of the cis diacid **29** (0.2 g, 0.005 mol) in methanol (20 ml) was added an excess of an alcoholic–ethereal solution of diazomethane. A colorless solid began to separate after 10 min. After stirring overnight, filtration yielded a colorless solid (0.15 g, 46%) identical[7] in all respects with authentic cis diester **25e**. No trans diester **25d** could be detected by tlc of the isolated solid or of its filtrate.

Oxidation of 25b with *m*-Chloroperbenzoic Acid. The 1:1 cycloadduct **25b** (1.0 g, 0.0018 mol), 85% *m*-chloroperbenzoic acid (0.36 g, 0.0018 mol), and methylene chloride (40 ml) were stirred together overnight at room temperature. Extraction with 10% sodium bicarbonate, water, separation of the methylene chloride layer, drying over sodium sulfate, evaporation under reduced pressure, and recrystallization of the residue from acetonitrile gave 5α,6β-dibenzoyl-1,2,3,4,5,6-hexahydro-1,2,4-triphenyl-1α,4α-epithiopyrid-2-one 7-oxide (**30**) as colorless prisms; 0.65 g (63%), mp 240–243° (Table III).

Oxidation of 25d with *m*-Chloroperbenzoic Acid. The trans diester **25d** (0.78 g, 0.0016 mol), 85% *m*-chloroperbenzoic acid (0.33 g, 0.0016 mol), and methylene chloride were stirred overnight at room temperature. Extraction in the usual manner and recrystallization of the resultant residue afforded a mixture of 5α,6β-di(methoxycarbonyl)-1,2,3,4,5,6-hexahydro-1,2,4-triphenyl-1α,4α-epithiopyrid-2-one 7-oxides (**31** and **32**) as colorless needles from ethanol; 0.5 g (62%), mp 202–205° (Table III).

Hydrolysis of *anhydro*-4-Hydroxy-2,3,5-triphenylthiazolium Hydroxide 1 (R = R¹ = Ph). From the reaction of the mesoionic compound with maleic acid in refluxing benzene was isolated after evaporation of the solvent, chromatography on preparative silica gel (chloroform), and recrystallization from ethanol, *S*-(*N*-phenylbenzimidoyl)mercaptophenylacetic acid as colorless needles: yield 25%; mp 165–167°; ir (KBr) 3280, 3050, 1660 cm^{-1}; λ_{max} (CH_3OH) 245 nm (log ε 4.38); nmr ($CDCl_3$) δ 7.03–8.33 (m, 15, aromatic), 5.60 (s, 1, CH).

Anal. Calcd for $C_{21}H_{17}NO_2S$: C, 72.59; H, 4.93; N, 4.03. Found: C, 72.39; H, 4.82; N, 3.93.

Registry No.—**1** (R = *p*-ClC_6H_4, R^1 = H), 52730-97-9; **1** (R = R^1 = Ph), 18100-80-6; **1** (R = *p*-ClC_6H_4, R^1 = Ph), 52730-98-0; **3** (R = *p*-ClC_6H_4), 52730-99-1; **3** (R = Ph), 52731-00-7; **7** (R = *p*-ClC_6H_4), 52731-01-8; **9** (R = $COCH_3$), 52731-04-1; **9** (R = COOEt), 52731-05-2; **13** (R = *p*-ClC_6H_4), 52731-06-3; **15** (R = Ph), 52746-61-9; **15** (R = *p*-ClC_6H_4), 52795-10-5; **16** (R = *p*-ClC_6H_4), 52731-03-0; **16** (R = Ph), 52731-02-9; **17**, 52731-07-4; **19** (R = $COCH_3$), 52731-08-5; **19** (R = CN), 52731-09-6; **20**, 52731-10-9; **21**, 52731-11-0; **22**, 52748-26-2; **24a**, 52718-86-2; **24b**, 52731-12-1; **24c**, 52731-13-2; **24d**, 52731-14-3; **25a**, 52731-15-4; **25b**, 52748-27-3; **25c**, 52731-18-7; **25d**, 52731-16-5; **25e**, 52746-62-0; **28**, 52731-19-8; **29**, 52731-17-6; **30**, 52731-20-1; **31**, 52731-21-2; **32**, 52746-63-1; *N*-phenylmaleimide, 941-69-5; *trans*-dibenzoylethylene, 959-28-4; methyl vinyl ketone, 78-94-4; ethyl acrylate, 140-88-5; maleic anhydride, 108-31-6; dimethyl fumarate, 624-49-7; dimethyl maleate, 624-48-6; diazomethane, 334-88-3; *m*-chloroperbenzoic acid, 937-14-4; 5α,6β-di(methoxycarbonyl)-1,2-diphenyl-1,2,3,4,5,6-hexahydro-1α,4α-epithiopyrid-2-one 7-*syn*-oxide, 52731-22-3; 5α,6β-di(methoxycarbonyl)-1,2-diphenyl-1,2,3,4,5,6-hexahydro-1α,4α-epithiopyrid-2-one 7-*anti*-oxide, 52746-64-2; ethyl crotonate, 10544-63-5; acrylonitrile, 107-13-1; ethyl methacrylate, 97-63-2; fumaronitrile, 764-42-1; *S*-(*N*-phenylbenzimidoyl)mercaptophenylacetic acid, 52731-23-4.

