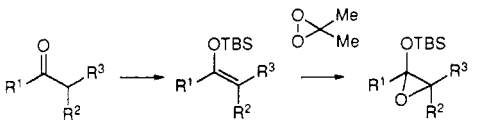
Scheme I



1a-g 2a-g 3a-g

	R^1	R^2	R^3
a	tBu	H	H
b	Ph	H	H
c	Et	H	Me
d	H	$-CH_2CH_2CH_2CH_2CH_2-$	
e	$-CH_2CH_2CH_2CH_2-$		H
f	$-CH_2CH_2CH_2CH_2-$		Me
g	Ph	Me	Me

In all cases, mass spectrometry showed incorporation of one atom of oxygen per molecule. Base peaks corresponded to $M^+ - 57$ (loss of *tert*-butyl radical). With one exception (the reaction of **2b**), NMR spectroscopy indicated quantitative formation of the siloxyoxiranes **3**; IR absorptions at 1250, 935–960, and 840 cm^{-1} were observed with little or no peaks attributable to carbonyl groups.

Reaction of **2b** gave as products a 1:1 mixture of siloxyoxirane **3b** and rearranged compounds (α-siloxy and α-hydroxy ketones), as evidenced by NMR spectroscopy. A carbonyl stretch (1700 cm^{-1}) was present in the product IR. This result was reproducible (two experiments) and presumably resulted from partial rearrangement of the initially formed siloxyoxirane during the time required to obtain the NMR spectrum (approximately 5 min from reaction).

We expected compounds **3b** and **3g** to be labile in comparison to the other siloxyoxiranes due to benzylic assistance to the opening of the epoxide. Indeed, **3b** and **3g** were the least stable of the products (vide infra). Compound **3g**, however, was stable enough to be observed pure by NMR. We presume steric interaction between the phenyl and *cis*-methyl groups obstructs alignment of the phenyl π-system and the σ^* orbital of the breaking C–O ring bond.

Rearrangement of the siloxyoxiranes to the corresponding α-siloxy (or hydroxy) carbonyl compounds in the wet acetone solutions (room temperature) was followed by ^1H NMR spectroscopy. Although no detailed kinetic analysis was performed, approximate half-lives of the siloxyoxiranes were <3 h (**3a**), 5 h (**3c**), 55 h (**3d**), 15 h (**3e**), 20 h (**3f**), and <3 h (**3g**).

We are investigating the possibility of carrying out other chemistry on these now available siloxyoxiranes, and the results will be described in due course.

Experimental Section

Materials and Methods. Organic chemicals from Aldrich were used without further purification. Silyl enol ethers were prepared by reaction of the parent ketones and aldehyde with *tert*-butyldimethylsilyl triflate in the presence of triethylamine[8] and purified by chromatography on silica gel (2–5% ethyl acetate in hexanes). Dimethyldioxirane-d_6 was prepared according to the small-scale procedure of Adam et al.[7] using 10 g of acetone-d_6 and was distilled as a solution in wet acetone-d_6. By ^1H NMR analysis, the reagent contained 4–5 volume % of water. It could be dried over $MgSO_4$ but was usually used wet since $MgSO_4$ catalyzed decomposition of the dioxirane. Solutions of dimethyldioxirane-d_6 in acetone-d_6 thus obtained were assayed by reaction with thioanisole and found to be around 0.1 M.

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Table I. ^1H NMR Data[a]

