reacted with 755 mg (5.23 mmol) of benzenesulfenyl chloride.[27] Purification by PLC utilizing ether ($R_f$ 0.6) gave 1.24 g (100%) of pure colorless oil: ir ($CCl_4$) 1655 and 1050 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 7.28–7.72 (5H, m), 5.4 (m, 2 H), 3.46 (d, $J$ = 6 Hz, 2 H), 2.00 (m, 2 H), 1.24 (bs, 6 H), 0.87 (t, $J$ = 5 Hz, 3 H); MS *m/e* (rel %) 236 (0.2), 222 (4), 218 (2), 126 (100), 111 (40), 110 (37), 78 (29), 77 (20), 69 (70), 55 (52); mol wt (calcd for $C_{14}H_{20}OS$, 236.1239) 236.1234.

**C. Preparation of (3-Hydroxy-1-octenyl) Phenyl Sulfide.** To 640 mg (6.35 mmol) of diisopropylamine in 15 ml of dry THF at −78° was added 4.23 ml of 1.50 *M* (6.35 mmol) *n*-butyllithium solution in hexane. After 15 min, 1.40 g (5.94 mmol) of sulfoxide was added in one portion. After stirring 1 hr at −78°, the anion solution was added to a solution of 1.53 g (7.00 mmol) of diphenyl disulfide in 10 ml of dry THF at 0°. The reaction was stirred 1 hr at 0°, poured into 75 ml of 10% aqueous hydrochloric acid, and extracted with 4 × 50 ml of chloroform. The combined organic portions were washed with 30 ml of 10% aqueous sodium bicarbonate, dried ($Na_2SO_4$), and evaporated at 25° in vacuo to leave a yellow oil. Purification by PLC (ether, $R_f$ 0.90) gave 1.20 g (86%) of pure colorless oil: ir ($CCl_4$) 3610, 3430, 1600, and 1580 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 7.31 (m, 5 H), 6.42 (d, $J$ = 16 Hz, 1 H), 5.86 (dd, $J$ = 16, 7 Hz, 1 H), 4.17 (q, $J$ = 7 Hz, 1 H), 2.15 (bs, 1 H), 1.1–1.8 (m, 8 H), 0.88 (t, $J$ = 7 Hz, 3 H); MS *m/e* (rel %) 236 (21), 218 (29), 165 (67), 123 (42), 110 (100), 109 (77), 91 (27), 78 (21), 77 (42), 65 (45), 57 (39), 55 (69), 51 (41), 45 (45); mol wt (calcd for $C_{14}H_{20}OS$, 236.1235) 236.1234.

**D. Preparation of (*E*)-2-Octenal.** To 236 mg (1.00 mmol) of (3-hydroxy-1-octenyl) phenyl sulfide in 10 ml of acetonitrile and 2 ml of water was added 286 mg (1.05 mmol) of mercuric chloride. The reaction was stirred at 50° for 17 hr, cooled to 25°, and filtered to remove precipitated mercury salts. The precipitate was washed with chloroform and the latter combined with the initial filtrate. The combined solution was washed with 25 ml of 10% aqueous sodium bicarbonate and extracted with 3 × 25 ml of chloroform. After drying ($Na_2SO_4$) the organic layer, it was evaporated in vacuo at 0° (20 mm) to leave a yellow oil which was purified by PLC ($CHCl_3$, two elutions, $R_f$ 0.2) to give 129 mg (93%) of pure (*E*)-2-octenal, whose spectral properties were identical with published data.[41]

**1-Cyclopentenecarboxaldehyde Series. A. Preparation of 1-(2-Pentylidenecyclopentyl) Phenyl Sulfoxide.** To 1.00 g of 1-cyclopentenecarboxaldehyde[42] (10.4 mmol) in 10 ml of dry THF at −78° was added 7.65 ml of 1.50 *M* (11.5 mmol) *n*-butyllithium solution in hexane. After 30 min, 1.67 g (11.5 mmol) of benzenesulfenyl chloride was added. After stirring 15 min at −78°, the reaction was stirred at 25° for 2 hr, poured into saturated aqueous sodium chloride, and washed with 3 × 50 ml of chloroform. The chloroform extracts were dried ($Na_2SO_4$) and evaporated in vacuo at 25° to leave a yellow oil. PLC (chloroform, $R_f$ 0.35) gave 2.68 g (99%) of pure product as a mixture of isomers: ir ($CHCl_3$) 1576 and 1020 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 7.38 (m, 5 H), 5.50 (m, 0.43 H), 5.08 (bt, $J$ = 6 Hz, 0.57 H), 3.69 (m, 0.43 H), 3.48 (m, 0.57 H), 1.1–2.6 (m, 12 H), 0.86 (m, 3 H).