References and Notes

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Synthesis of Olefins from Thionocarbonates by an Alkylation–Reduction Sequence

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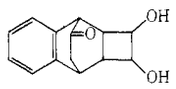
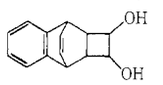
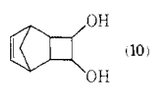
Thionocarbonates are alkylated at sulfur with concomitant ring cleavage by iodide to give vicinal iodo thiocarbonates. The latter are reductively cleaved to olefins by zinc dust reduction. Alkylation with methyl iodide at 90° gives the highest yields of thionocarbonate cleavage products. The method is well suited for preparation of cyclobutenes from the thionocarbonates. Stereochemistry of the starting diol is lost during the two-step procedure. Thus, either *meso*- or *dl*-hydrobenzoin thionocarbonates afford predominantly *trans*-stilbene, and either *cis*- or *trans*-cyclooctanediol thionocarbonates give only *cis*-cyclooctene.

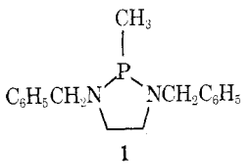
Vicinal diol thionocarbonates are useful synthetic precursors to olefins. The procedure developed by Corey, *et al.*,[1] for thionocarbonate fragmentation with trivalent phosphorus reagents has been used successfully to generate highly strained alkenes including *trans*-cycloheptene,[1a] bicyclo[3.2.1]oct-1-ene,[2a] cyclobutene derivatives,[2b,c] as well as more routine olefins.[2d,f,g] The most common variation employs trialkyl phosphite at 110–160°, but lower reaction temperatures are feasible using 1,3-dibenzyl-2-methyl-1,3-diazaphospholidine (**1**) for desulfurization.[1b] Thionocarbonate decomposition can also be accomplished with zerovalent nickel and iron complexes.[3]

Table I
Olefins from Thionocarbonates and Isopropyl Iodide

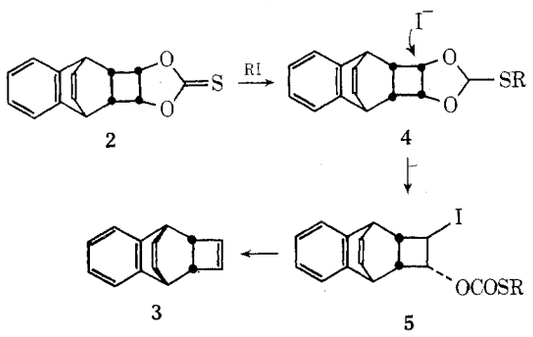
Thionocarbonate derived from	Yield of olefin after alkylation, %	Total yield of olefin after Mg–Hg reduction, %
meso-Hydrobenzoin	86 (*trans*-stilbene)	
dl-Hydrobenzoin	80 (*trans*-stilbene)	
cis-1,2-Dihydroxycyclooctane	32	42 (*cis*-cyclooctene
trans-1,2-Dihydroxycyclooctane	28	54 (*cis*-cyclooctene
1-Methyl-*trans*-1,2-dihydroxycyclohexane	20	30
1-Methyl-*cis*-1,2-dihydroxycyclohexane	27	28
	0	84[a]
	0	60[a]
 (10)	0	54[a]

[a] Zinc dust was used to reduce the iodo thiocarbonate.

As part of a synthetic project,[4] we had planned to prepare the cyclobutene **3** from the thionocarbonate **2.** The reaction with triethyl phosphite proved to be hopelessly slow in this sterically demanding case, and no trace of alkene was found even after 4 days at 120°. The desired conversion did occur when **2** was treated with the diazaphospholidine **1,** but the reaction was still very slow at 155° (84 hr, 57% yield). Also, we experienced considerable difficulty in handling the air-sensitive diazaphospholidine since conversion to the oxide occurred with exceptional ease. It proved necessary to manipulate **1** under argon and to carry out the thionocarbonate reaction under argon in a sealed tube.



1

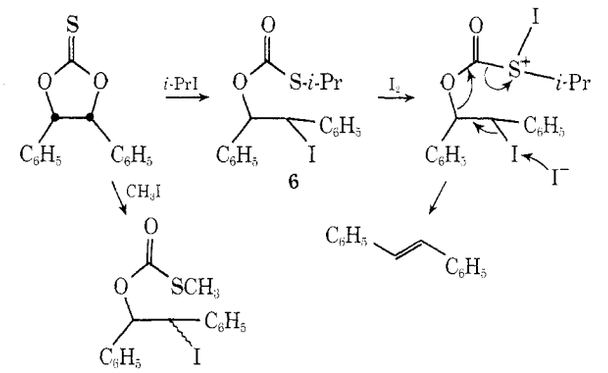


2 **4** **3** **5**

In the hope of finding a more practical alternative route from **2** to **3,** we considered a two-step method for thionocarbonate fragntation. By analogy to the high nucleophilic reactivity of thio amides compared to their oxygen counterparts, it seemed probable that thionocarbonates would be alkylated at sulfur by methyl iodide. Subsequent nucleophilic attack by iodide would then convert the intermediate **4** into **5** which would be reduced easily to the olefin by zinc dust.

Table II
Olefins from Thionocarbonates and Methyl Iodide

Thionocarbonate derived from	Overall yield of olefin after zinc reduction, %
meso-Hydrobenzoin	90 (*trans*-stilbene)
dl-Hydrobenzoin	92 (*trans*-stilbene)
cis-1,2-Dihydroxycyclooctane	72 (*cis*-cyclooctene)
10	84



7a, b

Figure 1.

Methyl iodide proved unreactive at its boiling point, but commercial isopropyl iodide reacted smoothly at 90° (5 hr) to afford an excellent yield of the reasonably stable adduct **5** (characterized by spectral data, see Experimental Section). After reductive elimination using zinc dust in ethanol, **3** was obtained in 60% overall yield from **2.** Although the yield was comparable to that obtained with the diazaphospholidine reagent, the isopropyl iodide method proved more convenient since the reaction is not air-sensitive, the conditions are milder, and the reagent is readily available.