compd	δ, ppm
3a	0.05 (s, 3 H), 0.11 (s, 3 H), 0.87 (s, 9 H), 0.95 (s, 9 H), 2.70 (d, J = 3.6 Hz, 1 H), 2.81 (d, J = 3.6 Hz, 1 H)
3b	0.06 (s, 3 H), 0.09 (s, 3 H), 0.91 (s, 9 H), 2.85 (d, J = 4.6 Hz, 1 H), 3.20 (d, J = 4.6 Hz, 1 H), 7.34–7.97 (m, 5 H)
3c	0.10 (s, 3 H), 0.17 (s, 3 H), 0.89 (s, 9 H), 0.92 (t, J = 7.5 Hz, 3 H), 1.23 (d, J = 5.2 Hz, 3 H), 1.50 (m, 1 H), 1.97 (m, 1 H), 2.83 (q, J = 5.2 Hz, 1 H)
3d	0.14 (s, 3 H), 0.15 (s, 3 H), 0.90 (s, 9 H), 1.34–1.69 (m, 10 H), 4.61 (s, 1 H)
3e	0.11 (s, 3 H), 0.14 (s, 3 H), 0.88 (s, 9 H), 1.22–2.00 (m, 8 H), 3.17 (d, J = 3.6 Hz, 1 H)
3f	0.10 (s, 3 H), 0.16 (s, 3 H), 0.88 (s, 9 H), 1.24–1.40 (m, 4 H), 1.27 (s, 3 H), 1.69 (m, 2 H), 1.96 (m, 2 H)
3g	−0.23 (s, 3 H), 0.00 (s, 3 H), 0.85 (s, 9 H), 0.92 (s, 3 H), 1.47 (s, 3 H), 7.32–7.45 (m, 5 H).

[a] 250 MHz spectrometer, samples in acetone-d_6, and peaks referenced to acetone-d_5 (δ 2.04 ppm).

Epoxidation of Silyl Enol Ethers. To 10 mg of silyl enol ether in 0.1 mL of acetone-d_6, −78 °C, was added dropwise 1.0 equiv of a chilled (−20 to 0 °C) solution of dimethyldioxirane-d_6 in acetone-d_6. After 2–5 min, the reaction solution was warmed to room temperature and examined by ^1H NMR spectroscopy (Table I) and low-resolution mass spectrometry (EI). A portion of the product was then freed of solvent by rotary evaporation at 0 °C, taken up in chloroform-*d*, and examined by infrared spectroscopy.

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Synthesis of Substituted Vinyl Sulfides by Reaction of [1-(Phenylthio)cyclopropyl]carbinyl Halides and Organocuprates[1]

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The longevity and scope of the work reported for cyclopropane derivatives attests to the interest and importance of these highly reactive molecules. In previous work we prepared cyclopropylcarbinyl halides (1) and showed they reacted with amines[3] in a ring-opening reaction best described as an homoallylic S_N2' reaction. Homoallylic substitution dominated when the halogen-bearing carbon was sterically hindered but direct S_N2' displacement was favored when that carbon was unencumbered. Halides 1 also react with lithium dialkylcuprates[4] to give the homoallylic alkene 2 with excellent selectivity for the *E* isomer.

(1) Presented at the Third Chemical Congress of North America, ORGN 193, 6/8/88; Toronto, Canada.
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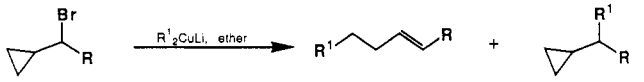
Posner had previously shown that cyclopropylcarbinyl tosylates give homoallylic ring opening on reaction with organocuprates.[5] Posner also showed that 6-chloro-3,5-cyclocholestane gave a mixture of S_N2 and S_N2' products on reaction with organocuprates.[5a] Minor amounts of the direct substitution product **3** were obtained with dimethyl- or diphenylcuprate.[4a] Prior to this work only cationic

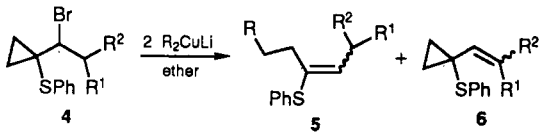


1 2 3

ring-opening reactions of cyclopropane derivatives[6] or Michael type additions of nucleophiles to cyclopropane derivatives containing *two* carbonyl groups[7] were known. We had clarified the nature of the S_N2' reaction with cyclopropylcarbinyl halides, but the synthetic utility was limited to the preparation of simple alkenes or alkenyl amines. We anticipated great enhancement in the synthetic utility of this process when applied to 1-(phenylthio)-1-(1-bromoalkyl)cyclopropanes, **4**. Homoallylic S_N2' substitution would generate substituted vinyl sulfides (**5**), which are important synthetic intermediates. Vinyl sulfides are readily hydrolyzed to ketones with mercuric salts.[8] They can be arylated by palladium salts and aryl halides in a Heck-like reaction[9] or by aryl diazonium salts in a Meerwein reaction.[10] Phenyl vinyl sulfides can be cyclized to benzothiophene derivatives by a thio-Claisen rearrangement.[11] Organolithium reagents react with vinyl sulfides to generate an α-lithio sulfide, which reacts with a variety of electrophiles.[12] Finally, vinyl sulfides function as 1,3-dipolarophiles to give the corresponding cycloadduct with a variety of reagents.[13]