**B. Sulfenylation of 1-(2-Pentylidenecyclopentyl) Phenyl Sulfoxide.** To 126 mg (1.73 mmol) of diethylamine in 8 ml of dry THF was added 1.24 ml of 1.39 *M* (1.73 mmol) *n*-butyllithium solution in hexane. After 20 min, 159 mg (0.61 mmol) of the sulfoxide dissolved in 1 ml of dry THF was added in one portion. After 30 min at −78° and 30 min at −25°, the anion solution was added via cannula to a solution of 146 mg (0.67 mmol) of diphenyl disulfide in 5 ml of THF at 0°. After 30 min at 0°, the reaction was worked up as before. PLC produced two fractions. The faster moving substance ($R_f$ 0.2) was identified as 1-phenylthio-2-(1′-hydroxypentyl) cyclopentene (85 mg, 35%): ir ($CCl_4$) 3625, 3460, 1640, and 1580 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 7.29 (ps, 5 H), 4.81 (t, $J$ = 6.5 Hz), 2.45 (m, 4 H), 1.18–2.18 (m, 8 H), 0.90 (t, $J$ = 6 Hz, 3 H); MS *m/e* (rel %) 262 (9), 244 (6), 205 (45), 187 (12), 154 (10), 123 (10), 110 (19), 96 (100), 79 (24), 67 (37). The slower moving substance ($R_f$ 0.1) was identified as [2-(1′-phenylthiopentyl)-1-cyclopentenyl] phenyl sulfoxide (155 mg, 49%): ir ($CCl_4$) 1635, 1610, 1580, and 1042 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 7.38 (m, 9 H), 6.93 (m, 1 H), 4.73 (t, $J$ = 7 Hz, 1 H), 2.60 (m, 4 H), 1.2–2.1 (m, 8 H), 0.93 (m, 3 H); MS *m/e* (rel %) 354 (16), 353 (57), 245 (28), 244 (27), 243 (100), 110 (57), 109 (51), 91 (33), 77 (34), 67 (30), 66 (23), and 55 (18).

**C. Preparation of 2-Pentylidenecyclopentanone. From 1-Phenylthio-2-(1′-hydroxypentyl)cyclopentene.** To 110 mg (0.42 mmol) of the hydroxy enol thioether in 4 ml of acetonitrile and 1 ml of water at 23° was added 125 mg 0.46 mmol) of mercuric chloride. After reaction and work-up as in the previous example, the crude product was purified by PLC ($R_f$ 0.25, chloroform) to give 43 mg (68%) of pure colorless oil:[30] ir ($CCl_4$) 1705 and 1640 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 6.55 (tt, $J$ = 7, 2 Hz, 1 H), 2.58 (bt, $J$ = 6 Hz, 2 H), 1.7–2.4 (m, 6 H), 1.4 (m, 4 H), 0.90 (t, $J$ = 7 Hz, 3 H); MS *m/e* (rel %) 152 (16), 123 (36), 107 (30), 81 (30), 67 (44), 55 (48), 43 (45), 41 (100); mol wt (calcd for $C_{10}H_{16}O$, 152.1203) 152.1201.

**From [2-(1′-Phenylthiopentyl)-1-cyclopentenyl] Phenyl Sulfoxide.** To 123 mg (0.33 mmol) of the vinyl sulfoxide in 8 ml of acetonitrile at 0° was added 131 mg (1.67 mmol) of acetyl chloride. After 5 min, 126 mg (0.67 mmol) of anhydrous stannous chloride was added in one portion. The reaction was stirred 1.5 hr at 0°, poured into 30 ml of 10% aqueous sodium bicarbonate, and extracted with 3 × 40 ml of ether. After drying ($MgSO_4$) and evaporating in vacuo, the combined ether extracts gave 110 mg (94%) of crude 1-phenylthio-2-(1′-phenylthiopentyl)cyclopentene. Mercuric chloride (252 mg, 0.93 mmol) was added to the crude vinyl sulfide in 7 ml of acetonitrile and 3 ml of water. After reaction and work-up as in the previous examples of hydrolysis, purification by PLC (chloroform, $R_f$ 0.25) gave 33 mg (71%) of pure product identical with the previous sample by ir and NMR spectroscopy.

**Norbornanone Series. A. Preparation of 2-(2′-Phenylsulfinylpropylidene)norbornane.** A solution of 1-propenylmagnesium bromide in 15 ml of dry THF was prepared by the method of Normant[39] from 0.96 g (40 mg-atoms) of magnesium turnings and 4.84 g (40 mmol) of 1-bromopropene. To this solution at 0° was added 2.20 g (20 mmol) of norcamphor dissolved in 5 ml of dry THF. The reaction was stirred 1 hr at 25°, quenched by the addition of a saturated aqueous solution of ammonium chloride, and worked up as usual to give 2.98 g (98%) of product.