The alkylation–reduction sequence is general, and gives satisfactory yields of cyclobutenes in the three cases studied (Table I). Simple olefins can also be prepared, although the yields are lower due to the sensitivity of the iodo thiocarbonate intermediates. Curiously, the initial alkylation step appears to be catalyzed by some impurity in commercial isopropyl iodide, probably iodine. Isopropyl iodide distilled from sodium thiosulfate does not react with thionocarbonates under the same conditions.

Subsequent experiments established that thionocarbonate alkylation with methyl iodide at 90° (sealed tube) in dimethoxyethane (DME) is faster, gives higher overall yields, and is not influenced by the purity of methyl iodide (Table II). A further difference between the methyl iodide and isopropyl iodide reactions is that the latter gives substantial yields of olefins directly from the alkylation step in cases where the olefin is unstrained.

Thus, reaction of *meso*-hydrobenzoin thionocarbonate with isopropyl iodide gives *trans*-stilbene in 86% yield without a zinc reduction step. Stilbene is probably derived from an intermediate **6** by iodide ion induced E2 elimination.[5] We suggest that iodine formed by decomposition of isopropyl iodide catalyzes the process as shown in Figure 1.

The above rationale is supported by the results of methyl iodide alkylations. Starting with the *meso*-hydrobenzoin thionocarbonate (DME, CH_3I, 90°) an intermediate **7** hav-

ing an SCH_3 singlet at δ 2.35 ppm is formed initially. The alkylation is complete after 14 hr, but a new SCH_3 singlet appears slowly at δ 2.18 ppm as the reaction proceeds. Starting with *dl*-hydrobenzoin thionocarbonate, the initial alkylation product has the δ 2.18 ppm singlet and the δ 2.35 ppm singlet appears more slowly. Stilbene is not present in the crude alkylation products from either *meso*- or *dl*-thionocarbonates. However, stilbene is formed in 85% yield if iodine is added to the methyl iodide reaction. The mixture of **7a,b** also gives stilbene upon treatment with iodine in DME, as does the parent thionocarbonate (75%). From this circumstancial evidence it appears that direct olefin formation is not possible unless a source of iodine is present in the alkylation step.

Reduction of different mixtures of **7a,b** with magnesium amalgam gives the same mixture of stilbenes (*ca.* 95% trans). Thus, even though the thionocarbonate ring cleavage by iodide is at least partly stereoselective,[6] the reductive elimination is not. Similar results are obtained with *cis*- or *trans*-1,2-cyclooctanediol thionocarbonates, either of which gives only the more stable *cis*-cyclooctene after reduction. Thus, the Corey procedure remains the method of choice for stereoselective olefin syntheses. However, the alkylation–reduction sequence should be considered where stereochemistry is not an issue, or where the lower reaction temperature may be advantageous. In particular, the alkylation method can be recommended for the preparation of cyclobutenes since the precursor thionocarbonates are more reactive toward alkyl iodides and the intermediate iodo thiocarbonates are comparatively stable.

Experimental Section

Preparations of Thionocarbonates. General Procedure for Preparing Thionocarbonates from Vicinal Diols. (a) A suspension of the vicinal diol (1 mmol) and *N,N'*-thiocarbonylbisimidazole (1.1 mmol) in dry toluene (6 ml) was refluxed (under nitrogen) for 1–2 hr. Toluene was removed under reduced pressure, and ether (20–30 ml) was added to the residue. The ether solution was washed with water and saturated brine solution, and dried (Na_2SO_4). Evaporation of the solvent usually afforded the corresponding thionocarbonate as yellow crystals. The thionocarbonates were purified by recrystallization from methanol, or by filtration chromatography over silica gel.

(b) Thionocarbonates were also prepared by reaction of the vicinal diol, *N,N'*-thiocarbonylbisimidazole, and a small amount of pyridine in toluene at room temperature for *ca.* 2 hr. Work-up was the same as in (a).

The Thionocarbonate[1a] of *meso*-Hydrobenzoin. Using method (b), *meso*-hydrobenzoin afforded the thionocarbonate in 92% yield: mp 157–158° (methanol); ir ($CHCl_3$) 1355, 1320, 1300, and 1270 cm^{-1} (s, C=S); nmr ($CDCl_3$, δ): 7.30–6.80 (10 H, m), 6.12 (2 H, s); *m/e* 256 (M^+).

The Thionocarbonate[1a] of *dl*-Hydrobenzoin. Method (a): 91% yield, mp 98–99° (methanol); ir ($CHCl_3$) 1320, 1310, 1300, and 1255 cm^{-1} (s); nmr ($CDCl_3$, δ) 7.60–7.18 (10 H, m), 5.50 (2 H, s); *m/e* 256 (M^+).

The Thionocarbonate[1a] of *cis*-1,2-Cyclooctanediol. Method (a): 81% yield, mp 140–141°; ir ($CHCl_3$) 1325 and 1280 cm^{-1} (s, C=S); nmr δ 5.02 (2 H, t, J = 4 Hz), 2.4–0.8 (12 H, m); *m/e* 186 (M^+).

The Thionocarbonate[1a] of *trans*-1,2-Cyclooctanediol. Method (a): 81% yield, mp 108–110°; ir ($CHCl_3$) 1335 and 1270 cm^{-1} (s, C=S); nmr ($CDCl_3$, δ) 4.94 (2 H, t, J = 4 Hz), 2.65–0.8 (12 H, m); *m/e* 186 (M^+).

