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Thiyl Radical Induced Cyclizations of Dienes. Cyclization of α-Acoradiene, α-Bulnesene, and Geranyl Acetate to Cedrane, Patchulane, and Cyclogeranyl Acetate Products

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Selected dienes reacted with ethanethiol, dimethyl disulfide, diphenyl disulfide, and bis(trifluoromethyl) disulfide, with radical initiation by photolysis of diphenyl disulfide or thermolysis of benzoyl peroxide, to give thiyl substituted cyclization products and acyclic adducts. These were desulfurized with Raney nickel. Thus diallylmalonate and diallylacetate gave good yields of *cis*- and *trans*-dimethylcyclopentanes (6:1 or total stereoselectivity), α-acoradiene was quantitatively coverted to cedrane, and α-bulnesene gave a modest yield of dihydro-α-patchulene in addition to tetrahydrobulnesene. Geranyl acetate led to various ratios of cyclic and acyclic adducts (5:1 to 1:17) depending on reaction conditions. No significant cyclization was found with aromatic olefins. The results suggest a stabilization of intermediate radicals with α-thiyl substituents not found with corresponding oxygen substituents.

While cyclizations of dienes and polyenes through carbonium ion intermediates have been extensively studied with respect to structural[2-5] and stereochemical[6-8] parameters and encompass major synthetic[9] and biomimetic[10,11] routes to carbocyclic systems, radical-initiated cyclizations of dienes have only been explored in recent years.[12-15] The two processes can differ fundamentally in synthetic direction, allowing alternative preferential ring size formation. In cationic cyclizations six-membered rings are generally obtained, with divergence to five-membered rings associated with examples of increased electronic stabilization of carbonium ion intermediates (increased alkyl substitution of cationic centers) when competing six-membered ring formation does not show this advantage.

In contrast, radical-initiated cyclizations generally lead to five-membered rings. Electronic stabilization of intermediate cyclized product radicals seems less important[14a] than considerations of steric compression in the cyclization process[16] or electronic stabilization of an initially reacting radical center,[14a] which may cause reversal of a kinetically favored five-membered ring closure. Thus six-membered rings can sometimes be obtained as a result of these two factors. Further control of cyclization arises from the required orbital overlap of the π system with the electron-deficient reacting center.[17] This results in the usual requirement of having at least three atoms between the double bond and the reacting center with consequent possibility of regiospecific direction of addition of an initiating agent in cyclizations of dienes.

The present study of thiyl radical induced cyclizations was undertaken because reductive desulfurization of cyclization products could allow alternatives to proton initiated cyclizations with respect to isomeric product type and/or compatibility with acid-sensitive functional groups, i.e., allylic oxygen or ketal functions. It was also of fundamental interest to see if the reversibility of thiyl radical addition to olefins[18] and the possibility of interaction of a radical center with a β-thiyl substituent[19,20] might furnish results which would reflect the energetic requirements of the radical cyclization process.

In order to get a comparison of cyclizations effected by representative thiyl radical species, dimethyl diallylmalonate (1) was subjected to reactions with ethanethiol without a radical initiating reagent and with radical initiation by photolysis with a small amount of diphenyl disulfide, or by initiation of the reaction with dibenzoyl peroxide. Thiyl radical addition and cyclization was also obtained by photolysis of

Scheme I. Reactions of Dimethyl Diallylmalonate with Thiyl Radicals Derived from Ethanethiol or Dialkyl Disulfides

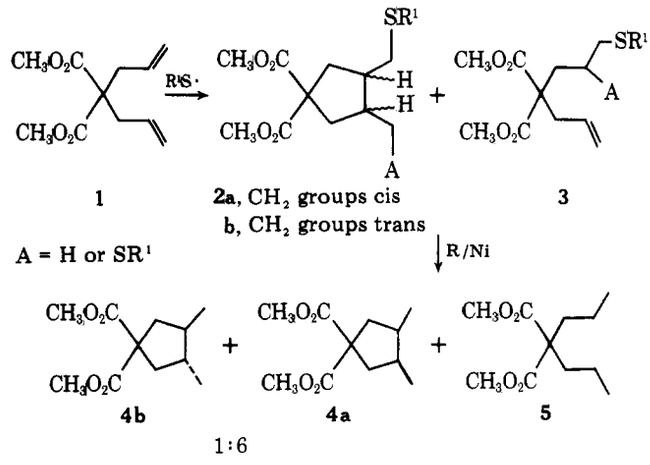


Table I. Reactions of Dimethyl Diallylmalonate with Thiyl Radicals

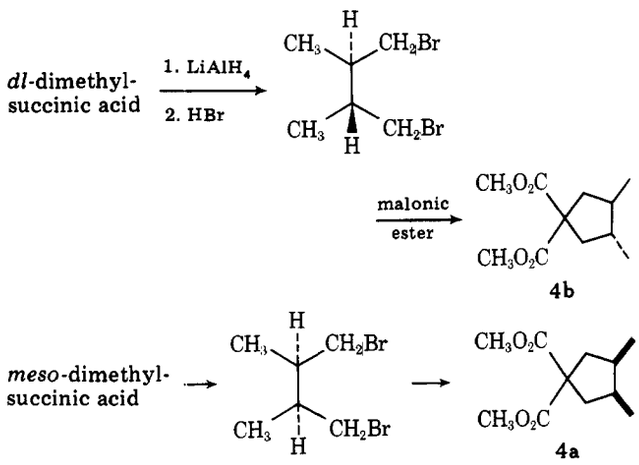
Reaction conditions	Yield, % Cyclic adducts 2 (a:b)	Acyclic adducts 3
Ethanethiol, diphenyl disulfide, $h\nu$, neat	85 (6:1)	6
Ethanethiol, diphenyl disulfide, $h\nu$, benzene	92 (6:1)	6
Ethanethiol, benzoyl peroxide, heat, neat	73 (4:1)	3
Ethanethiol, benzoyl peroxide, heat, benzene	<1[a]	
Ethanethiol, RT, dark 15 h, neat	25[b] (1:trace)	15
Dimethyl disulfide, $h\nu$, neat	83[c] (only 2a)	7
Bis(trifluoromethyl) disulfide, $h\nu$, neat	48[d]	14

[a] >90% recovery of starting material. [b] 60% recovery of starting material. [c] Mixture of methanethiol and some dimethyl disulfide adducts. [d] Estimated from desulfurization products of 11-component mixture.

dimethyl disulfide. Reductive desulfurization of the reaction products **2a,b** and **3** on Raney nickel gave 3,4-dimethyl-1,1-dicarbomethoxycyclopentanes (**4a,b**) as a stereoisomeric mixture with the cis dimethyl compound as the major (6:1) or only isomer as well as dimethyl dipropylmalonate (**5**) as a minor product. While an analogous reaction with bis(trifluoromethyl) disulfide gave a product mixture with at least 11 components, subsequent reduction of this mixture again led primarily to the dimethylpentane product **4a.** These results are summarized in Table I.

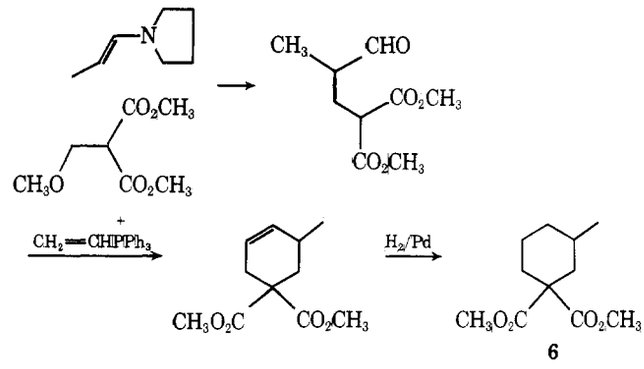
Adducts **2a,b** and **3** were characterized by mass fragmentography. Products **5** and **4a,b** were identified by VPC comparison with authentic samples, prepared respectively by hydrogenation of the diallyl compound **1** and the reaction sequence shown below,[21,22] which established the stereochemical assignment of epimers **4a,b.** Products **2a** and **4a** also

Scheme II. Syntheses of *cis*- and *trans*-3,4-Dimethylcyclopentanedicarboxylic Esters



gave NMR spectra consistent with dimethyl cyclopentanedicarboxylic esters. In order to rule out formation of a minor six-membered cyclization product, dicarbomethoxy-3-methylcyclohexane (**6**) was prepared from the enamine derivative of propionaldehyde, dimethyl methoxymethylmalonate, and triphenylvinylphosphonium bromide by the indicated reactions. The final product **6** of this reaction sequence was not found among the desulfurized thiyl radical cyclization products.