The crude product (2.60 g, 17.1 mmol) was converted to the allylic sulfoxide in 25 ml of dry THF in the usual way by first forming the alkoxide with 13.5 ml of a 1.39 *M* solution (18.8 mmol) of *n*-butyllithium in hexane followed by 2.71 g (18.8 mmol) of benzenesulfenyl chloride. The product was purified utilizing dry column chromatography (3% 2-propanol in hexane, $R_f$ 0.25) to give 3.86 g (88%): ir ($CCl_4$) 1673 and 1047 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 7.47 (ps, 5 H), 4.96 (m, 1 H), 3.24 (m, 1 H), 2.03 (m, 1 H), 2.24 (m, 2 H), 0.9–2.1 (m, 10 H).

**B. Preparation of 2-Hydroxy-2-(2′-phenylthio-1′-propenyl)norbornane.** Sulfenylation was performed as previously described utilizing lithium diethylamide, generated from 264 mg (3.62 mmol) of diethylamine and 2.5 ml of a 1.45 *M* solution (3.62 mmol) of *n*-butyllithium in hexane, 471 mg (1.81 mmol) of sulfoxide, and 394 mg (1.81 mmol) of diphenyl disulfide. After purification by PLC, 302 mg (65%) of pure product was obtained as an oil: ir ($CCl_4$) 3610 and 3470 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 7.26 (m, 5 H), four broad singlets at $\delta$ 6.23, 6.14, 5.98, 5.92 (total 1 H), 2.04 (3 H), s superimposed on multiplet at 1.64–2.44 (4 H), 0.9–1.6 (m, 6 H).

**C. Preparation of 1-(2′-Norbornylidene)propan-2-one.** Hydrolysis of the vinyl sulfide alcohol (207 mg, 0.79 mmol) was performed as usual with 238 mg (0.88 mmol) of mercuric chloride in 4 ml of acetonitrile and 1 ml of water. Purification by PLC ($R_f$ 0.6, 1:1 ether:hexane) gave 103 mg (87%) of pure product as a colorless oil: ir ($CCl_4$) 1688 and 1617 $cm^{-1}$; NMR ($CCl_4$) two bs at $\delta$ 6.17 and

5.98 (total 1 H), 3.95 and 2.79 (two multiplets, total 1 H), 2.48 (m, 2 H), 2.17 (s, 3 H), 1.2–1.9 (m, 7 H); MS *m/e* (rel %) 150 (48), 135 (31), 122 (100), 107 (37), 79 (40); mol wt (calcd for $C_{10}H_{14}O$, 150.1045) 150.1044.

**Pinacolone Series. A. Preparation of 2-(4,5,5-Trimethylhex-3-enyl) Phenyl Sulfoxide.** Addition of 1-propenylmagnesium bromide prepared from 4.84 g (40 mmol) of 1-bromopropene and 0.96 g (40 mg-atoms) of magnesium turnings to 2.00 g (20 mmol) of pinacolone in 10 ml of dry THF gave 2.72 g (95%) of allylic alcohol. Quenching of the alkoxide, generated from 1.80 g (12.7 mmol) of alcohol and 10 ml of a 1.39 *M* solution (13.9 mmol) of *n*-butyllithium in hexane, with 1.94 g (13.9 mmol) of benzenesulfenyl chloride in the usual way gave 2.44 g (78%) of the allylic sulfoxide after purification by dry column chromatography (3% 2-propanol in hexane): ir ($CCl_4$) 1643, 1586, and 1049 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 7.43 (m, 5 H), 4.86 (m, 1 H), 3.51 (m, 1 H), 1.1–1.5 (m, 5 H), 0.97 and 1.00 (two singlets, 9 H); MS *m/e* (rel %) 250 (1), 234 (1), 124 (87), 110 (62), 109 (47), 83 (28), 78 (38), 69 (100), 41 (47); mol wt (calcd for $C_{15}H_{22}OS$, 250.1391) 250.1391.

**B. Preparation of 2-Phenylthio-4,5,5-trimethylhex-2-en-4-ol.** Sulfenylation of 151 mg (0.60 mmol) of allylic sulfoxide with 131 mg (0.60 mmol) of diphenyl disulfide in 16 ml of dry THF utilizing lithium diethylamide, generated from 88 mg (1.21 mmol) of diethylamine and 0.84 ml of 1.45 *M* solution (1.21 mmol) of *n*-butyllithium in hexane, was performed as usual. Purification by PLC ($R_f$ 0.65, 1:1 ether:hexane) gave 130 mg (81%) of pure oil: ir ($CCl_4$) 3620, 3400, 1623, and 1585 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 7.23 (m, 5 H), 5.80 (s, 1 H), 2.16 (s, 3 H), 1.34 (bs, 1 H), 1.27 (s, 3 H), 0.97 (s, 9 H); MS *m/e* (rel %) 250 (0.1), 232 (9), 218 (8), 155 (26), 125 (48), 110 (22), 57 (100), 43 (61); mol wt (calcd for $C_{15}H_{22}OS$, 250.1391) 250.1392.