The Thionocarbonate from 1-Methyl-*trans*-1,2-dihydroxycyclohexane.[7] Method (a): 80% yield, mp 107–108° (methanol); ir ($CHCl_3$) 1320, 1300, and 1290 cm^{-1} (s, C=S); nmr ($CDCl_3$, δ) 4.22 (1 H, dd, J = 12, 4 Hz), 2.40–1.20 (8 H, m), 1.37 (3 H, s); exact mass determination 172.055900 (calcd for $C_8H_{12}O_2S$, 172.055800).

The Thionocarbonate from 1-Methyl-*cis*-1,2-dihydroxycyclohexane.[7] Method (a): a liquid (71% yield); ir 1340 and 1340 cm^{-1} (s, C=S); nmr ($CDCl_3$, δ) 4.57 (1 H, t, J = 4 Hz), 2.40–1.20 (8 H, m), 1.55 (3 H, s); exact mass determination 172.05595 (calcd for $C_8H_{12}O_2S$, 172.05580).

***endo*-Tricyclo[4.2.1.$0^{2,5}$]non-7-ene-*endo*-3,4-diol.** *endo*-3,4-Bis(trimethylsiloxy)tricyclo[4.2.1.$0^{2,5}$]nona-3,7-diene[8] (3.14 g, 10.66 mmol) was stirred with absolute ethanol (10 ml) at room temperature (under nitrogen). After 2 hr, it was completely hydrolyzed to the corresponding acyloin: ir (neat) 3600 and 3450 (s, OH), 1770 cm^{-1} (s, C=O); nmr ($CDCl_3$, δ) 6.12 (2 H, bs), 4.50 (1 H, m, *CH*OH), 3.97 (1 H, br, OH), 3.75–2.50 (4 H, m), 1.77 and 1.53 (2 H, J = 9 Hz, AB quartet) after removal of solvent.

Sodium borohydride (1.5 g) was added to the crude ethanol solution of acyloin from above at −78°, and the resulting mixture was warmed to 0° for 2 hr and then to room temperature (2 hr). Work-up with 5% sodium potassium tartrate and ether extraction produced white crystals (1.2 g, 74%). The diol crystallized from ethanol–hexane as white prisms: mp 135–136°; ir ($CHCl_3$) 3520 and 3400 cm^{-1} (s, OH); nmr ($CDCl_3$, δ) 6.40 (2 H, t, J = 1.7 Hz), 4.35 (2 H, bs), 3.05 (4 H, m), 2.25 (2 H, m, OH), 1.45 and 1.08 (2 H, AB quartet, J = 9 Hz); exact mass determination 134.07294 ($M^+ - H_2O$, calcd for $C_9H_{10}O$, 134.07312).

The Thionocarbonate. Method (a) from the diol (92% yield): mp 89–91°; ir ($CDCl_3$) 1322, 1310, 1270, and 1255 cm^{-1}; nmr ($CDCl_3$, δ) 6.30 (2 H, bs), 5.22 (2 H, t, J = 3 Hz), 3.12 (4 H, bs), 1.60 and 1.16 (2 H, AB quartet, J = 2 Hz); exact mass determination 194.04065 (calcd for $C_{10}H_{10}O_2S$, 194.04018).

Thionocarbonate Reactions with Isopropyl Iodide. Thionocarbonate of *meso*-Hydrobenzoin. A solution of the thionocarbonate (51 mg, 0.2 mmol) in isopropyl iodide (2 ml, commercial sample from Aldrich) was gently heated under reflux for 24 hr. The resulting solution was evaporated, diluted with $CHCl_3$ (5 ml), stirred with a few crystals of $Na_2S_2O_3$, and filtered. The filtrate was concentrated and purified by tlc over silica gel using hexane as eluent. *trans*-Stilbene (31 mg, 86%) was obtained, R_f 0.14.

A solution of the thionocarbonate (26 mg) in purified isopropyl iodide (distilled from $Na_2S_2O_3$) was refluxed for 12 hr. Evaporation of isopropyl iodide afforded starting material (22 mg). If the reaction was continued (2–4 days), evaporation of isopropyl iodide afforded a mixture of starting material, *trans*-stilbene, and uncharacterized labile products containing isopropyl methyls. Upon attempted chromatography, the latter decomposed with liberation of iodine.

When sodium iodide was added to the reaction mixture, the rate of reaction was unchanged.

Reaction of *meso*-Hydrobenzoin Thionocarbonate with Iodine. The thionocarbonate (52 mg, 0.2 mmol), iodine (29 mg, 0.11 mm), and glyme (2 ml) were heated for 20 hr, and the solvent was evaporated. The residue was purified by tlc (hexane), giving *trans*-stilbene (27 mg, 75%; no cis isomer was detected by nmr) and an unidentified product (5.5 mg, yellow crystals, R_f 0.9). When 0.22 mmol of iodine was used, *trans*-stilbene was isolated in 60% yield.

Reactions of the Thionocarbonate of *dl*-Hydrobenzoin with *i*-PrI and Iodine. A solution of thionocarbonate (25 mg, 0.1 mmol) in isopropyl iodide (1 ml) was refluxed for 24 hr. The usual work-up gave *trans*-stilbene (14 mg, 80%).

The reaction was also carried out by using purified isopropyl iodide and stopped after 2–4 days. Removal of isopropyl iodide gave a complex mixture of starting material, *trans*-stilbene, and uncharacterized labile products containing the isopropyl group.