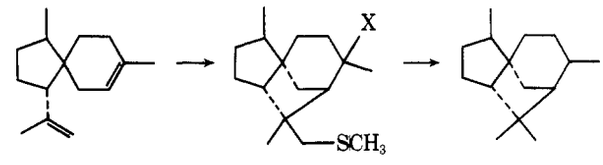
Scheme III. Synthesis of 1,1-Dicarbomethoxy-3-methylcyclohexane



The results conform with analogous, stereochemically unclassified, radical-initiated cyclizations of diallyl compounds.[21,23] The stereospecificity of the cyclization leading to the thermodynamically unfavored cis dialkylcyclopentane product **2a** may be contrasted with the predominant formation of trans substituted cyclopentane products from cyclization of benzylic 6-arylhex-1-enyl radicals,[24] and the previously assumed formation of trans substituted cyclopentanes as other diallyl cyclization products.[14b,g] Generation of cis-disubstituted cyclopentane products can be presumed to arise from a kinetic control based on stereoelectronic factors. The latter may be complex since the cis–trans ratio was found to vary for the same reactants with changes in experimental conditions and thus several alternative postulates may have to be considered.[25]

Irradiation of solutions of α-acoradiene (**7**)[26] and dimethyl disulfide in benzene or cyclohexane yielded nearly quantitatively 1:1 adducts **8** of the diene and methanethiol (96%, *m/e* 252) and dimethyl disulfide (4%, *m/e* 298). Raney nickel desulfurization of this product gave a saturated hydrocarbon **9** (*m/e* 206) which was identified as dihydrocedrene by com-

Scheme IV. Reaction of α-Acoradiene with Dimethyl Disulfide and Desulfurization



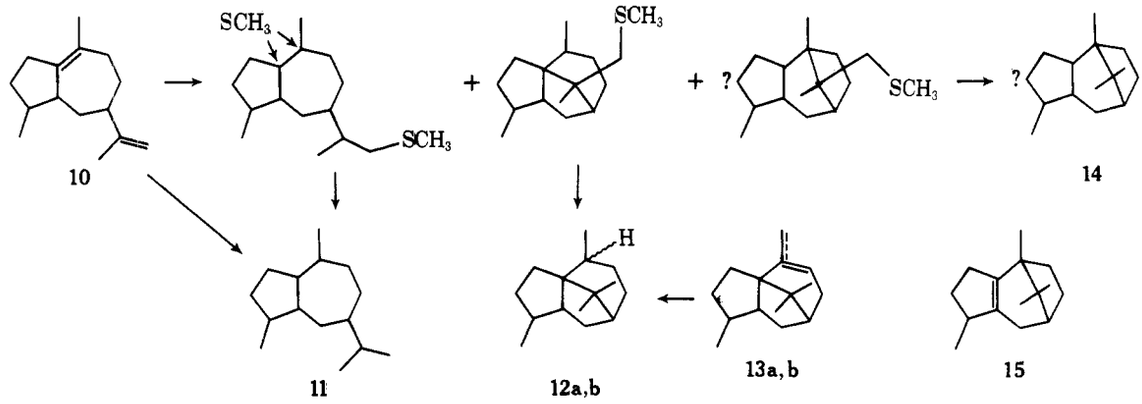
X = H and SCH_3

parison of IR and NMR spectra, the mass fragmentation pattern, and VPC retention times with those of the hydrogenation product of natural cedrene. Tetrahydroacoradiene was not found.

Photolysis of dimethyl disulfide and α-bulnesene[27] (**10**) in cyclohexane or benzene gave complex mixtures of products. Desulfurization of these yielded tetrahydrobulnesene (**11**) as a major component and at least five other compounds. One of these was identified as a dihydro-α-patchulene **12a,b** by comparison of its mass fragmentation with that of one of the two epimeric products obtained on hydrogenation of a mixture of α- and γ-patchulenes **13a,b.** A further isolated isomeric saturated product could not be definitely assigned the alternative dihydro-β-patchulene structure **14** because of failure to obtain a stereoisomerically corresponding pure product from β-patchulene (**15**).

The extensive formation of uncyclized adducts of bulnesene contrasts with the preceding examples of five-membered ring formation in high yields. It may be ascribed to strain in the bridged ring systems[28] **12** and **14** and to steric compression

Scheme V. Reactions of Bulnesene with Dimethyl Disulfide and Desulfurization

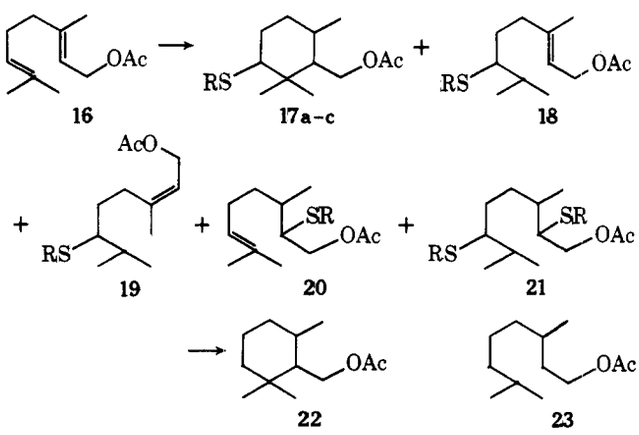


arising from four geminal substituents on the generated five-membered ring. Avoidance of such 1,2-tetrasubstituted cyclopentane products was again found in the following radical cyclizations.

In reactions of geranyl acetate (16) with thiyl radicals, attack at the less substituted position of the terminal double bond produces a tertiary radical which could undergo cyclization to five- or six-membered rings. If steric compression by four adjacent geminal substituents is a barrier to the former course, the alternative (otherwise slower) cyclization to a six-membered ring and competing hydrogen abstraction by the radical, with formation of acyclic thiol adducts, can be anticipated as preferred reaction pathways. Acyclic addition products rather than cyclization should also result from thiyl radical addition to the internal double bond since the tertiary radical thus formed would have poor overlap with the terminal double bond (only two carbons between the double bond and radical center). Table II shows the ratio of acyclic to cyclic compounds obtained after desulfurization of reaction products formed in various thiyl radical reactions with geranyl acetate.

Generally six monothioether fractions were obtained from reactions of ethanethiol or dimethyl disulfide, consisting of three epimeric cyclization products **17a–c** and three acyclic fractions containing the adducts **18–20** (with the last possibly

Scheme VI. Reactions of Geranyl Acetate with Thiyl Radicals



as an epimeric mixture). A seventh fraction corresponding to epimeric diadducts **21** was formed in substantial amount in photolyses of dimethyl disulfide and geranyl acetate in cyclohexane or benzene. The product fractions were separated by VPC and characterized by NMR spectra and mass fragmentography.

Desulfurization of the thioethers with Raney nickel yielded cyclogeranyl acetate (**22**) and tetrahydrogeranyl acetate (**23**),

Table II. Ratios of Cyclic to Acyclic Product in the Reaction of Geranyl Acetate with Thiyl Radicals

RS source	Conditions	Acyclic	Cyclic	% reaction
EtSH	$h\nu$,[f] Pyrex,[g] PhSSPh, 15 h	9.4	1[a]	31
	$h\nu$, Pyrex, 68 h, PhH, PhSSPh	(95% starting material)		
	$(PhCO_2)_2$, 85 °C, 15 h	(92% starting material)		
	$(PhCO_2)_2$, 85 °C, 15 h, PhH	(99% starting material)		
$(CH_3S)_2$	$h\nu$, Pyrex, 17 h	4.75	1[a]	50
	$h\nu$, Pyrex, cyclohexane, 24 h	2.45	1[d]	45
		1	1.8[b]	
		1	0[c]	
	$h\nu$, Pyrex, benzene, 24 h	1.95	1[d]	33
PhSSPh	$h\nu$, Vycor, CH_3CN, 24 h	1	1.84[a]	18[e]
	$h\nu$, Pyrex, benzene, 24 h	1	5.1[a]	20[e]
	$h\nu$, Pyrex, cyclohexane, 24 h	1.25	1[a]	68
$(CF_3S)_2$	2537 Å, 15 h	16.6	1[d]	46[e]
	$h\nu$, Pyrex, 8 h	16.6	1[d]	56[e]
	$h\nu$, Pyrex, cyclohexane, 24 h	2.75	1[d]	56[e]
t-Bu_2S_2	$h\nu$, Vycor,[g] CH_3CN, 24 h	3.21	1[a]	17

[a] Based on desulfurization of starting-material-free product fraction. [b] Based on desulfurization of fraction corresponding to diene + CH_3SH. [c] Based on desulfurization of fraction corresponding to diene + $2CH_3SH$. [d] Based on desulfurization of total reaction mixture. [e] Recovery of volatile materials. [f] All photolyses with a 450-W Hg high-pressure lamp. [g] Light filter.