We anticipated that reaction of organocuprates with cyclopropylcarbinyl halides would lead to the homoallylic substituted vinyl sulfides. The requisite cyclopropylcarbinyl bromides were prepared from the corresponding cyclopropylcarbinyl alcohols. The alcohols were prepared by treatment of (phenylthio)cyclopropane[14] with *n*-butyllithium followed by condensation with the desired aldehyde.[15] Reaction with propanal or 2-methylpropanal, for example, provided the corresponding cyclopropylcarbinyl alcohol in 75% and 71% yield, respectively.

Table I. Synthesis of 1,2-Disubstituted Vinyl Sulfides via Homoallylic Ring Opening of Cyclopropylcarbinyl Bromides



4 5 6

4	R^1	R^2	R	5, %[a,b]	E:Z[c]	% 6
4a	H	Me	*n*-Bu	**5a**, 66	53:47	11
			Me	**5b**, 55	70:30	15
			Ph	**5c**, 57	55:45	5
			t-Bu	**5d**, 48	60:40	28
4b	Me	Me	*n*-Bu	**5e**, 71	70:30	10
			Me	**5f**, 50	80:20	8
			Ph	**5g**, 64	95:5	7
			t-Bu	**5h**, 66	90:10	25

[a] Percent yield determined by VPC analysis with phenyl vinyl sulfide as an internal standard. [b] Satisfactory analyses for all new compounds. [c] The *E*:*Z* ratio was determined by capillary VPC/MS analysis.

Attempts to convert the alcohol to the bromide via treatment with bromine/triphenylphosphine in DMF or to the chloride with hexachloroacetone and triphenylphosphine failed. This methodology was successful in our previous work but required thermolysis to produce the halide. Presumably, the phenylthio derivatives are insufficiently volatile or thermally unstable. We solved the problem by treating the alcohol with thionyl bromide at −10 °C, which gave **4a** in 44% and **4b** in 61% yield. This was an interesting result since Trost observed that similar reaction at elevated temperatures led to ring expansion and formation of a 1-(phenylthio)cyclobutene.[15a] We also obtained the chlorides in somewhat higher yield by reaction with thionyl chloride. The chlorides were significantly less reactive, giving less than 10% homoallylic substitution on reaction with organocuprates. In all cases the halide (**3**) was sufficiently stable to isolate and use in reactions with organocuprates. The halides decomposed on prolonged standing at ambient temperatures, however.

Reaction of organocuprates with alkyl halides is well known,[16] and we had previously shown their facile reactivity with cyclopropylcarbinyl halides.[4] The phenylthio derivative, **4**, reacted in an analogous manner with organocuprates to give **5** (see Table I). When **1** reacted with diphenyl- or dimethylcuprate, small amounts of the direct substitution product **3** were observed, but no trace of this product was apparent with **4a** or **4b**. Elimination during the reaction gave small amounts of **6**. Posner had observed some elimination in reactions of cyclopropylcarbinyl tosylates with organocuprates,[5] but we observed no elimination of **1**. Halides **1** gave only the *E* isomer **2**, except when the alkyl group (R) was methyl. Although the ring opening of **4** was regiospecific, the stereoselectivity was poor for **4a**, giving **5a–d** as a 1.1:1 → 2.3:1 mixture of *E*:*Z* isomers. The isopropyl derivative, **4b**, gave **5e–h** with moderate to good selectivity, ranging from 70:30 and 80:20 *E*:*Z* in **5e** and **5f** to 95:5 and 90:10 in **5g** and **5h**. The selectivity of **1**, the poor selectivity of **4a**, and the modest selectivity of **4b** can be explained by invocation of conformational intermediates analogous to those proposed by Julia[3a] and Johnson[3b] for the cationic ring opening of cyclopropylcarbinyl alcohols. Conformation **7** is required for conversion to the *E* isomer when X = H (**1**). This repre-

