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.

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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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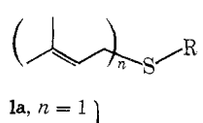
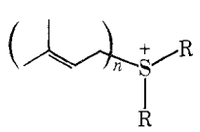
Preparation and reactions of 2-(2-hydroxy-2,6-dimethyl-5-heptenyl)-1,3-dithiane (**3a**) and its conversion to linaloyl oxide (**15**) are described. The alcohol **3a** was prepared in quantitative yield from the reaction of 2,6-dimethyl-1,2-epoxy-5-heptene with 2-lithio-1,3-dithiane. Selective transformations 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.

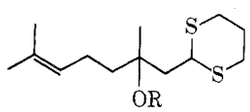
The prenyl,[1] geranyl,[2,3] and farnesyl[4,5] sulfides **1a–c** and the related sulfonium salt **2**[1] have been extensively used in syntheses of biological active terpenoids, juvenile hormones, and sex attractants. We have been interested in developing novel syntheses of terpenoids from 2-(2-hydroxy-2,6-dimethyl-5-heptenyl)-1,3-dithiane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



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

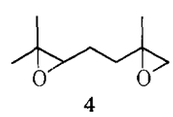


2, $n = 1$; R = alkyl



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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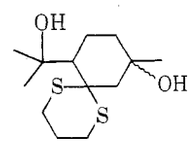

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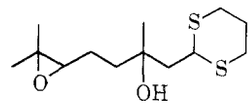

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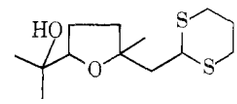
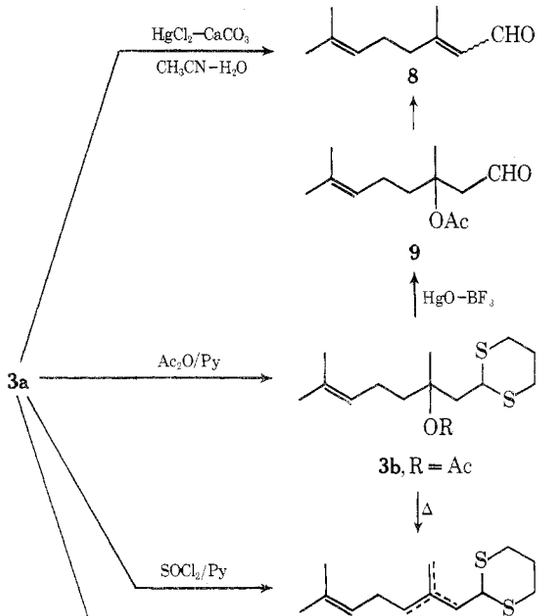


7

ducing the cyclic compounds **5** along with **6** and **7**. This paper deals with the chemistry of **3a** and its selective conversion into linaloyl oxide (**15**).

The utility of 1,3-dithiane in organic synthesis is well documented in the literature.[7] Above all, the reaction of 2-lithio-1,3-dithiane with epoxides provides a promising route to derivatives of secondary or tertiary alcohols.[8] Thus, reaction of 2,6-dimethyl-1,2-epoxy-5-heptene with 2-lithio-1,3-dithiane in dry tetrahydrofuran at −30° provided the alcohol **3a**, homogeneous by tlc, ir, and nmr, in 98% yield after chromatography on silica gel.

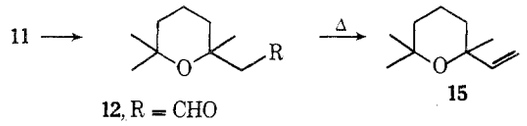
Exclusive conversion of **3a** into citral (**8**) was carried out by refluxing in aqueous 80% acetonitrile in the presence of 1 equiv of mercuric chloride and calcium carbonate, whereas hydrolysis of the acetate **3b** using mercuric oxide and boron trifluoride gave the corresponding acetate **9**[9] in 84% yield. Deacetoxylation of the acetate **9** occurred smoothly on elution over silica gel, affording citral in good yield.