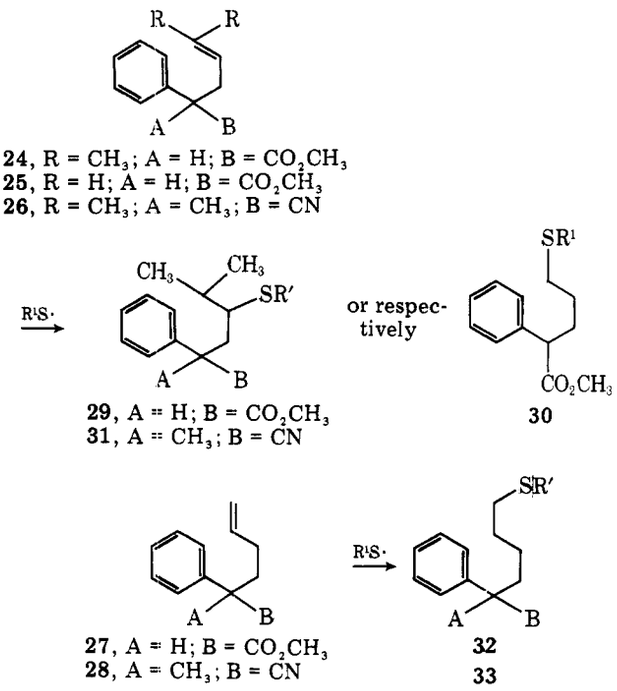
identified by comparison with authentic samples. In all of these thiyl radical reactions additional nonvolatile material was formed. Raney nickel desulfurization of these distillation residues did not produce volatile products.

Photolysis of diphenyl disulfide and geranyl acetate in benzene gave a higher cyclization ratio (5:1) than ethanethiol or dimethyl disulfide. While expectation of retarded hydrogen abstraction by intermediate radicals was rewarded and cyclization was favored under these conditions, more complex reaction products also resulted and the overall yield of volatile products decreased. Reactions with bis(trifluoromethyl) disulfide gave 12–15 volatile products in benzene, acetonitrile, or cyclohexane and the cyclization ratio, found after desul-

furization, was particularly low for the first two solvents. Irradiation of thiophenol, diphenyl disulfide, and geranyl acetate gave the acyclic adduct **18** in 42% yield.[29]

Reactions of the aromatic olefins **24–28** with ethanethiol and radical initiation by photolysis with diphenyl disulfide or by thermolysis of benzoyl peroxide and photolysis with dimethyl disulfide gave the acyclic adducts **29–33** in 50–83%

Scheme VII. Reactions of Arylalkenes with Thiyl Radicals



yields. The uncyclized products were identified by NMR spectra and their molecular ions. Cyclization products, if formed, were obscured in uncharacterized minor product mixtures (2–8%).

The present study shows that thiyl radical initiated cyclizations of dienes occur readily when unstrained cyclopentane products can be formed but that cyclization yields decrease in favor of formation of olefinic addition products when cyclizations are forced toward energetically less favored, strained or six-membered ring closure and that no significant cyclization arises from attack on an aromatic ring. Chain transfer (H transfer) is expected to be competitive in reactions of thiols with dienes. This process leads to more acyclic adducts as the energetic requirement for the cyclization increases. The chain transfer process is less competitive for the dialkyl disulfide reactions but products derived from alkyl hydrogen transfer then predominate. These results may be compared with those of benzoyloxy radical induced cyclizations of dienes and aryl olefins where the energetically more demanding cyclizations have been achieved. The difference in ease of such cyclizations initiated by thiyl vs. benzoyloxy radicals may lie in a decreased electrophilic reactivity of radicals generated with thioalkyl vs. benzoyloxy substituents on the adjacent carbon. However, most of the benzoyloxy radical initiated cyclizations were also obtained under conditions less favorable for hydrogen transfer.

Experimental Section

Reaction of Dimethyl Diallylmalonate with Ethanethiol. A. Diphenyl Disulfide Initiated Photolysis. A mixture of 122 mg (0.576 mmol) of dimethyl diallylmalonate, bp 120–122 °C (17 mm) (one VPC peak on column below), 2 mg (0.0092 mmol) of diphenyl disulfide, and 43 μL (35 mg, 0.57 mmol) of ethanethiol in a Pyrex tube was purged with nitrogen and sealed under a nitrogen atmosphere. The mixture was then irradiated for 15 h using a 450-W Hg high-pressure lamp. Distillation of the reaction mixture at 100–120 °C (0.03 mm) gave 105 mg of a clear liquid. A VPC of this liquid on a 5 ft × 0.125 in. 10% Carbowax 20M on Chromosorb W column at 190 °C showed some remaining starting material and three products with the following retention times and relative areas: starting material, 2.25 min (2.93); **3**, 20.5 min (1); **2b**, 23.5 min (1.18); **2a**, 28 min (7.15). The mixture was fractionated by preparative VPC on a 10 ft × 0.25 in. 20% Carbowax 20M on Chromosorb W column at 195 °C. Three fractions were collected corresponding to the three products listed above: **2a**, NMR ($CDCl_3$) δ 3.87 (s, 3 H), 1.4–2.7 (broad, complex pattern, 10 H), 1.28 (t, J = 7.5 Hz, 3 H), 0.9 (d, J = 7.5 Hz, 3 H), m/e 274 (M^+); **3**, m/e 274 (M^+); **2b**, m/e 274 (M^+). Irradiation of the same reactants for 68 h in 7 mL of benzene gave 96 mg of oil, distilled at 100–120 °C (0.03 mm), with VPC showing a trace of starting material and components **2a,b** with relative areas of 1 and 7.05. Reactions with 1.2 g of diallylmalonate and 10% excess of ethanethiol gave results shown in Table I.

B. Benzoyl Peroxide Initiated Thermolysis. A mixture of 116 mg (0.545 mmol) of dimethyl diallylmalonate, 3.4 mg (0.014 mmol) of benzoyl peroxide, and 35 μL (29 mg, 0.47 mmol) of ethanethiol was purged with nitrogen, sealed in a Pyrex tube, and then heated overnight in an oven at 85 °C. Distillation of the reaction mixture at 100–120 °C (0.03 mm) gave 102 mg of a clear liquid. VPC showed some remaining starting material and three products with retention times corresponding to those from the diphenyl disulfide initiated photolysis. Relative areas follow: starting material (5.95), **3** (1), **2b** (3.75), and **2a** (14.7).

A similar reaction in 7 mL of benzene gave 92 mg of oil, distilled at 100–120 °C (0.03 mm), with VPC showing mostly starting material with very small amounts (<1%) of two products, corresponding by VPC to those of the photolysis in benzene.

C. Uninitiated Reaction. A mixture of 127 mg (0.60 mmol) of dimethyl diallylmalonate and 44 μL (37 mg, 0.59 mmol) of ethanethiol was placed in a Pyrex tube, purged with nitrogen, sealed, and stored in the dark overnight. VPC of the reaction mixture showed starting material and three products corresponding to those seen in the photolytic reaction. Relative areas follow: starting material (3.96); **3** (1); **2b** (trace); **2a** (1.67).

Raney Nickel Desulfurization of the Dimethyl Diallylmalonate–Ethanethiol Adduct. The major product from the diphenyl disulfide initiated photolysis of ethanethiol and dimethyl diallylmalonate was treated with an excess of W4 Raney nickel in 5 mL of refluxing methanol for 24 h. The reaction mixture was filtered and the catalyst was triturated three times with 5-mL portions of boiling methanol. The methanol solution was concentrated to give a clear liquid which had only one component, **4a** by VPC (5 ft × 0.125 in. 10% Carbowax 20M on Chromosorb W at 195 °C): NMR ($CDCl_3$) δ 3.72 (s, 6 H), 1.8–2.6 (broad, complex pattern, 6 H), 0.87 (d, J = 7 Hz, 6 H). This compound corresponded to the *cis*-dimethylcyclopentane product obtained by the following alternative synthesis. Desulfurization of the entire product mixture obtained on photolysis with ethanethiol allowed matching with dimethyl dipropylmalonate[30] (**5**) and the *cis*- and *trans*-dimethylcyclopentanes **4a,b** by VPC on DEGS or Carbowax columns. No methylcyclohexane product could be seen.

Reaction of Dimethyl Diallylmalonate with Dimethyl Disulfide. Dimethyl diallylmalonate (0.114 g, 0.538 mmol) and dimethyl disulfide (47 μL, 0.53 mmol) were placed in a Pyrex tube, purged with nitrogen, and sealed. The mixture was then irradiated for 12 h using a 450-W high-pressure Hg lamp. Distillation of the reaction mixture at 100–130 °C (0.03 mm) gave 0.124 g of a clear, colorless liquid. A VPC of this liquid on a 5 ft × 0.125 in. 10% Carbowax 20M on Chromosorb W column at 190 °C showed no starting material but two components with the following retention times and relative areas: A, 8.5 min (1); B, 10 min (11.7). This product was fractionated by preparative VPC on a 10 ft × 0.25 in. 20% Carbowax 20M on Chromosorb W column at 190 °C. The second fraction showed NMR ($CDCl_3$) δ 3.68 (s, 6 H), 1.9–2.6 (broad multiplet, 5 H), 2.08 (s, 3 H), 0.88 (d, J = 6 Hz, 3 H); m/e 260 (M^+, corresponds to dimethyl diallylmalonate plus methanethiol); small peaks were also seen at m/e 275, 291, and 306 (corresponding to 1:1 adduct).