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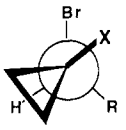
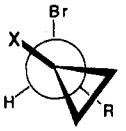
sents a less sterically encumbered conformation relative to 8 in which the cyclopropyl group interacts with the R group. When R is a small methyl group, the *E*:*Z* selectivity was poor.[4] As the size of R increased, the *E* selectivity increased due to the greater R ↔ cyclopropyl interaction in 8. When X = SPh, however, 7 is the precursor to the



7



8

Z isomer and 8 leads to the *E* isomer. In **4a**, the X ↔ R (R = Ethyl, X = SPh) interaction is not significantly greater than the ethyl ↔ cyclopropyl interaction. This leads to a slight preference for 8 and the *E* isomer. With **4b**, the X ↔ R interaction (R = isopropyl, X = SPh) is significant and conformation 8 is greatly preferred, leading to good selectivity for the *E* isomer. It is apparent that diphenylcuprate and di-*tert*-butylcuprate show greater selectivity than di-*n*-butylcuprate or dimethylcuprate. This is probably due to differences in aggregate state and binding to the halide for the bulkier organocuprates. This may influence the relative proportions of 8 and 7 and, therefore, the stereoselectivity of the ring opening process.

Reaction of **4a** with lithium di-*n*-butylcuprate in THF gave no appreciable increase in the yield of **5a** nor significant improvement in selectivity. In reactions of 1, we found that reaction with higher order mixed cuprates $[Li_2Cu(CN)R_2]$[17] gave *poorer* yields of homoallylic substitution with cyclopropylcarbinyl halides, and similar reaction with **4a** showed similar behavior. We therefore focused our attention on the Gilman type reagents in ether. We used cuprous bromide to generate the organocuprate. In our previous work cuprous iodide and the dimethyl sulfide complex of cuprous bromide ($CuBr{\cdot}SMe_2$) gave significantly lower yields of the homoallylic substitution product.[4] We found that freshly prepared cuprous bromide[18] gave the best yields in all organocuprate reactions.

We have demonstrated the viability of preparing highly substituted vinyl sulfides by the homoallylic S_N2' reaction with cyclopropylcarbinyl halides. The reaction is regiospecific but shows reasonable selectivity for the *E* isomer only when the haloalkyl group is rather large. This result led to a rational explanation for the *E*:*Z* selectivity exhibited by cyclopropylcarbinyl halides on reaction with organocuprates. The ability of convert vinyl sulfides to the corresponding ketone or to use them in known cyclization, arylation, alkylation, or cycloaddition reactions greatly expands the synthetic utility of the homoallylic S_N2' reaction.

Experimental Section

All ^1H and ^{13}C NMR spectra were recorded on an IBM 270 NMR spectrometer at 270.133 and 67.925 MHz, respectively. All NMR spectra are reported in ppm, downfield from tetramethylsilane. The infrared spectra were determined neat or in $CDCl_3$ on a Perkin-elmer Model 283 spectrophotometer. The mass spectra were recorded at 70 eV on a Hewlett-Packard 5970-B gas chromatographic/mass spectrometric system utilizing a methylsilicon capillary column (12.0 m × 0.2 mm, i.d.), and the high-resolution mass spectra were determined on an AEI MS-902 mass spectrometer by Marvin Thompson. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected, as are the boiling points. All apparatus used for anhydrous experiments were flame-dried and flushed with argon prior to use. Absolute ether and THF were distilled from sodium/benzophenone under argon immediately prior to use, and the pentane was distilled from calcium hydride. *n*-Butyllithium, methyllithium, *tert*-butyllithium, and phenyllithium were obtained from Aldrich Chemical Co. and standardized with diphenylacetic acid[19] prior to each use. The cuprous bromide was freshly prepared by the method of Corey[18a] and Kende.[18b] Thionyl bromide, pyridine, cuprous bromide, 1-bromo-3-chloropropane, propanal, and 2-methylpropanal were also obtained from Aldrich. Liquid chromatography separations employed silica gel 60 (70–230 mesh) obtained from E. Merck. The 1-chloro-3-(phenylthio)-propane was prepared from 1-bromo-3-chloropropane by the method of Truce.[14] Cyclization to 1-(phenylthio)cyclopropane was accomplished by treatment with potassium amide.[14]