Dehydration of **3a** to the dienes **10** proceeded smoothly on treatment with thionyl chloride or methanesulfonyl chloride in pyridine. Thermal deacetoxylation of **3b** also occurred at 200° to afford **10** in 95% yield. Without further purification, the dienes **10** were hydrolyzed to give citral.

Acid-catalyzed cyclization of olefinic alcohols to cyclic ethers has been reported in the literature,[10] but few such references outline the preferred reaction conditions for selective cyclization without producing by-products. Hence, careful examination of the reaction conditions is required for obtaining satisfactory product selectivity. Indeed, reaction temperature was found to be the most critical factor influencing the yield of the cyclic ether **11**. Treatment of **3a** with 2 equiv of boron trifluoride etherate in benzene and dichloromethane (2:1) at −10° for 12 hr yielded 81% of **11**. Higher temperature (over 0°) favored the dehydration product **10**. In fact, the reaction of **3a** in benzene at 7–10° gave 10% of **10** and 60% of **11**, while on refluxing in benzene **10** was isolated as a sole product. The structural assignment of **11** was based on spectral data.

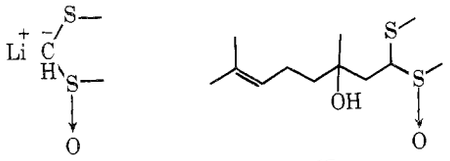
Conversion of **11** to the corresponding aldehyde **12**[11] was

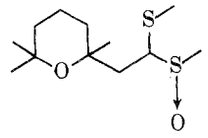


12, R = CHO
13, R = CH_2OH
14, R = $CH_2OC(S)SCH_3$

performed using boron trifluoride and mercuric oxide in aqueous tetrahydrofuran[12] in 84% yield. Reduction of **12** with lithium aluminum hydride furnished the alcohol **13**[13] in quantitative yield, which was converted into the corresponding xanthate **14** efficiently. Thermolysis of **14** took place instantaneously at *ca.* 320° to give linaloyl oxide (**15**)[14] as a colorless oil in 79% yield (45% overall yield from 6-methylheptenone). The spectral data (ir, nmr, and mass spectrum) of **15** were identical with those reported.[10e]

Similarly, 2,6-dimethyl-1,2-epoxy-5-heptene reacted smoothly with the lithio sulfoxide **16**[15] in tetrahydrofuran at −30° to afford **17** in excellent yield. The adduct **17** was





converted to **12** by cyclization (94% yield) and hydrolysis (70% yield) in the same manner as the dithiane derivative **3a**.

Experimental Section

Boiling points were indicated by an air or an oil bath temperature without correction. Nmr spectra were recorded on a Hitachi R-24 instrument using tetramethylsilane as an internal standard. Ir spectra were taken with a Hitachi EPI-S2 instrument. Mass spectral analyses were carried out at 70 eV with a Hitachi RMS-4 mass spectrometer. Microanalysis was performed by Mr. Tsutomu Okamoto of our laboratory.