**C. Preparation of (*E*)-4,5,5-Trimethylhex-3-en-2-one.** Hydrolysis of 62 mg (0.25 mmol) of the vinyl sulfide alcohol with 74 mg (0.27 mmol) of mercuric chloride in 3 ml of acetonitrile and 1 ml of water as usual gave 24 mg (71%) of pure colorless oil[29] after purification by PLC ($R_f$ 0.70, 1:1 ether:hexane): ir ($CCl_4$) 1690 and 1608 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 6.04 (s, 1 H), 2.10 (s, 3 H), 2.07 (d, J = 1 Hz, 3 H), 1.13 (s, 9 H); MS *m/e* (rel %) 140 (23), 125 (100), 97 (36), 67 (25), 57 (41), 55 (77); mol wt (calcd for $C_9H_{16}O$, 140.1201) 140.1198.

**Cyclohexenone Series. A. Preparation of 1-Phenyl-3-cyclohexenyl Phenyl Sulfoxide.** Following the procedure described for 1-cyclopentenylcarboxaldehyde, 11.0 mmol of a commercial solution of phenyllithium in 70:30 benzene–ether was added to 0.96 g (10.0 mmol) of cyclohexenone in dry THF and quenched with 1.59 g (11.0 mmol) of benzenesulfenyl chloride to give 2.67 g (93%) of the desired pure sulfoxide after dry column chromatography ($R_f$ ~0.2, $CHCl_3$): ir ($CCl_4$) 1600, 1585, and 1048 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 7.2–7.8 (m, 10 H), 6.14 (dt, *J* = 4, 1.5 Hz), 3.62 (m, 1 H), 2.43 (m, 2 H), 1.4–2.2 (m, 4 H).

**Preparation of 1-Phenylthio-3-phenyl-1-cyclohexen-3-ol.** Sulfenylation of 340 mg (1.21 mmol) of the above sulfoxide was carried out as previously described utilizing lithium diethylamide, generated from 177 mg (2.42 mmol) of diethylamine and 1.67 ml of a 1.45 *M* solution (2.42 mmol) of *n*-butyllithium in hexane, and 264 mg (1.21 mmol) of diphenyl disulfide in 10 ml of dry THF. Purification by PLC ($R_f$ 0.6, 1:1 ether:hexane) gave 391 mg (83%) of pure product: ir ($CHCl_3$) 3610, 3360, and 1600 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 7.36 (m, 10 H), 5.78 (s, 1 H), 2.22 (m, 3 H), 1.5–2.1 (m, 4 H).

**Preparation of 3-Phenyl-2-cyclohexen-1-one.** Hydrolysis of 190 mg (0.487 mmol) of vinyl sulfide alcohol was achieved as previously described utilizing 263 mg (0.97 mmol) of mercuric chloride in 4 ml of acetonitrile and 1 ml of water to give 76 mg (92%) of enone after purification by PLC ($R_f$ 0.3, 1:1 ether:hexane). Its spectral properties agreed with published data.[43]

**Carvone Series. A. Preparation of *n*-Butyl-5-isopropenyl-2-methyl-3-cyclohexenyl Phenyl Sulfoxide.** Following the procedure described for 1-cyclopentenylcarboxaldehyde, 7.33 mmol of a commercial 1.45 *M* solution of *n*-butyllithium in hexane was added to 1.00 g (6.67 mmol) of carvone in 20 ml of dry THF and quenched with 1.06 g (7.33 mmol) of benzenesulfenyl chloride to give 1.80 g (85%) of product after purification by dry column chromatography ($R_f$ ~0.4, 1:1 ether:hexane): ir ($CCl_4$) 1642, 1580, and 1048 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 7.43 (m, 5 H), 4.72 (m, 2 H), 3.0–3.6 (m, 1 H), 2.03 (m, 5 H), 1.1–1.8 (m, 12 H), 0.92 (t, *J* = 7 Hz, 3 H).

**B. Preparation of 3-*n*-Butyl-5-isopropenyl-2-methyl-1-phenylthio-1-cyclohexen-3-ol.** Sulfenylation of 343 mg (1.09 mmol) of the above sulfoxide was carried out as previously described utilizing lithium diethylamide, generated from 160 mg (2.20 mmol) of diethylamine and 1.52 ml of a 1.45 *M* solution (2.20 mmol) of *n*-butyllithium in hexane, and 240 mg (1.10 mmol) of diphenyl disulfide in 8 ml of dry THF. Purification by PLC ($R_f$ 0.65, 1:1 ether:hexane; $R_f$ 0.3, $CHCl_3$) gave 274 mg (80%) of pure product: ir ($CCl_4$) 3610, 3430, 1641, and 1580 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 7.24 (ps, 5 H), 4.70 (m, 2 H), 1.0–2.4 (m, 15 H), 0.92 (bt, *J* = 7 Hz, 3 H).