A solution of thionocarbonate (51 mg, 0.2 mmol), iodine (56 mg, 0.22 mmol), and glyme (2 ml) was heated at 90° for 16 hr. The usual work-up (tlc) yielded *trans*-stilbene (19 mg, 52%).

Reaction of the Thionocarbonate of *cis*-1,2-Cyclooctanediol. A solution of thionocarbonate (44 mg, 0.23 mmol) and *i*-PrI (0.5 ml) in a sealed tube was heated at 90° for 19 hr. The total mixture was analyzed by vpc (0.25 in. × 10 ft 10% Carbowax on Chromosorb P 60–80 mesh using 4-methylcyclohexene as internal standard). *cis*-Cyclooctene was formed in 32% yield.

Upon evaporation of the solvent and any olefin formed under vacuum, a residue (70 mg) was obtained: nmr ($CDCl_3$, δ) 5.5 (1 H, m), 4.6 (1 H, m), 3.65 (1 H, m), 1.42 (6 H, d), 1.0–2.4 (10 H, m). The residue was sealed in a glass tube with Mg(Hg) (prepared from 0.2 g of Mg and 0.3 g of $HgCl_2$ in 10 ml of THF and stirred for 15 min at room temperature) in THF (2 ml), and the mixture was stirred at room temperature overnight. The reduction mixture was analyzed by vpc (0.25 in. × 10 ft 20% TCEP on Chromosorb P 60–80 mesh; standard was 1-methylcyclohexene). *cis*-Cyclooctene was produced in 10% yield from this reduction step. Total yield was 42%. No *trans*-cyclooctene was observed in either step.

Reaction of the Thionocarbonate of *trans*-1,2-Cyclooctanediol. A solution of thionocarbonate (30 mg, 0.16 mmol) and *i*-PrI (0.4 ml) in a sealed tube was heated at 90° for 19 hr. It gave *cis*-cyclooctene in 28% yield (0.25 in. × 10 ft 20% TCEP column on

Chromosorb P, 4-methylcyclohexene as standard). Evaporation of the solvent produced a residue. The nonvolatile residue contained the expected iodo thiocarbonate and unknown side products (nmr analysis). Reduction of the residue was carried out as described above to afford *cis*-cyclooctene in 26% yield or 54% combined yield over both steps. *trans*-Cyclooctene was not observed in either step.

Reaction of the Thionocarbonate of 1-Methyl-*trans*-1,2-dihydroxycyclohexenediol. The thionocarbonate was heated at 90° with *i*-PrI for 24 hr and gave 1-methylcyclohexene in 20% yield (0.25 in. × 10 ft 20% TCEP–Chromosorb P, *cis*-cyclooctene as standard). Evaporation of *i*-PrI afforded a residue with a very complicated nmr spectrum. 1-Methylcyclohexane was obtained in 10% yield (20% TCEP, *cis*-cyclooctene as standard), when the residue was reacted with Mg(Hg) by the usual procedure.

Reactions of the Thionocarbonate of 1-Methyl-*cis*-1,2-dihydroxycyclohexane. By the method described above for reaction of the trans diol, 1-methylcyclohexene was obtained in 27% yield directly from the reaction with *i*-PrI. Reduction of the residue with Mg(Hg) as usual gave only 1% 1-methylcyclohexene.

Reaction of the Thionocarbonate of *endo*-Tricyclo[4.2.1.0^{2,5}]non-7-ene-*endo*-3,4-diol. When a solution of the thionocarbonate (58 mg, 0.3 mmol) and *i*-PrI (2 ml) was refluxed for 30 hr the corresponding iodo thiocarbonate was obtained as an oil (112 mg): ir ($CHCl_3$) 1700 cm^{-1} (s, C=O); nmr ($CDCl_3$, δ) 6.33 (1 H, m), 6.20 (1 H, m), 5.15 (1 H, dd, $J \approx 8.6$ Hz, CHO), 4.00 (1 H, dd, J = 6 and 4 Hz, CHI), 3.52 (1 H, quintet, CHS), 3.07 (4 H, bs), 1.36 (6 H, d, J = 8 Hz), 1.53 and 1.14 (2 H, AB quartet). Reduction with zinc dust (0.4 g) in refluxing ethanol (1.5 ml) and water (0.15 ml) for 24 hr, afforded *endo*-tricyclo[4.2.1.0^{2,5}]nona-3,7-diene in 54% yield. The olefin was identified by comparison of its retention time with that of the corresponding exo isomer (20% TCEP, 1-methylcycloheptene as standard).

When purified isopropyl iodide was used, the starting thionocarbonate was recovered. Addition of sodium iodide did not accelerate the reaction.

Reactions with Methyl Iodide. Reaction of *meso*-Hydrobenzoin Thionocarbonate. A mixture of the thionocarbonate (75 mg, 0.3 mmol), purified methyl iodide (0.8 ml), and dry glyme (0.8 ml) in a sealed tube was heated at 90° for 6 hr. White crystals (110 mg) were obtained after evaporation of methyl iodide and glyme. The nmr spectrum of the crystals indicated a mixture of starting thionocarbonate (20%) and the iodo thiocarbonate **7**: nmr δ 7.15 (bs, 10 H), 6.22 (1 H, d, J = 10 Hz, CHO), 5.32 (1 H, d, J = 10 Hz, CHI), 2.35 (3 H, s, CH_3).

A solution of the thionocarbonate (28 mg, 0.11 mmol), methyl iodide (0.5 ml), and glyme (0.5 ml) in a sealed tube was heated for 14 hr. A mixture of **7a,b** was obtained (no starting material was detected by tlc) as evidenced by a major methyl singlet at δ 2.35 ppm and a minor singlet at δ 2.18 ppm.