2-(2-Hydroxy-2,6-dimethyl-5-heptenyl)-1,3-dithiane (3a). Into a solution of 120 mg (1 mmol) of 1,3-dithiane and 3 ml of dry THF 2 mmol of *n*-butyllithium was added dropwise with stirring at −30° and the mixture was stirred for 1.5 hr. Following addition of 140 mg (1 mmol) of 2,6-dimethyl-1,2-epoxy-5-heptene, the mixture was stirred for 15 min at −30° and then for 12 hr at room temperature. Into the ice-cooled reaction mixture 2 ml of ether and 2 ml of saturated NH_4Cl were added. The organic layer was extracted with ether, washed twice with 2 ml of brine, dried (Na_2SO_4), and concentrated *in vacuo*. The residue was chromatographed over silica gel (Wakogel C-200, dichloromethane) to yield 254 mg (98%) of **3a** as a colorless oil: bp 55–60° (0.005 mm); ir (neat) 3446 (OH), 3050 (C=CH) cm^{-1}; nmr (CCl_4) δ 4.88–5.24 (m, 1 H, CH=C), 4.11 (t, J = 7 Hz, 1 H, S–CH–S), 2.73–2.98 (m, 4 H, S–CH_2), 2.40 (s, 1 H, OH), 1.30–2.26 (m, 8 H, CH_2), 1.66 (s, 3 H, CH_3), 1.62 (s, 3 H, CH_3), 1.20 (s, 3 H, CH_3); mass spectrum *m/e* 260 (M^+, 21), 242 (M − 18, 15), 119 (base peak).

Anal. Calcd for $C_{13}H_{24}S_2O$: C, 59.98; H, 9.29. Found: C, 59.84; H, 9.21.

2-(2,6,6-Trimethyl-2-tetrahydropyranyl)methyl-1,3-dithiane (11). Into a stirred solution of 260 mg (1 mmol) of **3a** in a mixture of 10 ml of dry benzene and 5 ml of dry dichloromethane was added dropwise 142 mg (1 mmol) of freshly distilled boron trifluoride etherate at −10° under nitrogen. The mixture was stirred at room temperature for 6 hr, treated again with 1 mmol of boron trifluoride etherate with stirring for an additional 6 hr, and quenched with 1 ml of cooled water. The organic phase was extracted with 5 ml of dichloromethane, washed twice with 2 ml of water, dried (Na_2SO_4), and concentrated *in vacuo*. The residue

was chromatographed over silica gel using a mixture of benzene and dichloromethane to yield 208 mg (81%) of **11** as a colorless oil, 2 mg (1%) of **10**, and 45 mg (17%) of the recovered **3a**. The physical data of **11** are as follows: bp 55–60° (0.005 mm); ir (neat) 1223 and 1118 (C–O) cm^{-1}; nmr (CCl_4) δ 4.09 (t, J = 6 Hz, 1 H, S–CH–S), 2.65–2.97 (m, 4H, S–CH_2), 1.80–2.14 (m, 2H, CH_2), 1.70 (d, J = 6 Hz, 2H, CH_2—C=S_2), 1.37–1.80 (m, 6 H, CH_2), 1.22 (s, 3 H, CH_3), 1.17 (s, 6 H, CH_3); mass spectrum m/e 260 (M^+, 68), 159 (base peak).

Anal. Calcd for $C_{13}H_{24}S_2O$: C, 59.98; H, 9.29. Found: C, 59.97; H, 9.10.

2,6,6-Trimethyltetrahydropyran-2-acetaldehyde (12). Into an ice-cooled mixture of 445 mg (2.1 mmol) of mercuric oxide (red) and 260.5 mg (1 mmol) of **11** in 2 ml of aqueous 85% THF solution was added dropwise 300 mg (2.1 mmol) of freshly distilled boron trifluoride etherate with stirring. The mixture was stirred for 1.5 hr at 7–10° and quenched by addition of 2 ml of ether to give a white solid, which was filtered off and rinsed three times with ether. The combined filtrates were washed with aqueous $NaHCO_3$, and twice with brine, dried (Na_2SO_4), and concentrated *in vacuo*. Distillation of the residue under reduced pressure gave 143 mg (84%) of **12** as a colorless oil: bp 78–82° (15 mm) (lit.[11] bp 76–78° (14 mm)); ir (neat) 2748 (CHO) and 1720 (C=O) cm^{-1}; nmr (CCl_4) δ 9.76 (t, J = 3 Hz, 1 H, CHO), 2.33 (d, J = 3 Hz, 2 H, CH_2C=O), 1.30–2.20 (m, 6 H, CH_2), 1.27 (s, 3 H, CH_3), 1.18 (s, 3 H, CH_3), 1.14 (s, 3 H, CH_3).