Raney Nickel Desulfurization of Dimethyl Disulfide–Dimethyl Diallylmalonate Adduct. A sample of the products from the photolysis of dimethyl disulfide and dimethyl diallylmalonate was stirred with an excess of W4 Raney nickel for 5 h. The mixture was filtered and the catalyst was washed several times with boiling methanol. The combined methanol solutions were concentrated and distilled at 80–100 °C (0.03 mm) to give a clear, colorless liquid. A VPC of this liquid on a 5 ft × 0.125 in. 10% Carbowax 20M on Chromosorb W column at 124 °C showed two peaks with retention times and rel-

ative areas of 8 min (1) and 10.5 min (4.58); NMR ($CDCl_3$) δ 3.72 (s, 6 H), 1.64–2.6 (broad pattern, 6 H), 0.88 (d, 6 H). The minor peak had the same VPC retention time as did methyl di-*n*-propylmalonate (**5**). The major peak had the same VPC retention time as the desulfurization product **4a** of the ethanethiol–dimethyl diallylmalonate reaction.

Reaction of Dimethyl Diallylmalonate with Bis(trifluoromethyl) Disulfide. A mixture of 0.545 g (2.57 mmol) of dimethyl diallylmalonate and 0.552 g (2.73 mmol) of bis(trifluoromethyl) disulfide was sealed in a Pyrex tube at 0.03 mm pressure and irradiated for 15 h using a 450-W high-pressure Hg lamp. Distillation of the reaction mixture at 100–130 °C (0.03 mm) gave 0.821 g of a pale yellow liquid. A VPC of this liquid on a 5 ft × 0.125 in. 10% Carbowax 20M on Chromosorb W column at 180 °C showed 11 well-resolved components with the following retention times and relative areas: 1.375 min (0.071), 2 min (0.035), 2.5 min (0.19), 3.5 min (0.032), 4.25 min (0.38), 6.75 min (0.071), 8.75 min (1), 10.25 min (0.17), 18 min (0.11), 25.25 min (0.45), 31 min (0.42); *m/e* (rel intensity) 414 (4.1), 383 (6.9), 345 (18.5), 313 (27), 151 (39), 93 (54.7), 91 (54), 79 (47.5), 77 (39.7), 59 (100), 41 (53.4), 39 (39.7).

Raney Nickel Desulfurization of Dimethyl Diallylmalonate–Bis(trifluoromethyl) Disulfide Reaction Mixture. A solution of 266 mg of the product from the above photolysis in 5 mL of methanol was heated at reflux overnight with an excess of W4 Raney nickel. The mixture was filtered and the catalyst was washed several times with boiling methanol. Distillation at 80–100 °C (0.03 mm) gave 115 mg of a clear liquid. A VPC of this liquid on a 5 ft × 0.125 in. 10% Carbowax 20M on Chromosorb W column at 140 °C showed five peaks with retention times and relative areas of 3.5 min (1), 4.75 min (1.62), 6.5 min (3.22), 8.25 min (0.665), 26 min (0.464). The major (6.5 min) component was identical by VPC with **4a**. The first component (3.5 min) had a retention time the same as that of dimethyl di-*n*-propylmalonate (**5**).

Reaction of α-Acoradiene with Dimethyl Disulfide. A solution of 70 mg (0.34 mmol) of α-acoradiene[26] and 30 μL (32 mg, 0.34 mmol) of dimethyl disulfide in 3 mL of cyclohexane was sealed in a Pyrex tube at 0.03 mm pressure. The solution was irradiated for 15 h using a 450-W high-pressure mercury lamp. Concentration of the solution gave a pale yellow oil which was distilled at 100–130 °C (0.03 mm) to give 65 mg of a clear liquid. A VPC of this liquid on a 5 ft × 0.125 in. 10% Carbowax 20M on Chromosorb W column at 190 °C showed traces of acoradiene, one very minor component, and one major component with retention times and relative peak areas of 0.75 min (trace), 2.875 min (0.036), 5.75 min (1). A mass spectrum of the distilled product showed peaks at *m/e* (rel intensity) 298 (0.8), 252 (16), 250 (8), 191 (100), 135 (34), 109 (36), 95 (77), 81 (62), 69 (36), 55 (40), 41 (45).

Raney Nickel Desulfurization of the α-Acoradiene–Dimethyl Disulfide Product. The product from the photolysis of dimethyl disulfide and α-acoradiene in cyclohexane was stirred for 8 h with an excess of W4 Raney nickel in 5 mL of refluxing ethanol. The mixture was then filtered, the catalyst was washed with boiling ethanol, and the combined filtrates were concentrated and distilled at 70–90 °C (0.03 mm) to give 36 mg of a clear liquid: *m/e* (rel intensity) 206 (61), 95 (50), 93 (56), 82 (100), 81 (46), 69 (46), 55 (49), 41 (76); NMR ($CDCl_3$) δ 2.1–1.1 (m), 1.1–0.7 (m), both multiplets had approximately the same integration. A VPC of this liquid on a 5 ft × 0.125 in. 10% Carbowax 20M on Chromosorb W column at 120 °C showed only one peak with a retention time of 3.5 min, identical with that of dihydrocedrene and differing from those of tetrahydro-α-acoradienes in respective enrichment VPC analyses. Dihydrocedrene and the present reaction product showed identical IR spectra.

An analogous reaction sequence with photolysis of dimethyl disulfide and α-acoradiene in benzene and subsequent desulfurization again gave mostly dihydrocedrene and 15% of an unidentified compound with longer VPC retention time (5.75 min vs. 4 min).

Catalytic Hydrogenation of α-Acoradiene. A solution of 66 mg (0.32 mmol) of α-acoradiene in 5 mL of ethanol was stirred with 10 mg of 10% palladium on charcoal under 1 atm of hydrogen until the theoretical amount of hydrogen (15 mL) had been taken up. The reaction mixture was then filtered, concentrated, and distilled at 70–90 °C (0.03 mm) to give 54 mg of a clear liquid. A VPC of this liquid on a 5 ft × 0.125 in. 10% Carbowax 20M on Chromosorb W column at 120 °C showed two peaks with retention times and relative areas of 2.75 min (1) and 3.125 min (2.8).

Catalytic Hydrogenation of Cedrene. A solution of 55 mg (0.27 mmol) of cedrene in 2 mL of ethanol was shaken overnight with 10% palladium on charcoal under 40 psi of hydrogen. The mixture was filtered, concentrated, and distilled at 70–90 °C (0.03 mm) to give 45 mg of a clear liquid: *m/e* (rel intensity) 206 (67), 163 (47), 122 (38), 121 (37), 95 (38), 82 (100), 55 (38), 41 (64); NMR ($CDCl_3$) δ 2.2–1.2 (m), 1.2–0.72 (m) (the multiplets have approximately a 1:1 integration).

Reaction of Bulnesene with Dimethyl Disulfide. A solution of 0.397 g (1.94 mmol) of bulnesene[27] and 171 μL (183 mg, 1.94 mmol) of dimethyl disulfide in 10 mL of cyclohexane was sealed in a Pyrex tube at 0.03 mm pressure and irradiated for 24 h using a 450-W high-pressure mercury lamp. Concentration of the reaction mixture gave a yellow-brown oil which was distilled at 120–180 °C (0.03 mm) to give 0.307 g of a pale yellow oil. A VPC of this oil on a 5 ft × 0.125 in. 10% Carbowax 20M on Chromosorb W column at 192 °C showed eight peaks with retention times and relative areas of 1 min (1.0 bulnesene), 1.75 min (0.10), 1.875 min (0.15), 3.5 min (0.14), 4.625 min (0.14), 6.5 min (0.77, several components), 9.75 min (0.014), 12.25 min (0.051). Preparative TLC of this material on a 20 × 20 cm silica gel coated plate developed with hexane gave four fractions: I, R_f 0–0.1; II, R_f 0.1–0.3; III, R_f 0.3–0.5; IV, R_f 0.5–0.9. Three fractions were analyzed by VPC using a 5 ft × 0.125 in. 10% Carbowax 20M on Chromosorb W column at 190 °C; fraction IV appeared to be almost pure bulnesene; fractions II and III were a mixture of products, including the major product, and appeared to be free of bulnesene; fraction I was mostly a product corresponding to the peaks with retention times of 1.75 or 1.875 min. Fractionation of fraction II by preparative VPC on a 10 ft × 0.375 in. 20% SE-30 on Chromosorb W column at 180 °C gave a sample of the major product: *m/e* (rel intensity) 252 (75), 237 (37), 204 (100), 190 (59), 108 (45), 81 (45), 61 (46), 41 (48).