Preparation of [1-(Phenylthio)cyclopropyl]carbinyl Alcohols. Using the method of Trost[15] a solution of of 1-(phenylthio)cyclopropane in 0.15 L of THF was treated with 2.4 M *n*-butyllithium in hexanes (40 mmol) via syringe at 0 °C. After 2.5 h the aldehyde was added via syringe, stirred for 1 h, and quenched with 10 mL of water. The reaction mixture was extracted with ether and dried ($MgSO_4$), and solvents were removed under reduced pressure. Chromatography on silica gel (hexane followed by 95:5 hexane–ether) gave the alcohol, in all cases.

1-[(Phenylthio)cyclopropyl]-1-propanol. Reaction of 3.7 g (24.7 mmol) of 1-(phenylthio)cyclopropane and 1.6 mL (18 mmol) of propanal gave 4.3 g (19.3 mmol, 78%) of 1-[(phenylthio)cyclopropyl]-1-propanal[15] (R_f, 0.4): ^1H NMR ($CDCl_3$) δ 0.93 (t, 3 H), 0.97–1.0 (m, 4 H), 1.73 (m, 2 H), 2.07 (s, 1 H), 3.20 (m, 1 H), and 7.1–7.65 ppm (m, 5 H); ^{13}C ($CDCl_3$) δ 10.6 (q), 13.8 (t), 13.9 (t), 28.1 (t), 31.1 (s), 77.9 (d), 125.9 (d), 129.1 (d), and 136.5 ppm (s); IR (neat) 3450, 3100–2800, 1580, 1470, 1430, 1380, 1080, 1020, and 730 cm^{-1}; mass spectrum (*m*/*z*, rel intensity) 208 (45, P), 190 (25), 179 (10), 99 (100), and 29 (45).

1-[(Phenylthio)cyclopropyl]-2-methyl-1-ethanol. Reaction of 3.0 g (20.0 mmol) of 1-(phenylthio)cyclopropane and 1.3 g (18.0 mmol) of 2-methylpropanal gave 3.2 g (14.2 mmol, 71%) of 1-[(phenylthio)cyclopropyl]-2-methyl-1-ethanol[15] (R_f, 0.3): ^1H NMR ($CDCl_3$) δ 0.9 (q, 3 H), 0.9–1.2 (m, 4 H), 1.9 (s, 1 H), 2.2 (m, 1 H), 2.8 (d, 1 H), and 7.1–7.6 ppm (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 13.6 (t), 16.3 (t), 18.7 (q), 20.1 (q), 30.0 (s), 33.4 (d), 83.0 (d), 126.4 (d), 128.8 (d), 130.3 (d), and 136.6 ppm (s); IR (neat) 3450, 3100–2800, 1575, 1450, 1370, 1040, and 735 cm^{-1}; mass spectrum (*m*/*z*, rel intensity) 222 (58, P), 179 (57), 161 (70), 149 (65), 117 (100), 91 (80), 73 (45), and 43 (95).

Preparation of 1-(Bromoalkyl)-1-(phenylthio)cyclopropanes. A solution of 2 equiv of thionyl bromide in dry pentane was added to 1 equiv of 1-(phenylthio)cyclopropylcarbinyl alcohol and stirred for 4 h at 25 °C. A solution of 1 equiv of dry pyridine in pentane was added, and the solution was refluxed for 3 h, cooled, and washed with 5% aqueous HCl. Extraction with ether and washing the ether phases with 5% aqueous NaOH was followed by drying ($CaCl_2$). Removal of solvents by bulb-to-bulb distillation under redued pressure gave the pure 1-(bromoalkyl)-1-(phenylthio)cyclopropane, in all cases.