2,6,6-Trimethyl-2-(2-hydroxy)ethyltetrahydropyran (13). The aldehyde **12** (170 mg, 1 mmol) was treated with 29 mg of lithium aluminum hydride in 2 ml of dry ether at room temperature. Usual work-up and distillation of the product gave 168 mg (98%) of **13** as a colorless oil: bp 90–94° (10 mm) (lit.[13] bp 62–63° (0.2 mm)); ir (neat) 3380 (OH), 1228 (C–O) cm^{-1}; nmr (CCl_4) δ 3.64 (t, J = 6 Hz, 2 H, CH_2O), 3.12 (s, 1 H, OH), 1.59 (t, J = 6 Hz, 2 H, CH_2CO), 1.36–1.80 (m, 6 H, CH_2), 1.24 (s, 3 H, CH_3), 1.21 (s, 3 H, CH_3), 1.17 (s, 3 H, CH_3).

2,6,6-Trimethyl-2-vinyltetrahydropyran (Linaloyl Oxide) (15). To an ice-cooled suspension of 72 mg (1.5 mmol) of sodium hydride in 3 ml of dry THF was added 172 mg (1 mmol) of **13** in 2 ml of dry THF under nitrogen. The mixture was stirred at room temperature for 3 hr, treated with 114 mg (1.5 mmol) of carbon disulfide at 0°, and further stirred at room temperature for 12 hr. Then, the ice-cooled mixture was treated with 214 mg (1.5 mmol) of methyl iodide, stirred at room temperature for 6 hr, and quenched with ice–water. The combined ether extracts were washed with water, dried (Na_2SO_4), and concentrated *in vacuo*. The residue was chromatographed over silica gel (Wakogel C-200, *n*-hexane–CH_2Cl_2 4:1) to yield 257 mg (98%) of **14** as a clean yellowish oil: ir (neat) 1250–1180, 1172, 1128, 1095–1040, 1011 cm^{-1}; nmr (CCl_4) δ 4.72 (t, J = 7 Hz, 2 H, CH_2O), 2.49 (s, 3 H, CH_3S), 1.91 (t, J = 7 Hz, 2 H, CH_2CO), 1.37–2.09 (m, 6 H, CH_2), 1.21 (s, 3 H, CH_3), 1.17 (s, 3 H, CH_3), 1.14 (s, 3 H, CH_3); mass spectrum m/e 262 (M^+, 0.8), 247 ($M^+ - CH_3$, 7), 69 (base peak). The xanthate **14**, without further purification, could be converted into linaloyl oxide in the following manner. To a 1-ml modified Claisen flask settled at 320° in an air bath, 80 mg (0.3 mmol) of **14** was dropped at 30-sec intervals by means of a 0.5-ml syringe. On adding **14** decomposition took place immediately to form a fumy vapor which was subsequently distilled out to give 39 mg of a colorless oil, whose vpc (neopentyl glycol, 3 m long, 4 ϕ, 90°) revealed that the oil contained 94% of **15**. The spectral data (ir, nmr, and mass spectrum) of the vpc separated sample were superimposable with those reported.[10e]

2-(2-Acetoxy-2,6-dimethyl-5-heptenyl)-1,3-dithiane (3b). The alcohol **3a** (130 mg, 0.5 mmol) was acetylated in a mixture of 1.5 ml of pyridine and 1.5 ml of acetic anhydride at 110° for 12 hr. Usual work-up and chromatography over silica gel (benzene) gave 128 mg (85%) of **3b** as a slightly yellowish oil: bp 68–72° (0.004 mm); ir (neat) 1737 (OAc) cm^{-1}; nmr ($CDCl_3$) δ 4.88–5.25 (m, 1 H, HC=C), 4.12 (t, J = 6 Hz, 1 H, S–CH–S), 2.75–3.03 (m, 4 H, CH_2S), 1.38–2.35 (m, 8 H, CH_2), 1.96 (s, 3 H, CH_3CO), 1.67 (s, 3 H, CH_3), 1.60 (s, 3 H, CH_3), 1.50 (s, 3 H, CH_3); mass spectrum m/e 242 (M^+ – AcOH, 8) and 119 (base peak).