Raney Nickel Desulfurization of the Bulnesene–Dimethyl Disulfide Adduct. Fraction III from the preparative TLC of the bulnesene–dimethyl disulfide reaction mixture was stirred for 12 h with an excess of W4 Raney nickel in refluxing ethanol. The solution was filtered and the catalyst was washed several times with boiling ethanol. The combined filtrates were concentrated and distilled at 70–90 °C (0.03 mm) to give 21 mg of a clear liquid. A VPC of this liquid on a 5 ft × 0.125 in. 10% Carbowax 20M on Chromosorb W column at 120 °C showed five poorly resolved peaks with retention times and relative peak heights of 2 min (0.5, shoulder), 2.25 min (1), 2.5 min (0.3), 3 min (0.3), 3.75 min (0.3). This material was shaken overnight in 1 mL of ethanol with a catalytic amount of 10% palladium on charcoal under 40 psi of hydrogen. No change in the VPC of the material was observed after this treatment. Fractions 2 and 3 showed molecular ions of *m/e* 208 (tetrahydrobulnesene). Of fractions 4 and 5 with *m/e* 206 (dihydropatchulenes) the latter could be matched in mass fragmentation with a dihydro-α,γ-patchulene sample obtained by hydrogenation (below). A corresponding reaction sequence using benzene as photolysis solvent also gave these four product fractions in similar amounts in addition to two minor components.

Catalytic Hydrogenation of γ-, α-, and β-Patchulenes. A solution of 243 mg of the isomeric patchulenes (1:3.8:1.6)[27a] in 15 mL of ethanol was stirred with 17 mg of 10% palladium on charcoal under hydrogen until uptake ceased (34 mL). The mixture was then filtered and concentrated to give an oil which was distilled at 70–90 °C (0.03 mm) to give 199 mg of a clear liquid. A VPC of this liquid on a 5 ft × 0.125 in. 10% Carbowax 20M on Chromosorb W column at 130 °C showed three peaks with retention times and relative areas of 1.75 min (1) (γ-patchulene, unreduced), 3.375 min (2.52), and 4 min (1.96). Samples of each component were collected by preparative VPC on a 10 ft × 0.25 in. 20% Carbowax 20M on Chromosorb W column at 180 °C. The first fraction showed peaks at *m/e* (rel intensity) 218 (31) contaminant, 204 (71), 184 (100), 151 (90), 133 (35), 119 (51), 93 (32), and 41 (44); fraction 2 had peaks at *m/e* (rel intensity) 206 (100), 191 (74), 163 (79), 107 (62), 95 (61), 82 (79), 81 (60), 41 (56); fraction 3 had peaks at *m/e* (rel intensity) 206 (77), 163 (100), 122 (75), 107 (81), 95 (100), 81 (82), 69 (63), 41 (91).

Reaction of Geranyl Acetate with Ethanethiol. A. Diphenyl Disulfide Initiated Photolysis. A mixture of geranyl acetate, bp 63–70 °C (0.1 mm)[31] (1.97 g, 0.01 mol), ethanethiol (0.74 mL, 0.62 g, 0.01 mol), and diphenyl disulfide (0.024 g, 0.098 mmol) was purged with nitrogen and sealed in a Pyrex tube. The mixture was irradiated with a 450-W high-pressure Hg lamp for 15 h. Distillation of the mixture gave three fractions: 1, 1.03 g, bp 55–75 °C (0.03 mm); 2, 0.21 g, bp 75–93 °C (0.03 mm); 3, 0.79 g, bp 94–180 °C (0.03 mm). A VPC of fraction 3 on a 5 ft × 0.125 in. 10% Carbowax 20M on Chromosorb W column at 190 °C showed the presence of starting material, three major products, and three very minor products with retention times and relative areas of A, 1.5 min (0.30, starting material); B, 6 min (1.03); C, 7 min (1); D, 8.5 min (2.13); E, 9.5 min (0.05); F, 12 min (0.09); G, 14 min (0.092). This material was fractionated by preparative VPC on a 10 ft × 0.25 in. 20% Carbowax 20M on Chromosorb W column at 190 °C. Three fractions were collected, corresponding to B, C, and D listed above. B, **20**, *m/e* 258, 260; NMR ($CDCl_3$) δ 5.28 (t, J = 8 Hz, 1 H), 4.28 (q, J = 6 Hz), 2.8–2.3 (5-line pattern, J = 7 Hz,

overlapping a broad absorption), 3.2 and 3.22 (singlets on one finely split doublet), 1.8–1.1 (complex pattern), 1.0 (5-line pattern, J = 4 Hz). C, **19**, m/e 258, 260; NMR ($CDCl_3$) δ 5.58 (t, J = 8 Hz, 1 H), 4.78 (d, J = 8 Hz, 2 H), 2.76–2.2 (complex pattern, 4–5 H), 1.02 (doublet of doublets, J = 4 and 8 Hz, 6 H). D, **18**, m/e 258; NMR ($CDCl_3$) δ 5.58 (t, J = 7 Hz, 1 H), 4.76 (d, J = 7 Hz, 2 H), 2.8–2.2 (complex pattern, 4–5 H), 2.12 (s, 3 H), 1.80 (s, 3 H), 1.28 (t, J = 7 Hz, 3–4 H), 1.01 (t, J = 6 Hz, 6 H). (Small m/e 260 peaks are due to contamination of geranyl acetate with small amounts of citronellyl acetate in this but not in subsequent experiments.)

An analogous reaction in 14 mL of benzene, purged with nitrogen, sealed in a Pyrex tube, and irradiated for 68 h gave 190 mg of a clear oil which by VPC appeared to be about 95% starting material, with about seven or eight products comprising the rest of the mixture.

B. Benzoyl Peroxide Initiated Thermolysis. A mixture of 107 mg (0.545 mmol) of geranyl acetate, 40 μL (33 mg, 0.54 mmol) of ethanethiol, and 3 mg (0.01 mmol) of diphenyl disulfide was purged with nitrogen and sealed in a Pyrex tube. The mixture was then heated in an oven at 85 °C for 15 h. Distillation of the mixture at 100–130 °C (0.03 mm) gave 98 mg of a clear liquid. A VPC of this liquid on a 5 ft × 0.125 in. 10% Carbowax 20M on Chromosorb W column at 190 °C showed the product to consist of about 92% starting material, with the remainder distributed approximately equally between four products with retention times of 4.75, 5.5, 6.75, and 8.5 min. A similar reaction in benzene gave 99% recovery of starting material.

Raney Nickel Desulfurization of Ethanethiol–Geranyl Acetate Reaction Mixture. The product from the diphenyl disulfide initiated photolysis of ethanethiol and geranyl acetate was fractionated by preparative VPC on a 10 ft × 0.375 in. 20% SE-30 on Chromosorb W column at 170 °C. One fraction was collected which contained all of the adducts and none of the starting material. This material (36 mg) was heated overnight in refluxing ethanol with an excess of W4 Raney nickel. The reaction mixture was then filtered and the catalyst was washed several times with boiling ethanol. The filtrate was concentrated and distilled at 50–70 °C (0.03 mm). A VPC of this liquid on a 5 ft × 0.125 in. 10% Carbowax 20M on Chromosorb W column at 127 °C showed two peaks with retention times and relative areas of 2.5 min (9.4) and 3.75 min (1). The major peak was identical by VPC with a sample of tetrahydrogeranyl acetate. The minor peak was identical by VPC with dihydrocyclogeranyl acetate.

Reaction of Geranyl Acetate with Dimethyl Disulfide. Geranyl acetate (1.96 g, 0.01 mmol) and dimethyl disulfide (0.88 mL, 0.94 g, 0.01 mol) were sealed in a Pyrex tube and irradiated for 17 h with 450-W high-pressure Hg lamp. The reaction mixture was then distilled and three fractions were collected: fraction 1, 0.52 g, bp 65–94 °C (0.08 mm); fraction 2, 1.06 g, bp 94–120 °C (0.08 mm); and fraction 3, 0.16 g, bp 120–160 °C (0.08 mm). Vapor phase chromatography using a 5 ft × 0.125 in. 10% Carbowax 20M on Chromosorb W column at 185 °C showed fraction 1 to be mainly starting material with small amounts of three products. Fraction 2 consisted of starting material, three major products with retention times and relative areas of 0.75 min (2.26); **20**, 3.25 min (1.67); **19**, 3.75 min (1); **18**, 4.5 min (2.78); and three minor products with retention times of 5, 6, and 7 min. Accurate measurement of the areas of these last three peaks was not possible. Fraction 3 consisted of the same components as fraction 2 with one additional component having a retention time of 14.5 min. The approximate relative peak areas were 1.00, 0.08, 0.47, 1.05, 0.036, 0.16, and 1.33. A portion of fraction 2 was fractionated by preparative VPC on a 10 ft × 0.25 in. 20% Carbowax 20M on Chromosorb W column at 180 °C. Six fractions were collected. A: m/e 244 (M^+); NMR ($CDCl_3$) δ 4.9 (t), 4.1 (m), 2.1 (s), 2.025 (s), 2.02 (s), 2.01 (s), 1.82 (s), 1.62 (d), 1.41 (d), 0.92 (t). B: m/e 244 (M^+); NMR ($CDCl_3$) δ 5.25 (t, J = 7 Hz, 1 H), 4.5 (d, J = 7 Hz, 2 H), 2.24 (m, 3 H), 2.03 and 2.01 (s, 9 H), 1.74 (s, 3 H), 0.94 (doublet of doublets, J = 6 and 2 Hz, 6 H). C: m/e 244 (M^+); NMR ($CDCl_3$) δ 5.24 (t, J = 7 Hz, 1 H), 4.48 (d, J = 7 Hz, 2 H), 2.08–2.28 (m, 3 H), 2.04 (s, 8–9 H), 1.68 (s, 3–4 H), 0.96 (doublet of doublets, J = 8 and 4 Hz, 6 H). D, E, and F, m/e 244 (M^+). Not enough material was obtained for an NMR of D, E, or F.