**C. Preparation of 3-*n*-Butyl-5-isopropenyl-2-methyl-2-cyclohexen-1-one.** Hydrolysis of 173 mg (0.55 mmol) of vinyl sulfide was achieved as previously described utilizing 224 mg (0.826 mmol) of mercuric chloride in 4 ml of acetonitrile and 1 ml of water to give 105 mg (92%) of product after purification by PLC ($R_f$ ~0.9, $CHCl_3$): ir ($CCl_4$) 1661, 1640, and 895 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 4.75 (m, 2 H), 2.0–2.7 (m, 7 H), 1.76 (bs, 6 H), 1.40 (m, 4 H), 0.94 (t, *J* = 7 Hz, 3 H); MS *m/e* (rel %) 205 (27), 165 (29), 149 (19), 121 (43), 106 (23), 105 (96), 96 (100), 93 (35), 91 (23), 67 (28), 53 (27), 41 (47); mol wt (calcd for $C_{14}H_{22}O$, 206.1671) 206.1673.

**Estrone Methyl Ether Series. A. Preparation of 3-Methoxy-17-phenylsulfinylisopropylidene-1,3,5(10)-estratriene.** To 436 mg (3.60 mmol) of 2-bromopropene in 8 ml of dry THF at −78° was added 7.20 mmol of *tert*-butyllithium (commercial solution in pentane).[44] After stirring 1 hr at −78°, 500 mg (1.76 mmol) of estrone methyl ether was added. Stirring was continued for 4 hr at −78° and for an additional hour during which time it was allowed to warm to room temperature. Addition of 3 ml of 2 *N* aqueous acetic acid solution quenched the reaction. The solution was made basic by addition of 50 ml of 10% aqueous sodium bicarbonate and extracted with 3 × 40 ml of ether. Drying ($MgSO_4$) and evaporating in vacuo left 561 mg of a foam. Purification by PLC (two elutions with chloroform) led to 261 mg (52%) of recovered estrone methyl ether ($R_f$ 0.5) and 253 mg (93% based upon recovered starting material) of adduct ($R_f$ 0.4) as a colorless foam.

The alkoxide generated from 252 mg (0.773 mmol) of alcohol and 0.78 mmol of commercial solution of *n*-butyllithium in hexane was converted to the sulfoxide with 113 mg (0.78 mmol) of benzenesulfenyl chloride in 20 ml of dry THF as previously described to give 268 mg (80%) of sulfoxide after PLC purification ($R_f$ 0.25, $CHCl_3$): ir ($CCl_4$) 1625, 1580, 1048, and 1028 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 7.28 (m, 6 H), 6.68 (m, 2 H), 3.77 (s, 3 H), 3.4–4.2 (m, 2 H), 2.82 (m, 2 H), 0.7–2.6 (m, 13 H).

**B. Preparation of 17-Hydroxy-17-(1′-phenylthio-2′-isopropenyl)-3-methoxy-1,3,5(10)-estratriene.** Sulfenylation of 260 mg (0.60 mmol) of the above sulfoxide was carried out as previously described utilizing lithium diethylamide, generated from 88 mg (1.20 mmol) of ethylamine and 1.20 mmol of a commercial solution of *n*-butyllithium in hexane, and 144 mg (0.66 mmol) of diphenyl disulfide in 7 ml of dry THF. Purification by PLC ($R_f$ 0.4, 1:1 ether:hexane) gave 165 mg (81%) of colorless foam: ir ($CCl_4$) 1621, 1581, and 1500 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 7.28 (m, 6 H), 6.68 (m, 2 H), 6.04 (s, 1 H), 3.77 (s, 3 H), 2.82 (m, 2 H), 1.95 (s, 3 H superimposed upon a multiplet from 1.0–2.3 (14 H), 0.97, s, 3 H.