Anal. Calcd for $C_{15}H_{26}S_2O_2$: C, 59.48; H, 8.67. Found: C, 59.46; H, 8.58.

Methyl 1-Methylthio-3-hydroxy-3,7-dimethyl-6-octenyl Sulfoxide (17). The sulfoxide **17** was prepared using methyl methylthiomethyl sulfoxide in a similar manner as for the preparation of **3a**. The epoxide (50 mg, 0.36 mmol) afforded 94 mg (100%) of **17** as a colorless oil after chromatographed over silica gel using chloroform–ethyl acetate (1:3): bp 76–79° (0.006 mm); ir (neat) 3376 (OH) and 1039 (S=O) cm^{-1}; nmr ($CDCl_3$) δ 4.90–5.29 (m, 1 H, HC=C), 3.67–4.12 (m, 1 H, SCHSO), 3.70–3.90 (br s, 1 H, OH), 2.71 (s, 1.5 H, $SOCH_3$), 2.58 (s, 1.5 H, $SOCH_3$), 2.30 (s, 1.5 H, CH_3S), 2.23 (s, 1.5 H, CH_3S), 1.83–2.42 (m, 4 H, CH_2), 1.68 (s, 3 H, CH_3), 1.62 (s, 3 H, CH_3), 1.34–1.77 (m, 2 H, CH_2), 1.26 (s, 3 H, CH_3); mass spectrum m/e 200 ($M^+ - CH_3SOH$, 4), 69 (base peak). Microanalysis for the sulfoxide **17** was not performed since it is very hygroscopic.

Methyl 1-Methylthio-2-(2,6,6-trimethyl-2-tetrahydropyranyl)ethyl Sulfoxide (18). The sulfoxide **18** was prepared in 95% yield by the same procedure as done in the preparation of **11**. Chromatography over silica gel (chloroform–ethyl acetate) and distillation gave a colorless oil: bp 70–75° (0.004 mm); ir (neat) 2923, 1447, 1378, 1223, 1119, 1054 (S=O) cm^{-1}; nmr ($CDCl_3$) δ 3.61–4.08 (m, 1 H, SCHSO), 2.56 (s, 3 H, CH_3SO), 2.35 (s, 1.5 H, CH_3S), 2.31 (s, 1.5 H, CH_3S), 1.20–2.20 (m, 8 H, CH_2), 1.18 (s, 3 H, CH_3), 1.23 (s, 6 H, CH_3); mass spectrum m/e 200 ($M^+ - CH_3SOH$, 4), 69 (base peak).

Anal. Calcd for $C_{12}H_{24}S_2O_2$: C, 54.53; H, 9.15. Found: C, 54.34; H, 9.32.

The Aldehyde 12 from 18. The sulfoxide **18** (50 mg, 0.19 mmol) was treated with 165 mg (0.76 mmol) of mercuric oxide (red) and 81 mg (0.57 mmol) of boron trifluoride etherate in 0.5 ml of aqueous 85% THF solution under nitrogen at 0° and the mixture was stirred for 36 hr at 15–20°. Usual work-up and distillation afforded 20 mg (70%) of **12**.