Raney Nickel Desulfurization of Photolysis Product. Fraction 2 from the distillation of the above photolysis product was fractionated by preparative VPC on a 10 ft × 0.375 in. 20% SE-30 on Chromosorb W column at 190 °C. Two fractions were collected, the first containing starting material and the second containing all of the products. A portion (92 mg) of the product fraction was heated in refluxing acetone for 6 h with an excess of W4 Raney nickel. The mixture was then filtered and the catalyst was washed several times with boiling acetone. The combined filtrates were concentrated on a rotary evaporator and distilled at 80–120 °C (0.03 mm) to give 55 mg of a clear, colorless liquid. This liquid was stirred in 10 mL of acetic acid with 6 mg of 10% palladium on charcoal under 1 atm of hydrogen until hydrogen uptake ceased. The mixture was then filtered, concentrated, and distilled to give 10 mg of a clear, colorless liquid: IR (liquid film) 3450 (m, broad), 2850–3000 (s), 1740 (s), 1700 (m, sh), 1350–1380 (m, b), 1200–1275 cm^{-1} (m). This liquid was heated at 90 °C with acetic anhydride and potassium carbonate in a sealed tube overnight. After cooling, the mixture was dissolved in benzene and washed with saturated sodium bicarbonate and saturated brine, dried ($MgSO_4$), and distilled at 80–120 °C (0.03 mm) to give 8.9 mg of a clear liquid. A VPC of this material on a 5 ft × 0.125 in. 10% Carbowax 20M on Chromosorb W column at 125 °C showed four peaks with retention times and relative areas for tetrahydrogeranyl acetate (**23**), 3.25 min (5.5); the epimeric dihydrocyclogeranyl acetates (**22**), 4 min (1), 4.5 min (0.16), and a peak at 6 min (0.07).

Reaction of Geranyl Acetate and Dimethyl Disulfide in Cyclohexane. Irradiation of geranyl acetate (0.49 g, 2.5 mmol), dimethyl disulfide (0.21 mL, 0.24 g, 2.5 mmol), and 5 mL of cyclohexane for 24 h, concentration, and distillation at 100–150 °C (0.025 mm) gave 0.273 g of a clear liquid and 0.351 g of a nonvolatile material. A VPC of the distillate on a 5 ft × 0.125 in. 10% Carbowax 20M on Chromosorb W column at 190 °C showed, in addition to a small trace of starting material, seven components with the following retention times and relative peak areas: starting material, 0.75 min (1); A, 3.25 min (6.92); B, 3.75 min (4.95); C, 4.5 min (5.39); D, 5.25 min (1.15); E, 5.75 min (1.24); F, 6.625 min (1.91); G, 14.5 min (17.75). This product mixture was fractionated by preparative VPC on a 10 ft × 0.375 in. 20% SE-30 on Chromosorb W column at 190 °C into 49.1 mg of components A–F, m/e 244 (M^+), and 108 mg of component G, m/e 290 and 292, corresponding to geranyl acetate plus dimethyl disulfide and geranyl acetate plus two molecules of methyl mercaptan: NMR ($CDCl_3$) δ 4.28 (d, J = 6 Hz, overlapping with another absorption), 2.74 (m), 2.16 (s), 2.08 (s), 1.76 (broad), 1.54 (broad), 1.25 (s), 0.98 (symmetrical multiplet). A reaction in benzene gave analogous results.

Raney Nickel Desulfurization of Photolysis Product. Components A–F from the preparative VPC of the distilled photolysis product were stirred in 5 mL of refluxing ethanol with an excess of W4 Raney nickel for 6 h. The mixture was then filtered and the catalyst washed with several portions of boiling ethanol. The resulting ethanol solution was concentrated on a rotary evaporator and distilled at 80–100 °C (0.03 mm) to give 32.1 mg of a clear, colorless liquid. A VPC of this material on a 5 ft × 0.125 in. 10% Carbowax 20M column at 125 °C showed four components with retention times and relative areas of 3 min (1), tetrahydrogeranyl acetate 3.75 min (1.78), and 4.25 min (0.05), dihydrocyclogeranyl acetate, and a peak at 5.375 min (0.13).

Component G from the preparative VPC of the photolysis product was similarly treated. Distillation gave 7 mg of a clear, colorless liquid. A VPC showed three components with retention times and relative areas of 1.75 min (1), 3 min (3.08), tetrahydrogeranyl acetate, 4.75 min (0.103).

Reaction of Geranyl Acetate with Diphenyl Disulfide. Photolysis in Acetonitrile. A solution of 1.97 g (0.011 mol) of geranyl acetate and 2.18 g (0.01 mol) of diphenyl disulfide in 160 mL of acetonitrile was purged with nitrogen and irradiated with a Hg high-pressure lamp through a Vycor filter for 24 h. The light immersion well became heavily coated with an ether- and acetone-insoluble material. The solution was concentrated and distilled to give two fractions: A, 1.99 g, bp 70–95 ° C (0.1 mm); B, 0.75 g, bp 95–250 °C (0.1 mm). Some nonvolatile material remained. A VPC of fraction B on a 5 ft × 0.125 in. 5% SE-30 on Chromosorb W column at 210 °C showed, in addition to a small amount of starting material, seven components with the following retention times and relative areas: 0.75 min (0.11), 1.25 min (0.08), 1.5 min (3.49), 1.75 min (0.36), 5.5 min (1.84), 10.5 min (6.5), 13 min (1). Fraction B was fractionated by preparative VPC on a 10 ft × 0.375 in. 20% SE-30 on Chromosorb W column at 220 °C. Five fractions were collected: 1, NMR ($CDCl_3$) δ 7.6 (d, J = 8 Hz), 7.35 (d, J = 7 Hz), 4.63 (d, J = 8 Hz), 2.7 (s), 1.64 (d, J = 9 Hz), 0.9 (broad); 2, m/e (rel intensity) 294 (2.6), 218 (3.2), 186 (100), 185 (41), 184 (19), 140 (2), 109 (13); NMR ($CDCl_3$) δ 7.38 (s), 2.28, 2.07, 1.8, 1.24, 0.9 (broad, weak absorptions); 3, m/e (rel intensity) 294 (4.8), 285 (1), 218 (100), 185 (37), 184 (65), 140 (67), 109 (28); NMR ($CDCl_3$) δ 7.3 (m), 4.26 (broad), 3.28 (broad), 2.04 (weak, broad), 1.64 (s), 1.2 (s), 0.9 (weak, broad); 4, m/e (rel intensity) 294 (28), 255 (13), 218 (69), 185 (36), 184 (56), 140 (44), 109 (100); NMR ($CDCl_3$) δ 7.3 (m, strong), 3.3 (broadened singlet), 1.65 (s), 1.28 (s), 0.9 (m, broad); 5, m/e (rel intensity) 294 (100), 285 (1.4), 218 (21), 185 (42), 184 (76), 140 (15), 109 (64); NMR ($CDCl_3$) δ 7.39 (m), weak absorptions at 4.27 (s), 3.3 (broadened singlet), 1.64 (s), 1.26 (s, broad), 0.9 (m, broad); IR ($CHCl_3$) 2910 (m, broad), 1565 (m-s), 1435 (sharp), 1475 cm^{-1} (sharp).

Raney Nickel Desulfurization of Photolysis Product. Fraction

B (68.5 mg) from the distillation of the crude photolysis product was treated with an excess of W4 Raney nickel in refluxing ethanol for 4 h. Distillation of the product at 100 °C (0.03 mm) gave 10.3 mg of a clear liquid: IR (thin film) 3400 (m, broad), 3070 (w, sh), 3035 (w, sh), 2960 (s, sh), 2935 (s, sh), 2860 (m, sh), 2810 (shoulder), 1730 (m, sh), 1450 (m, broad), 1365 (m, broad), 1235 (m, broad), 1050 cm^{-1} (m, broad). This liquid was added to acetic anhydride (10 μL) and a few crystals of anhydrous sodium acetate in a Pyrex tube which was sealed and heated in an oven at 110 °C for 6 h. Distillation at 100 °C (0.03 mm) gave 5.2 mg of a clear liquid. A VPC of this liquid on a 5 ft × 0.125 in. 10% Carbowax 20M on Chromosorb W column at 125 °C showed six peaks with the following retention times and relative areas: A, 3 min (1), B, 4 min (0.078), C, 5 min (1.76), D, 7 min (0.167), E, 8.25 min (5.34), F, 21.5 min (2.22). A VPC of a mixture of this product and tetrahydrogeranyl acetate showed enhancement of component A. A VPC of the product with added dihydrocyclogeranyl acetate showed enhancement of components B and C.