The mixture of **7a,b** was then treated with iodine (18 mg, 0.07 mmol) in glyme (1 ml) and heated at 90° for 6 hr. The reaction mixture was stirred with crystalline sodium thiosulfate to remove excess of iodine, filtered, and passed through Na_2SO_4. Evaporation of the solvent gave yellow prisms (20 mg, 95%). The product was further purified by filtration through a short silica gel column (eluted with hexane) to afford *trans*-stilbene as white prisms (15 mg, 70%).

A mixture of **7a,b** (26 mg, 0.1 mmol) was stirred with Mg(Hg)/THF (2 ml) (prepared from 0.4 g of Mg and 0.4 g of $HgCl_2$ in 10 ml of THF, stirred for 15 min) for 1 hr at room temperature. The total mixture was passed through a short silica gel column and eluted with hexane to give stilbene containing *ca.* 5% of *cis*-stilbene (nmr analysis) in 90% yield (16.2 mg).

A solution of the *meso* thionocarbonate (25 mg, 0.1 mmol), methyl iodide (0.5 ml), glyme (0.5 ml), and iodine (17 mg, 0.067 mmol) was heated for 6 hr. The usual work-up yielded *trans*-stilbene (85%).

Reaction of *dl*-Hydrobenzoin Thionocarbonate. A solution of the thionocarbonate (26 mg, 0.1 mmol), methyl iodide (0.5 ml), and glyme (0.5 ml) in a sealed tube was heated at 90° for 6 hr. The mixture contained starting thionocarbonate and **7a,b** (2:1 in favor of the δ 2.18 ppm methyl singlet relative to the δ 2.35 methyl singlet).

If the reaction was heated for 12 hr, it gave a mixture of equal amounts of **7a** and **7b**. The reaction intermediate was then treated with Mg(Hg)/THF (2 ml), prepared as usual, for 1 hr at room temperature. The reduced mixture was worked up as before to produce stilbene (*ca.* 5% cis) (16.5 mg, 92%).

Reaction of *cis*-1,2-Cyclooctanediol Thionocarbonate. The thionocarbonate (32 mg, 172 mmol) in glyme (0.5 ml) with CH_3I (0.5 ml) at 90° for 8 hr gave the corresponding iodo thiocarbonate: ir ($CHCl_3$) 1700 cm^{-1}; nmr ($CDCl_3$, δ) 5.35 (1 H, m, CHO), 4.50 (1 H, m, CHI), 2.36 (3 H, s, CH_3), 1.0–2.4 (10 H, m). Reduction of the iodo thiocarbonate with Mg(Hg)/THF (2 ml) (prepared from 0.4 g of Mg and 0.4 g of $HgCl_2$ in 10 ml of THF, stirred for 15 min) gave cyclooctene (72%) (10% Carbowax, 1-methylcycloheptene as standard).

Reaction of the Thionocarbonate of Tricyclo[4.2.1.0^{2,5}]non-7-ene-*endo*-3,4-diol. A solution of the thionocarbonate (58 mg, 0.3 mmol), glyme (0.6 ml), and methyl iodide (0.6 m) (at 90° for 12 hr) afforded the iodo thiocarbonate (100 mg): ir ($CHCl_3$) 1700 (s, C=O), 1140 cm^{-1} (s); nmr ($CDCl_3$, δ) 6.32 (1 H, m), 6.15 (1 H, m), 5.17 (1 H, dd, J = 9 and 6 Hz, CHO), 4.00 (1 H, dd, J = 6 and 4 Hz, CHI), 3.05 (4 H, m), 2.31 (3 H, s, CH_3), 1.50 and 1.10 (2 H, two doublets, J = 9 Hz, AB quartet). A mixture of the iodo thiocarbonate, zinc (0.4 g), ethanol (1.5 ml), and water (0.15 ml) in a sealed tube was heated at 85° for 24 hr. It gave the corresponding olefin in 84% yield (20% TCEP, 1-methylcycloheptene as standard).

1,3-Dibenzyl-2-methyl-1,3-diazaphospholidine. A mixture of *N,N'*-tetramethylmethylphosphonous diamide (7.5 g, 39.4 mmol) and *N,N'*-dibenzylethylenediamine (9.3 g, 38.5 mmol) in a 50-ml flask, which was attached to a distillation apparatus, was stirred and heated at 110–120° in the presence of nitrogen. Diethylamine (4.62 g) was distilled and was collected over a 7-hr period. Excess of the phosphonousdiamide was removed under vacuum and the diazaphospholidine was obtained (10.6 g, 96%): bp 142° (0.09 mm) (lit.[1b] 135° (0.04 mm)); nmr ($CDCl_3$) 7.28 (19 H, s), 4.02 (4 H, d, J = 9.5 Hz), 3.00 (4 H, m), 0.99 (3 H, d, J = 6 Hz).

***syn*-7,8-Benzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene.**[4] (a) A mixture of the olefin thionocarbonate **2**[9] (26 mg, 0.1 mmol) in trimethyl phosphite (173 mg, 1.4 mmol) and benzene-d_6 (100 μl) in a sealed nmr tube was heated at 120° and the reaction was monitored by nmr. After being heated for 4 days, it did not give any change in the spectrum except for appearance of a doublet at about δ 1.0, which was not identifiable. The phosphite was removed and the starting thionocarbonate (24 mg) recovered.