3-Acetoxy-3,7-dimethyl-6-octenal (9). The desulfurization of **3b** was carried out in the similar manner as done in the preparation of **12** from **11**. Starting from 80 mg (0.26 mmol) of **3b**, 47 mg (85%) of **9** was obtained as a colorless oil after capillary distillation: bp 58–62° (2 mm); ir (neat) 2740 (CHO), 1740 (AcO), 1730 (CHO), 1246 cm^{-1}; nmr ($CDCl_3$) δ 9.77 (t, J = 2 Hz, 1 H, CHO), 4.92–5.27 (m, 1 H, HC=C), 3.06 and 2.72 (q, J_1 = 16 Hz, J_2 = 2 Hz, 2 H, CH_2CO), 2.01 (s, 3 H, CH_3CO), 1.88–2.13 (m, 4 H, CH_2), 1.69 (s, 3 H, CH_3), 1.62 (s, 3 H, CH_3), 1.57 (s, 3 H, CH_3); mass spectrum m/e 152 (M^+ – AcOH, 7), 69 (base peak).

Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 68.14; H, 9.50.

The acetate **9** was eluted through silica gel column using benzene–ethyl acetate (5:1) affording citral (trans/cis = 3:1) in 80% yield.

Pyrolysis of 3b. The acetate **3b** (61 mg, 0.2 mmol) was heated at 200° for 1.5 hr and the eliminated acetic acid was removed continuously. The residue was chromatographed over silica gel using *n*-hexane–benzene (1:1) to afford 45 mg (93%) of an isomeric mixture **10**. The separation of the isomers was not successful by column chromatography (silica gel): ir (neat) 2921, 1647 (C=C), 1424, 1378, 1276, 908 cm^{-1}; nmr (CCl_4) δ 4.76–5.33 (m, 2 H, vinyl), 4.07 (t, 1 H, SCHS), 2.62–3.07 (m, 4 H, CH_2S), 1.80–2.62 (m, 6 H, CH_2), 1.62–1.74 (m, 9 H, CH_3); mass spectrum m/e 242 (M^+, 5), 119 (base peak).

Anal. Calcd for $C_{13}H_{22}S_2$: C, 64.44; H, 9.15. Found: 64.70; H, 9.25.

Dehydration of 3a. Into the ice-cooled solution of 50 mg (0.19 mmol) of **3a** in 0.7 ml of dry pyridine was added 42 mg (0.35 mmol) of freshly distilled thionyl chloride with stirring under nitrogen and the mixture was stirred for 2 hr at 0°. After addition of 2 ml of ether and 1 ml of cooled 5% HCl with vigorous stirring, the organic phase was extracted with ether, washed with 1 ml of 5% HCl and twice with water, dried (Na_2SO_4), and concentrated. The residue was chromatographed over silica gel using *n*-hexane–benzene (1:1) to afford 34 mg (74%) of an isomeric mixture of **10**, whose spectral data were quite similar with those of the mixture obtained from thermolysis of **3b**.

Conversion of 3a into Citral. A mixture of 50 mg (0.19 mmol) of **3a**, 114 mg (0.42 mmol) of mercuric chloride, and 42 mg (0.42 mmol) of calcium carbonate in 1 ml of aqueous 80% acetonitrile was stirred under nitrogen at 85–90° for 6 hr. The mixture was filtered to remove a white precipitate and the filtrate was concentrated. The residue was rinsed with ether and filtered and the slight yellow precipitate was washed twice with ether. The combined filtrates were washed with brine, dried (Na_2SO_4), and concentrated to give a yellow oil (32 mg), which was chromatographed over silica gel using *n*-hexene–ethyl acetate (10:1) affording 21 mg (72%) of citral (trans/cis = 2:1).

Registry No.—**3a**, 52920-86-2; **3b**, 52920-87-3; **9**, 52920-88-4; **10** isomer a, 25094-26-2; **10** isomer b, 52920-89-5; **10** isomer c, 52920-90-8; **11**, 52920-91-9; **12**, 2259-20-3; **13**, 52920-92-0; **14**, 52920-93-1; **15**, 7392-19-0; **17**, 52977-08-9; **18**, 52920-94-2; 1,3-dithiane, 505-

23-7; 2,6-dimethyl-1,2-epoxy-5-heptene, 50340-32-4; methyl methylthiomethyl sulfoxide, 33577-16-1.