**C. Preparation of 17-(1′-Formyl-1′-ethylidene)-3-methoxy-1,3,5(10)-estratriene.** Hydrolysis of 140 mg (0.323 mmol) of the vinyl sulfide alcohol was achieved as previously described utilizing 176 mg (0.65 mmol) of mercuric chloride in 4:1 v/v acetonitrile–water to give 95 mg (92%) of product after PLC purification ($R_f$ 0.4, 1:1 ether–hexane) as a mixture of isomers: ir ($CCl_4$) 1665, 1625, 1585, and 1500 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 10.28 and 10.01 (two s, 1 H), 7.20 (d, *J* = 8 Hz, 1 H), 6.72 (m, 2 H), 3.80 (s, 3 H), 2.88 (m, 4 H), two narrow (*J* ~1 Hz) triplets at $\delta$ 1.85 and 1.72 for 3 H superimposed on multiplet at 1.2–2.6 for 11 H, 1.11 and 1.00 (two s, 3 H); MS *m/e* (rel %) 324 (100), 226 (61), 199 (30), 186 (45), 174 (85), 173 (74), 172 (37), 171 (71), 160 (44), 147 (54), 110 (53), 91 (45); mol wt (calcd for $C_{22}H_{28}O_2$, 324.2089) 324.2088.

**Progesterone Ethylenedioxy Ketal Series. A. Preparation of 3,3-Ethylenedioxy-23-phenylsulfinyl-24-norchola-5,20(22)-diene.** In the usual manner, vinylmagnesium bromide prepared from 1.50 g (14.0 mmol) of vinyl bromide and 337 mg (14.0 mg-atoms) of magnesium turnings was added to 1.00 g (2.81 mmol) of the monoketal of progesterone[45] in 25 ml of dry THF to give 1.01 g (94%)

of adduct after PLC purification ($R_f$ 0.2, $CHCl_3$).

The alkoxide generated from 1.00 g (2.60 mmol) of the above alcohol and 2.60 mmol of a commercial solution of *n*-butyllithium in hexane was converted to the allylic sulfoxide with 375 mg (2.60 mmol) of benzenesulfenyl chloride in 25 ml of dry THF as previously described to give 1.00 g (77%) of product, mp 154–157° after PLC purification ($R_f$ 0.10, 1:1 ether–hexane): ir ($CCl_4$) 1640, 1585, and 1054 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 7.52 (m, 5 H), 5.33 (m, 1 H), 5.08 (t, $J$ = 7 Hz, 1 H), 3.96 (s, 4 H), 3.64 (bd, $J$ = 7 Hz, 2 H), 2.56 (m, 1 H), 1.65 (s, 3 H superimposed upon multiplet at 1.0–2.1 for 17 H), 1.03 (s, 3 H), 0.52 (s, 3 H).

**B. Preparation of 3,3-Ethylenedioxy-20-hydroxy-23-phenylthio-24-norchola-5,22-diene.** Sulfenylation of 500 mg (1.01 mmol) of the above sulfoxide was carried out as previously described utilizing 3.03 mmol of lithium diethylamide generated in the usual way and 440 mg (2.02 mmol) of diphenyl disulfide in 6 ml of dry THF. Purification by PLC ($R_f$ 0.5, 1:1 ether–hexane) gave 398 mg (80%) of pure product as a foam: ir ($CHCl_3$) 3600, 3450, 1612, and 1585 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 7.28 (m, 5 H), 6.41 and 6.33 (two d, $J$ = 16 Hz, 1 H), 6.00 (d, $J$ = 16 Hz, 1 H), 5.31 (m, 1 H), 3.95 (s, 4 H), 2.53 (m, 1 H), 0.9–2.1 (m, 20 H), 1.25 and 1.36 (two s, 3 H), 1.05 (s, 3 H), 0.81 and 0.84 (two s, 3 H).

**C. Preparation 3-Oxo-24-norchola-4,20(22)-dien-23-ol.** Hydrolysis of 200 mg (0.405 mmol) of vinyl thioether alcohol with 220 mg (0.81 mmol) of mercuric chloride in 6:1 v/v acetonitrile–water in the usual way gave 103 mg (75%) of crystalline product, mp 162–165°, after PLC purification ($R_f$ 0.5, ether): ir ($CHCl_3$) 1668 and 1630 $cm^{-1}$; NMR ($CDCl_3$) 10.03 (d, $J$ = 7 Hz, 1 H), 5.90 (d, $J$ = 7 Hz, 1 H), 5.71 (s, 1 H), 0.9–2.5 (m, 20 H), 2.20 (s, 3 H), 1.20 (s, 3 H), 0.66 (s, 3 H); MS *m/e* (rel %) 340 (0.3), 272 (3), 172 (30), 144 (12), 109 (6), 100 (100), 83 (14), 72 (79), 58 (75), 44 (27); mol wt (calcd for $C_{23}H_{32}O_2$, 340.2402) 340.2403.