Analogous cyclization reactions and desulfurizations were carried out in benzene and cyclohexane with diphenyl disulfide and with trifluoromethyl disulfide and di-*tert*-butyl disulfide. The results are listed in Table II.

Preparation of Dihydrocyclogeranyl Acetate (22). α-Cyclogeraniol[32] (1.014 g, 6.6 mmol) and 70 mg of 10% palladium on charcoal were stirred in 20 mL of ethanol under 1 atm of hydrogen until the calculated amount of hydrogen (148 mL) had been absorbed. The mixture was then filtered, concentrated, and distilled to give 0.433 g (42%) of dihydrocyclogeraniol distilled at 80–100 °C (block temperature) at 0.04 mm: NMR ($CDCl_3$) δ 3.76 (d, J = 6 Hz), 2.0 (broad singlet), 1.68–1.08 (complex pattern), 1.0 (s), 0.88 (s).

Dihydrocyclogeraniol (0.119 g, 0.767 mmol), acetic anhydride (72.3 μL, 0.0782 g, 0.767 mmol), and sodium acetate (85.2 mg, 1.04 mmol) were heated in a sealed tube for 4 h at 150 °C. The tube was then cooled and the contents added to cold water. After standing for 15 min, the mixture was extracted several times with ether. The ethereal solutions were combined, washed with saturated aqueous sodium bicarbonate and saturated aqueous sodium chloride, dried ($MgSO_4$), concentrated, and distilled at 80–100 °C (0.04 mm) to give 105.6 mg (69%) of a clear oil: NMR ($CDCl_3$) δ 4.04 (d, J = 4 Hz, 2 H), 1.98 (s, 3 H), 1.8–1.1 (complex pattern, 8 H), 1.0–0.8 (complex pattern, 9 H); IR (thin film), 1735 cm^{-1}; VPC (5 ft × 0.125 in. 10% Carbowax 20M on Chromosorb W, 125 °C), 4 min (1) and 4.5 min (0.65).

Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18; O, 16.14. Found: C, 72.96; H, 11.30.

1,1-Dicarbomethoxy-3-methylcyclohexane (6). Following a procedure developed in our laboratory by Reider for an analogous compound, a solution of 3.0 g (2.0 mmol) of methoxymethyl dimethylmalonate and 2.2 g (2.0 mmol) of *N*-pyrrolidino-1-propene in 10 mL of acetonitrile was stirred under nitrogen at room temperature for 20 h. Then 3 mL of acetic acid in 12 mL of water was added and after 5 h the mixture was extracted with dichloromethane and concentrated. Distillation at 95–110 °C (0.003 mm) gave 2.0 g of crude 4,4-dicarbomethoxy-2-methylbutyraldehyde. A solution of 0.90 g (5.0 mmol) of this compound in 6 mL of dry tetrahydrofuran was added over 1 h to a stirred suspension of 2.0 g (5.4 mmol) of triphenylvinylphosphonium bromide and 0.14 g (6.0 mmol) of sodium hydride in 4 mL of tetrahydrofuran. After stirring for 20 h the mixture was filtered through Celite and concentrated and the residue triturated with five 30-mL portions of hexane. Concentration and distillation at 120–130 °C (18 mm) gave 0.24 g of 4,4-dicarbomethoxy-6-methylcyclohexene: NMR ($CDCl_3$) δ 1.05 (d, 3 H), 1.5–3.0 (m, 5 H), 3.80 (s, 6 H), 5.7 (m, 2 H); *m/e* (rel intensity) 212 (7), 211 (58), 151 (81), 136 (68), 92 (89), 91 (96), 90 (100), 78 (84), 58 (75).

Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.37; H, 7.70.

Catalytic hydrogenation of 0.10 g of the cyclohexene diester in 3 mL of methanol with 0.14 g of 5% palladium on charcoal catalyst resulted in 11 mL uptake of hydrogen in 10 min. Distillation of the product at 120–140 °C (18 mm) gave 0.10 g of **6** which showed only one VPC peak on a DEGS on Chromosorb W 13-ft column at 160 °C with retention time at 7.7 min (as compared with 7.1 min for the *meso*-dimethylcyclopentane diester **4a**) and *m/e* (rel intensity) 214 (0.6), 213 (4), 153 (21), 144 (100), 113 (51), 95 (100), 82 (43), 59 (21), 55 (21), 42 (28).

1,1-Dicarbomethoxy-3,4-dimethylcyclopentanes (4a,b). To a mixture of 0.22 g (0.91 mmol) of *meso*- or *dl*-1,4-dibromo-2,3-dimethylbutane and 0.12 g (0.92 mmol) of dimethyl malonate in 5 mL of refluxing methanol was added 0.11 g (2.0 mmol) of sodium methoxide in 10 mL of methanol, over 1.5 h. After an additional 1.5 h at reflux the solvent was evaporated under vacuum and the product dissolved in ether. Concentration and distillation at 120–140 °C (18 mm) gave 50 mg of product with the meso or *dl* compounds **4a,b** in respective experiments showing VPC peaks at 7.0 and 5.5 min on a 5-ft 20% Carbowax 20M on Chromosorb W column at 175 °C (15 mL/min) or at 7.1 and 5.8 min on a 13-ft DEGS on Chromosorb W column at 160 °C (25 mL/min): *m/e* 214; NMR ($CDCl_3$) δ 3.7 (s, 6 H), 1.6–2.6 (b, 6 H), 0.85 (d, 6 H) for cis dimethyl compound **4a** and 0.94 (d, 6 H) for trans dimethyl compound **4b**. In addition two compounds with shorter VPC retentions and solid products (2:1 alkylation) were found.

Preparation of Methyl 2-Phenylpent-4-enoate (25). Methyl phenylacetate (6.0 g, 0.04 mol) was added dropwise to a solution of triphenylmethylpotassium prepared from 9.76 g (0.04 mol) of triphenylmethane, 1.56 g (0.04 g-atom) of potassium, 35 mL of 1,2-dimethoxyethane, and 3 mL of butadiene.[33] To the resulting suspension was added 4.84 g (0.04 mol) of allyl bromide in 5 mL of 1,2-dimethoxyethane. After stirring for 1 h, the mixture was filtered and the residual potassium bromide was washed with ether. The combined organic solution was washed with water and saturated aqueous sodium chloride, dried over magnesium sulfate, and concentrated to a yellow semisolid material. Distillation gave 6.50 g [bp 110–204 °C (14 mm)]. The distillate was chromatographed on silica gel using first hexane and then methanol as the eluent. The methanol fraction was concentrated and distilled to give 5.50 g (73.3%) of a clear liquid: bp 66–67 °C (0.25 mm); NMR ($CDCl_3$) δ 7.14 (s, 5 H), 5.8–5.4 (m, 1 H), 5.08–4.8 (m, 2 H), 3.56 (s, 3 H, overlapping with a triplet, 1 H), 2.9–2.3 (m, 3 H); IR (liquid film) 3080 (w), 3020 (w), 3000 (w), 2955 (w-m), 1730 (s) 1635 (m), 1600 cm^{-1} (m-w).

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42; O, 16.82. Found: C, 75.76; H, 7.48.

Preparation of Methyl 2-Phenyl-5-methyl-4-hexenoate (24). Using the preceding procedure and 7.64 g (31.3 mmol) of triphenylmethane, 1.22 g (0.0313 g-atom) of potassium, 35 mL of 1,2-dimethoxyethane, 2 mL of butadiene, 4.69 g (31.3 mmol) of methyl phenylacetate, and 1-bromo-3-methyl-2-butene (4.69 g, 31. mmol), gave 4.85 g (71%) of a clear, colorless, chromatographed liquid: bp 79–80 °C (0.025 mm); NMR ($CDCl_3$) δ 7.14 (s, 5 H), 4.94 (t, J = 6 Hz, 1 H), 3.56 (s, 3 H), 3.48 (t, J = 8 Hz, 1 H), 1.6 (s, 3 H), 1.54 (s, 3 H); IR (liquid film) 3020, 2960, 2950, 2910, 1735, 1600 cm^{-1}.

Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31; O, 14.66. Found: C, 76.90; H, 8.42.