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A Convenient Means of Generating Alkyl-Substituted Isobenzofurans as Reactive Intermediates

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A tautomeric equilibrium is demonstrated to exist between 1-benzalphthalan and 1-benzylisobenzofuran. This equilibrium is exploited as a convenient means of generating alkyl-substituted isobenzofurans as reactive intermediates and the same principle is employed to prepare 1-*tert*-butyl-3-phenylisobenzofuran. Examples are given of the use of these isobenzofuran derivates to prepare substituted naphthalenes and a naphthol. The generation of substituted isobenzofurans by the procedure described here has the advantage that the initial reagents are readily prepared and the generation of the isobenzofuran is not accompanied by any coproduct.

The facile oxidation[1,2] of benzalphthalan, **1a**, is inconsistent with its structure. However, this reactivity suggested that an equilibrium might exist between **1a** and its tautomer 2-benzylisobenzofuran, **2a**. Subsequent reactions then proceed through this reactive[3] intermediate.

The existence of this equilibrium was established by capturing the intermediate **2a** through a Diels–Alder reaction with dimethyl acetylenedicarboxylate to provide **3a**. Attempts to observe directly this equilibrium by nmr or uv spectroscopy were unsuccessful.

In pursuit of a directly observable equilibrium, compounds containing one phenyl substituent were prepared. Thus dehydration of the hydroxyphthalan **5b** gave **1b** which in the presence of dimethyl acetylenedicarboxylate formed the Diels–Alder adduct **3b**. Unfortunately, the isobenzofuran **2b** could not be detected spectroscopically.

In the case of the hydroxyphthalan **5c**, dehydration of necessity produced the corresponding isobenzofuran **2c**, isolated as a reactive yellow oil with a brilliant fluorescence under uv light. The isobenzofuran structure was supported by its uv spectrum, by its easy oxidation[4] to the diketone **6**, and by the reaction of **2c** with dimethyl acetylenedicarboxylate and dimethyl maleate to produce **3c** and **4c**, respectively (maleic anhydride also reacts).

The accessibility of isobenzofurans as reactive intermediates has important synthetic consequences. Thus substituted naphthols can be formed by acid-catalyzed ring opening[5] of **3** and the reaction **3a** to **8** was effected here. Again, substituted naphthalenes[5,6] can be obtained by ring opening of compounds such as **4**, which, in turn, are prepared from **2** and dimethyl maleate (*e.g.*, **4c**) or by hydrogenation of **3** (*e.g.*, **3a** and **3b**). The ring openings are sensitive to the substituent groups present. While **4b** was transformed smoothly to **7b**, **4c** resisted conversion to the corresponding naphthalene perhaps because of the steric crowding which would arise in the product from the coplanarity of the substituent groups, the peri interactions being exaggerated by the buttressing effects of the carbomethoxy groups. On the other hand, **4a** was converted to a mixture containing **7a** as the major product and **9** as the minor product. Since **7a** and **9** are not in equilibrium, these products must arise by competitive eliminations. This suggests that the stereochemistry of **4** or the conformation of the intermediates are an important factor in this reaction.

In this regard, **4a** has the endo configuration since coupling is observed between the bridgehead hydrogen and the hydrogen α to the carbomethoxy group. It is suggested that **4b** and **4c** have the more stable exo configuration since attempts to isomerize these compounds have been unsuccessful.

The utilization of isobenzofuran[3,6b,7] as a reactive intermediate in syntheses has been reported elsewhere. These methods generally involve the initial preparation of Diels–Alder adducts which decompose photolytically or thermally to provide the desired intermediate. The approach described here has the advantage that the initial reagents are readily prepared and no coproduct is generated on forming the isobenzofuran.