(b) A solution of the thionocarbonate **2** (40 mg, 0.156 mmol) in 1,3-dibenzyl-2-methyl-1,3-diazaphospholidine (0.5 ml or 645 mg) in a sealed tube (under argon) was stirred and heated at 155° for 84 hr. The mixture was dissolved in toluene (20 ml) and then treated with 1 N HCl dropwise until no more precipitate was found. The solid was filtered off and the filtrate, after being passed through a mixture of Na_2SO_4 (anhydrous) and K_2CO_3 (anhydrous) and evaporated, yielded a yellow liquid (143 mg). Purification of the liquid by tlc gave white needles of the hydrocarbon product (16 mg, 57%): mp 41–42°; ir (CCl_4) 3050, 2950, 2920, 1450, 1320, 1280, 680 cm^{-1}; nmr (CCl_4) δ 6.97 (4 H, s, aromatic protons), 6.50 (2 H, dd, J = 4 and 3 Hz, olefinic protons at C_9 and C_{10}), 5.78 (2 H, s, protons at C_3 and C_4), 3.74 (2 H, m, bridgehead protons), 2.72 (2 H, m, protons at C_2 and C_5); mass spectrum *m/e* (%) 47 (40), 48 (10), 49 (17), 50 (8), 51 (17), 52 (62), 63 (10), 76 (10), 83 (86), 84 (62), 85 (59), 86 (40), 87 (10), 101 (35), 127 (11), 128 (64), 129 (7), 152 (17), 165 (47), 178 (35), 179 (100), 180 (74, M^+), 181 (10, $(M+1)^+$); exact mass determination 180.093680 (calcd for $C_{14}H_{12}$, 180.093900).

(c) A solution of the thionocarbonate **2** (13 mg, 0.05 mmol) in isopropyl iodide (1 ml) was refluxed for 5 hr (under nitrogen). Evaporation of the solvent gave a reddish brown residue (22.5 mg, 105%) containing 99% of the iodo thiocarbonate **5** (R = *i*-Pr) by nmr: ir ($CHCl_3$) 2960, 2940, 2870, 1695, 1460, 1259, 1130, 1058, 1000 cm^{-1}; nmr ($CDCl_3$, δ) 7.16 (4 H, m), 6.54 (2 H, bt, J = 6 Hz), 5.11 (1 H, bt, HCO), 4.08 (2 H, m), 3.49 (1 H, m); 3.15 (1 H, t, J = 6 Hz, HCl), 2.88 (2 H, m), 1.36 (6 H, t, J = 8 Hz).

A mixture of the crude iodo thiocarbonate **2**, zinc dust (0.3 g), absolute ethanol (2 ml), and water (0.2 ml) was stirred overnight (12 hr) at room temperature and the hydrocarbon (5.5 mg, 60%) was obtained after usual work-up and tlc purification.

Conversion of the Thionocarbonate[9] of 9-Keto-*syn*-7,8-benzotricyclo[4.2.2.0^{2,5}]dec-7-ene-*cis*-3,4-diol to *syn*-7,8-Benzotricyclo[4.2.2.0^{2,5}]deca-3,7-dien-9-one. (a) A mixture of the keto thionocarbonate (27 mg, 0.01 mol) in trimethyl phosphite was refluxed for 84 hr in a sealed tube (under argon). There was no spot above the base line of the analytic tlc plate when ether was used as mobile phase.

(b) A solution of the keto thionocarbonate (20 mg, 0.073 mmol) and commercial isopropyl iodide (1.5 ml) under nitrogen was heated under reflux for 5 hr. Evaporation of the isopropyl iodide gave 38 mg (100%) of brown residue consisting of a mixture of iodo thiocarbonates: ir ($CHCl_3$) 2960, 2870, 1725 (C=O), 1700 (S—C=O), 1450, 1125, 1055; nmr ($CDCl_3$, δ) 7.32 (4 H, m), 5.32 (1 H, m,

HCO), 4.0–3.0 (6 H, m), 2.20 (2, H, m), 1.37 (6 H, overlapping doublets, J = 7 Hz, CH_3).

The crude iodo thiocarbonates were treated with zinc dust (0.3 g), absolute ethanol (2 ml), and water (0.2 ml) (under nitrogen) and the mixture was refluxed for 14 hr. The zinc was filtered off and the solution was concentrated and purified by tlc (hexane–ether 10:1), affording the cyclobutene product (12 mg, 84%) as white crystals: mp 48°; ir (CCl_4) 3060, 2920, 1725, 1297, 1138, 112 cm^{-1}; nmr (CCl_4) 7.24 (4 H, bs), 5.76 (2 H, ABX, J = 12, 2.5 Hz, olefinic protons), 3.98 (1 H, d, J = 3 Hz, CHC=O), 3.1–3.45 (3 H, m, $CHCH_2$ and C_2H and C_5H), 2.10 (2 H, bs, CH_2C=O); mass spectrum m/e (%) 115 (12), 128 (25), 152 (23), 153 (79), 154 (100, 155 (13), 165 (11), 167 (13), 196 (42, M^+), 197 (7, $(M + 1)^+$); exact mass determination 199.08906 (calcd for $C_{14}H_{12}O$, 196.08875).