**Dehydro-β-ionone Series. A. Preparation of Metastigma-4,6,8-trienyl Phenyl Sulfoxides.** To 1.50 g (7.90 mmol) of 3,4-dehydro-β-ionone[32] in 40 ml of benzene at 0° was added 2.25 g (15.8 mmol) of diisobutylaluminum hydride as a solution in hexane. After stirring for 6 hr at 0°, the reaction was quenched by sequential addition of 2 ml of methanol, 1 ml of water, and 5 g of anhydrous sodium sulfate in 10-min intervals. Stirring continued an additional hour, and then the reaction was filtered. The solution was extracted with 10 × 30 ml of ether and the organic phase washed with 30 ml of saturated aqueous sodium chloride. Drying ($MgSO_4$), evaporation in vacuo, and PLC purification ($R_f$ 0.25, $CHCl_3$) gave 890 mg (60%) of colorless oil.

Conversion of 720 mg (3.74 mmol) to the sulfoxide in the usual manner utilizing 4.12 mmol of a commercial solution of *n*-butyllithium in hexane and 597 mg (4.12 mmol) of benzenesulfenyl chloride in 20 ml of dry THF gave 730 mg (65%) of oil after PLC purification ($R_f$ 0.3, 1:1 ether–hexane) as a complex isomeric mixture: ir ($CCl_4$) 1650, 1620, 1610, 1600, and 1050 $cm^{-1}$; NMR ($CDCl_3$) 7.70 (m, 5 H), 5.38–6.95 (m, 4 H), 3.57 (m, 1 H), 0.8–2.7 (m, 14 H).

**B. Preparation of 3,4-Dehydro-3-phenylthio-β-ionol.** Sulfenylation of 336 mg (1.12 mmol) of the above sulfoxide was carried out as previously described utilizing 2.30 mmol of lithium diethylamide generated in the usual way and 268 mg (1.23 mmol) of diphenyl disulfide in 5 ml of dry THF. Purification by PLC ($R_f$ 0.4, 1:1 ether–hexane) gave 210 mg (63%) of pure product: ir ($CCl_4$) 3600, 3415, 1650, 1635, and 1575 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 7.28 (m, 5 H), 6.00 (d, $J$ = 16 Hz, 1 H), 5.82 (s, 1 H), 5.55 (dd, $J$ = 16, 6 Hz, 1 H), 4.28 (dq, $J$ = 6, 6 Hz, 1 H), 2.30 (bs, 1 H), 2.06 (s, 2 H), 1.78 (s, 3 H), 1.28 (d, $J$ = 6 Hz, 3 H), 0.98 (s, 6 H); MS *m/e* (rel %) 300 (11), 299 (22), 282 (12), 218 (65), 158 (36), 133 (32), 119 (34), 110 (68), 109 (100), 105 (33), 91 (55), 77 (66), 65 (59), 51 (41); mol wt (calcd for $C_{19}H_{24}OS$, 300.1548) 300.1548.

**C. Preparation of Metastigma-4,6,8-trienone.** Hydrolysis of 89 mg (0.30 mmol) of vinyl thioether alcohol in the usual way with 105 mg (0.387 mmol) of mercuric chloride in 4:1 v/v acetonitrile–water gave 21 mg (38%) of product after PLC purification ($R_f$ 0.75, $CHCl_3$) as a mixture of isomers whose spectral (ir and NMR) properties agree with published data.[34]

**Ethyl Vinyl Ketone Series. A. Preparation of 3-Ethyl-3-hydroxy-1-phenylthio-1-heptane.** To 500 mg (5.96 mmol) of ethyl vinyl ketone in 8 ml of dry THF at −25° was added 4.51 ml of a 1.45 *M* solution (6.55 mmol) of *n*-butyllithium in hexane. After 30 min, 950 mg (6.55 mmol) of benzenesulfenyl chloride was added and the resulting solution stirred 1 hr at −20°. The reaction was added to a solution of 13.1 mmol of lithium diethylamide prepared in the usual way in 10 ml of dry THF at −20°. This reaction was stirred 1 hr to ensure complete anion generation and then added to 1.30 g (5.96 mmol) of diphenyl disulfide in 8 ml of dry THF at 0°. After 1 hr, the reaction was poured into 32 ml of saturated aqueous sodium chloride containing 2 ml of 10% aqueous hydrochloric acid and extracted into 3 × 40 ml of ether. The combined ether portions were washed with 10 ml of 10% aqueous sodium bicarbonate, dried ($MgSO_4$), and evaporated in vacuo to leave a brown oil. Purification by PLC ($R_f$ 0.4, 1:1 ether–hexane) gave 762 mg (51%) of colorless oil: ir ($CCl_4$) 3610, 3470, and 1583 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 7.4 (m, 5 H), 6.37 (d, $J$ = 15 Hz, 1 H), 5.81 (d, $J$ = 15 Hz, 1 H), 1.87 (b, 1 H), 1.0–1.8 (m, 8 H), 0.91 (~t, $J$ = 7 Hz, 6 H).