Preparation of 2-Phenyl-5-methyl-4-hexenonitrile. A solution of 6.0 g (0.05 mol) of phenylacetonitrile and 11.20 g (0.075 mol) of 1-bromo-3-methyl-2-butene in 5 mL of dimethyl sulfoxide and 20 g of a 50% aqueous sodium hydroxide solution were simultaneously added slowly to 40 mL of dimethyl sulfoxide in a 250-mL flask. Stirring was continued for 1 h after which the reaction mixture was diluted with 100 mL of water and extracted with two 40-mL portions of benzene and one 40-mL portion of ether. The combined organic solution was washed with saturated aqueous sodium bicarbonate and saturated aqueous sodium chloride, dried over magnesium sulfate, and concentrated. Distillation of the residual oil gave three fractions: fraction 1, 1.13 g, bp 65–85 °C (0.05 mm); fraction 2, 5.21 g, bp 85–115 °C (0.05 mm); NMR ($CDCl_3$) δ 7.16 (s, 5 H), 5.04 (t, J = 8 Hz, 1 H), 3.66 (t, J = 6 Hz), 2.50 (t, J = 6 Hz), 1.66 (s, 3 H), 1.48 (s, 3 H); fraction 3, 2.47 g, bp 115–140 °C (0.05 mm) (contains dialkylated product).

Preparation of 2,5-Dimethyl-2-phenyl-4-hexenonitrile (26). A solution of 2-phenyl-5-methyl-4-hexenonitrile (2.70 g, 0.0146 mol) and methyl iodide (10.35 g, 0.073 mol) in 3 mL of dimethyl sulfoxide and 5.84 g of a 50% aqueous sodium hydroxide solution were simultaneously added to 12 mL of dimethyl sulfoxide. Stirring was continued for 1 h after which the reaction mixture was diluted with 40 mL of water and extracted with two 20-mL portions of benzene and one 20-mL portion of ether. The combined organic solution was washed with saturated aqueous sodium bicarbonate and saturated aqueous sodium chloride and dried ($MgSO_4$), concentrated, and distilled to give 2.23 g (77.5%) of a clear liquid: bp 78–90 °C (0.04 mm); NMR ($CDCl_3$) δ 7.22 (m, 5 H), 5.02 (t, J = 7 Hz, 1 H), 2.52 (d, J = 7 Hz), 1.66 (s, 6 H), 1.52 (s, 3 H); IR (thin film) 3060 (w), 2980 (m), 2235 (w), 1600 cm^{-1} (w).

Anal. Calcd for $C_{14}H_{17}N$: C, 84.37; H, 8.60; N, 7.03. Found: C, 84.41; H, 8.55; N, 6.89.

Preparation of 2-Phenyl-5-hexenonitrile. Following the above procedure for 2-phenyl-5-methyl-4-hexenonitrile, a mixture of phenylacetonitrile (6.0 g, 0.05 mol) and 1-bromo-3-butene (10.13 g, 0.075 mol) in 5 mL of dimethyl sulfoxide and 20 g of 50% aqueous sodium hydroxide gave fraction 1, 1.37 g, bp 30–136 °C (8 mm); fraction 2, 5.31 g, bp 136–147 °C (8 mm); NMR ($CDCl_3$) δ 7.12 (s, 5 H), 5.8–5.3 (m, 1 H), 5.0 (d, J = 6 Hz, 1 H), 4.88 (s, 1 H), 3.70 (t, J = 8 Hz, 1 H), 2.3–1.8 (m, 4 H); fraction 3, 1.18 g, bp 147–155 °C (8 mm).

Preparation of 2-Methyl-2-phenyl-5-hexenonitrile (28). A mixture of 2-phenyl-5-hexenonitrile (5.31 g, 0.031 mol) and methyl iodide (6.6 g, 0.0465 mol) in 5 mL of dimethyl sulfoxide, and 12.4 g of a 50% aqueous sodium hydroxide solution, by the preceding procedure, gave 5.25 g (91%) of a clear liquid: bp 59–69 °C (0.03 mm); NMR ($CDCl_3$) δ 7.14 (m, 5 H), 5.76–5.36 (m, 1 H), 4.88 (d, J = 6 Hz, 1 H), 4.74 (s, 1 H), 1.96 (m, 4 H), 1.66 (s, 3 H); IR (liquid film) 3060 (m), 2980 (m), 2935 (m), 2235 (w), 1640 (w-m), 1600 cm^{-1} (w). Preparative VPC on a 10 ft × 0.375 in. SE-30 on Chromosorbe W column at 190 °C afforded the analytical sample.

Anal. Calcd for $C_{13}H_{15}N$: C, 84.28; H, 8.16; N, 7.56. Found: C, 84.47; H, 8.23; N, 7.38.

Attempted Aryl Olefin Cyclizations. The preceding compounds (**24–28**) were subjected to reactions with ethanethiol with radical initiation by photolysis of diphenyl disulfide or thermolysis of benzoyl peroxide in benzene, or without solvent, in each case. Alternatively, dimethyl disulfide or di-*tert*-butyl disulfide were used as thiyl precursors. Procedures analogous to those used for the dienes, or reaction times extended to 4 days, led to olefin addition products and no significant cyclization. Crude and fractionated reaction products and Raney nickel desulfurized, hydrogenated products were examined by mass fragmentation, using characteristic m/e = M of aryl olefin + RS − H and m/e = M of aryl olefin, respectively, to find cyclization products.

Since no significant product fractions with such molecular ions were found but instead only products with m/e = M + RSH and m/e = M + 2 were obtained for the thiol adducts and their desulfurization products, experimental descriptions of these cyclization failures are omitted.

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Registry No.—**1**, 35357-77-8; **2a** (R′ = Et; A = H), 61558-92-7; **2a** (R′ = Me; A = SMe), 61558-93-8; **2a** (R′ = Me; A = H), 61559-00-0; **2b** (R′ = Et; A = H), 61558-94-9; **3** (R′ = Et; A = H), 61558-95-0; **3** (R′ = Me; A = SMe), 61558-96-1; **4a**, 61558-97-2; **4b**, 61558-98-3; **5**, 16644-05-6; **6**, 61558-99-4; **7**, 24048-44-0; **8** (X = H), 61559-01-1; **8** (X = SMe), 61559-02-2; **9**, 13567-54-9; **9** dehydro derivative, 546-28-1; **10**, 3691-11-0; **10** CH_3SSCH_3 adduct 1, 61559-32-8; **10** CH_3SSCH_3 adduct 2, 61559-03-3; **11**, 21073-70-1; **12a**, 25491-20-7; **12b**, 3724-42-3; **13a**, 560-32-7; **13b**, 508-55-4; **15**, 514-51-2; **16**, 105-87-3; **17** (R = Et), 61559-04-4; **17** (R = Me), 61559-05-5; **17** (R = Ph), 61559-06-6; **18** (R = Et), 61559-07-7; **18** (R = Me), 61559-08-8; **18** (R = Ph), 61559-09-9; **19** (R = Et), 61559-10-2; **19** (R = Me), 61559-11-3; **19** (R = Ph), 61559-12-4; **20** (R = Et), 61559-13-5; **20** (R = Me), 61559-14-6; **20** (R = Ph), 61559-15-7; **21** (R = Et), 61559-16-8; **21** (R = Me), 61559-17-9; **21** (R = Ph), 61559-18-0; **22**, 61559-19-1; **22** free alcohol, 34026-01-2; **23**, 20780-49-8; **24**, 61559-20-4; **25**, 14815-73-7; **26**, 51559-21-5; **28**, 61559-22-6; ethanethiol, 75-08-1; dimethyl disulfide, 624-92-0; bis(trifluoromethyl) disulfide, 372-64-5; diphenyl disulfide, 882-33-7; methyl iodide, 74-88-4; di-*tert*-butyl disulfide, 110-06-5; methoxymethyl dimethylmalonate, 61559-23-7; *N*-pyrrolidino-1-propene, 13937-88-7; 4,4-dicarbomethoxy-2-methylbutyraldehyde, 61559-24-8; triphenylvinylphosphonium bromide, 5044-52-0; 4,4-dicarbomethoxy-6-methylcyclohexene, 61559-25-9; *meso*-1,4-dibromo-2,3-dimethylbutane, 59635-00-6; *dl*-1,4-dibromo-2,3-dimethylbutene, 59634-99-0; dimethyl malonate, 108-59-8; methyl phenylacetate, 101-41-7; triphenylmethylpotassium, 1528-27-4; butadiene, 106-99-0; allyl bromide, 106-95-6; 1-bromo-3-methyl-2-butene 870-63-3; phenylacetonitrile, 140-29-4; 2-phenyl-5-methyl-4-hexenonitrile, 38179-48-5; 2-phenyl-5-hexenonitrile, 61559-26-0; 1-bromo-3-butene, 5162-44-7.

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(27) Samples of bulnesene and patchouli alcohol were provided by Dr. T. A. Narwid of Hoffmann-La Roche, Inc., Nutley, N.J., and a sample of bulnesol was furnished by Dr. W. I. Taylor of International Flavors and Fragrances, Union Beach, N.J. The isomeric patchulenes were prepared from these compounds according to reported methods: (a) G. Buchi, R. E. Erickson, and N. Wakabayashi, *J. Am. Chem. Soc.*, **83**, 927 (1961); (b) E. von Rudloff, *Can. J. Chem.*, **39**, 1860 (1961); (c) R. B. Bates and R. C. Slagel, *J. Am. Chem. Soc.*, **84**, 1307 (1962).
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