Registry No.—**1,** 52718-74-8; **2,** 52718-70-4; **3,** 41791-25-7; **5,** 52718-71-5; *meso*-**7,** 52748-16-0; *dl*-**7,** 52730-77-5; *meso*-hydrobenzoin, 579-43-1; *meso*-hydrobenzoin thionocarbonate, 39247-13-7; *dl*-hydrobenzoin, 655-48-1; *dl*-hydrobenzoin thionocarbonate, 39247-17-1; *cis*-1,2-cyclooctanediol, 27607-33-6; *cis*-1,2-cyclooctanediol thionocarbonate, 50300-29-3; *trans*-1,2-cyclooctanediol, 42565-22-0; *trans*-1,2-cyclooctanediol thionocarbonate, 35859-00-7; 1-methyl-*trans*-1,2-dihydroxycyclohexane, 19534-08-8; 1-methyl-*trans*-1,2-dihydroxycyclohexane thionocarbonate, 52718-64-6; 1-methyl-*cis*-1,2-dihydroxycyclohexane, 52718-65-7; 1-methyl-*cis*-1,2-dihydroxycyclohexane thionocarbonate, 52718-66-8; *endo*-3,4-bis(trimethylsiloxy)tricyclo[4.2.1.$0^{2,5}$]nona-3,7-diene, 39762-43-1; *endo*-tricyclo[4.2.1.$0^{2,5}$]non-7-en-*endo*-3-ol-4-one, 52748-15-9; *endo*-tricyclo[4.2.1.$0^{2,5}$]non-7-ene-*endo*-3,4-diol, 52718-67-9; *endo*-tricyclo[4.2.1.$0^{2,5}$]non-7-ene-*endo*-3,4-diol thionocarbonate, 52718-68-0; isopropyl iodide, 75-30-9; *trans*-stilbene, 103-30-0; iodine, 7553-56-2; *cis*-cyclooctene, 931-87-3; 1-methylcyclohexane, 108-87-2; *endo*-tricyclo[4.2.1.$0^{2,5}$]non-7-ene iodo thiocarbonate, 52718-69-1; *endo*-tricyclo[4.2.1.$0^{2,5}$]nona-3,7-diene, 15564-44-0; methyl iodide, 74-88-4; *cis*-stilbene, 645-49-8; *cis*-1,2-cyclooclane iodo thiocarbonate, 52718-72-6; tricyclo-[4.2.1.$0^{2,5}$]non-7-ene iodo thiocarbonate, 52718-73-7; *N,N'*-tetramethyl methylphosphonous diamide, 14937-39-4; *N,N'*-dibenzylethylenediamine, 140-28-3; 9-keto-*syn*-7,8-benzotricyclo[4.2.2.$0^{2,5}$]dec-7-ene-*cis*-3,4-diol thionocarbonate, 52746-00-6; *syn*-7,8-benzotricyclo[4.2.2.$0^{2,5}$]deca-3,7-dien-9-one, 50849-00-8; 9-keto-*syn*-7,8-benzotricyclo[4.2.2.$0^{2,5}$]dec-7-ene iodo thiocarbonate, 52748-21-7; *N,N*-thiocarbonylbisimidazole, 52718-75-9.

References and Notes

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(6) In the case of the solvolytically unreactive cyclobutene precursors, the product of alkyl iodide thionocarbonate cleavage is clearly the *trans*-iodo thiocarbonate on the basis of nmr evidence. Ring cleavage by iodide ion undoubtedly involves an SN2 process in all cases. Subsequent loss of stereochemistry in the iodo thiocarbonate **7** may be due to SN2 attack by iodide at the carbon–iodine bond of **7.**

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Preparation and Reaction of 2-(2-Hydroxy-2,6-dimethyl-5-heptenyl)-1,3-dithiane. A Synthesis of Linaloyl Oxide (2,6,6-Trimethyl-6-vinyltetrahydropyran)

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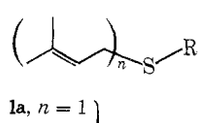
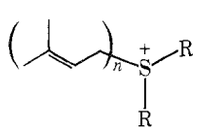
Preparation and reactions of 2-(2-hydroxy-2,6-dimethyl-5-heptenyl)-1,3-dithiane (**3a**) and its conversion to linaloyl oxide (**15**) are described. The alcohol **3a** was prepared in quantitative yield from the reaction of 2,6-dimethyl-1,2-epoxy-5-heptene with 2-lithio-1,3-dithiane. Selective transformations of **3a** into citral (**8**) and its key precursors **9** and **10,** and the tetrahydropyran derivative **11** were carried out. Linaloyl oxide was synthesized in 45% overall yield from 6-methyl-5-hepten-2-one by the following steps: hydrolysis of **11** yielding aldehyde **12,** reduction of **12** to alcohol **13,** and pyrolysis of the xanthate of **13.** Instead of 2-lithio-1,3-dithiane, lithio methyl methylthiomethyl sulfoxide (**16**) could be used for the preparation of linaloyl oxide.

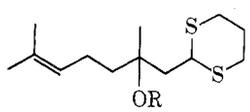
The prenyl,[1] geranyl,[2,3] and farnesyl[4,5] sulfides **1a–c** and the related sulfonium salt **2**[1] have been extensively used in syntheses of biological active terpenoids, juvenile hormones, and sex attractants. We have been interested in developing novel syntheses of terpenoids from 2-(2-hydroxy-2,6-dimethyl-5-heptenyl)-1,3-dithiane (**3a**) instead of from the sulfides and the sulfonium salt.



1a, $n = 1$
b, $n = 2$
c, $n = 3$
} R = alkyl

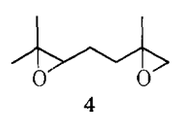


2, $n = 1$; R = alkyl



3a, R = H

In a previous communication,[6] we described a new ring closure of the diepoxide **4** with 2-lithio-1,3-dithiane pro-



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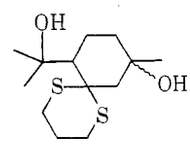

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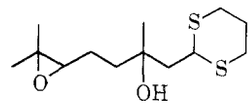

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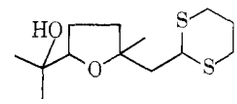

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