**B. Preparation of 3-Ethyl-2-heptenal.** Hydrolysis of 276 mg (1.10 mmol) of the above vinyl thioether alcohol with 895 mg (3.30 mmol) of mercuric chloride under the usual conditions in 6:1 v/v acetonitrile–water gave 101 mg (65%) of enal after PLC purification ($R_f$ 0.2, $CHCl_3$) as an isomer mixture: ir ($CCl_4$) 2730, 1679, and 1628 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 9.87 (d, $J$ = 8 Hz, 1 H), 5.72 (d, $J$ = 8 Hz, 0.55 H), 5.68 (d, $J$ = 8 Hz, 0.45 H), 2.57 (q, $J$ = 7 Hz, 2 H), 2.22 (q, $J$ = 7 Hz, 2 H), 0.7–1.7 (m, 10 H); MS *m/e* (rel %) 140 (5), 139 (55), 114 (81), 111 (46), 110 (49), 109 (48), 100 (32), 96 (51), 81 (62), 71 (48), 69 (65), 57 (62), 55 (100), 43 (98); mol wt (calcd for $C_9H_{16}O$, 140.1201) 140.1174.

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# A New Photochemical Rearrangement. A Cyclopropyl-π-methane Rearrangement. Mechanistic and Exploratory Organic Photochemistry[1,2]

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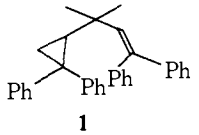
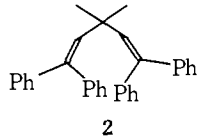
**Abstract:** The photochemistry of 3-(2,2-diphenylcyclopropyl)-3-methyl-1,1-diphenyl-1-butene was investigated in order to ascertain the reactivity of a system having one π moiety and one cyclopropyl ring attached to a saturated carbon. Only the singlet excited state proved reactive. As photochemical products there were obtained 1,1-diphenylethylene, 2-methyl-1,1-diphenyl-1-propene, 1,1-diphenylbutadiene, 4-methyl-1,1-diphenyl-1,3-pentadiene, and 3-(2,2-diphenylvinyl)-2,2-dimethyl-1,1-diphenylcyclobutane. The cyclobutane product was considered as a potential reaction intermediate in the formation of the other products, and its photochemistry was investigated. Irradiation of the cyclobutane was found to afford 2-methyl-1,1-diphenyl-1-propene and 1,1-diphenyl-1,3-butadiene but no diphenylethylene or 4-methyl-1,1-diphenyl-1,3-pentadiene. This evidence required that the diphenylethylene and the 4-methyl-1,1-diphenyl-1,3-pentadiene be primary photolysis products of the cyclopropylvinylmethane. Furthermore, extrapolation of the product distribution to zero time revealed an initial absence of 2-methyl-1,1-diphenyl-1-propene and diphenylbutadiene, thus showing these to be secondary photoproducts deriving from reaction of the cyclobutane. One a priori mechanism for formation of diphenylethylene and 4-methyl-1,1-diphenyl-1,3-pentadiene was carbene fragmentation followed by rearrangement. This was ruled out by independent study of the behavior of the carbene generated thermally and photochemically. A mechanism is postulated accounting both for formation of these products and the cyclobutane. This mechanism parallels that of the ubiquitous di-π-methane rearrangement but leads instead to the cyclobutane. Diversion of the reaction mechanism along the reaction coordinate leads to the fragmentation products.

Organic photochemistry is at a stage of development where its repertoire of established reactions consists of less than a score. Of these one is the di-π-methane rearrangement which has proved both extraordinarily general and synthetically useful.[3] It thus seemed worthwhile to investigate the possibility of effecting a parallel rearrangement in which one π moiety has been replaced by a three-membered ring, thus affording a cyclopropyl-π-methane or homo-di-π-methane rearrangement.

For this study, we selected 3-(2,2-diphenylcyclopropyl)-3-methyl-1,1-diphenyl-1-butene (**1**) because of its close structural relationship to the well-studied[3b,4] 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene (**2**).




**1**




**2**

## Results

**Synthesis of Reactant.** The synthesis devised for cyclopropylvinylmethane **1** is outlined in Chart I. This route began with 2,2-diphenylcyclopropyl methyl ketone[5] (**3**) and its reaction with the conjugate base of triethyl phosphonoacetate. The phosphonate reaction[6] required somewhat more strenuous conditions than normal but proceeded in excellent yield. Otherwise the synthesis was unexceptional.

**Exploratory Photochemistry of the Cyclopropylvinylmethane.** Exploratory photolyses were run on a Rayonet[7] type of reactor consisting of 32 15-W low-pressure mercury lamps arranged in a cylindrical array surrounding a quartz vessel. It was observed that direct irradiation (sensitization led to no reaction) under these conditions led to five prod-