1-(Bromopropyl)-1-(phenylthio)cyclopropane (4a). Reaction of 2.4 g (16.3 mmol) of [(phenylthio)cyclopropyl]-1-propanol with 3.8 g (36 mmol) of $SOBr_2$ and 1.3 mL (16.3 mmol) of dry pyridine gave 1.9 g (7.2 mmol, 44%) of **4a** (Kugelrohr distillation, 180–185 °C, 5 mmHg): ^1H NMR ($CDCl_3$) δ 0.7–2.5 (m, 9 H), 3.9 (m, 1 H), and 6.9–7.7 ppm (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 12.5 (t), 16.2 (q), 19.7 (t), 30.1 (s), 126.3 (d), 128.9 (d), 130.0 (d), and 136.0 ppm (s); IR (neat) 3080, 2960, 2890, 1570, 1450, 1430, and 650 cm^{-1}; mass spectrum (*m*/*z*, rel intensity) 273 (26, P + 2), 271 (27, P), 191 (100), 158 (60), 135 (62), 109 (62), 91 (75), 81 (99), and 65 (85).

1-Bromo-2-(methylpropyl)-1-(phenylthio)cyclopropane (4b). Reaction of 0.57 g (2.3 mmol) of 2-methyl-1-[(phenylthio)cyclopropyl]-1-propanol, 0.5 g (4.6 mmol) of $SOBr_2$, and 0.18

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mL (2.3 mmol) of dry pyridine gave 0.3 g (0.9 mmol, 41%) of **4b** (Kugelrohr distillation, bp 182–187 °C, 5 mmHg): ^{1}H NMR ($CDCl_3$) δ 0.9–1.2 (d, 1 H), 2.4 (d, 1 H), 3.9 (d, 1 H), and 7.2 ppm (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 18.0 (q), 19.8 (q), 38.2 (s), 52.5 (d), 71.0 (d), 128.3 (d), 129.0 (d), 133.1 (d), and 137.0 ppm (s); IR (neat) 3100, 2980, 1465, 1450, 1375, and 660 cm^{-1}; mass spectrum (*m/z*, rel intensity) 284 (43, P + 2), 282 (30, P), 205 (87), 189 (23), 161 (41), 149 (54), 109 (57), 95 (100), 77 (83), and 69 (72).

Reaction with Lithium Dialkylcuprates. A solution of 2 equiv of the appropriate lithium dialkylcuprate in anhydrous ether was treated with the appropriate bromide at −20 °C and stirred for 15 h. The reaction was quenched with water and filtered through a 0.25-in. pad of Celite. Separation of the phases was followed by drying the ether phase ($MgSO_4$) and removal of solvents under reduced pressure. The products were purified by chromatography on silica gel with pentane.

In each case a "standard" concentration of dialkylcuprate was used. A solution of 13.4 mL of 2.4 M *n*-butyllithium in 30 mL of ether was treated with 2.3 g (16.1 mmol) of CuBr at −78 °C, warmed to −40 °C for 15 min, and treated with bromide. The reaction was then warmed to −20 °C. Similarly, a solution of 5.9 mL of 1.4 M methyllithium was treated with 0.6 g (4.1 mmol) of CuBr at −78 °C and warmed to 0 °C for 10 min. The slurry was cooled to −20 °C and treated with bromide. The diphenylcuprate was prepared similarly by reaction of 15 mL of 1.1 M phenyllithium and 2.93 g (20.4 mmol) of CuBr. Reaction of 13.0 mL of 1.2 M *tert*-butyllithium and 1.75 g (12.2 mmol) of CuBr at −78 °C for 30 min was followed by treatment with bromide at −78 °C, stirring for 1 h, and slow warming to −20 °C.

4-(Phenylthio)-3-decene (5a). Reaction of 0.5 g (1.8 mmol) of **4a** with the lithium di-*n*-butylcuprate slurry gave 0.27 g (1.1 mmol, 66%) of **5a** as a colorless oil (R_f, 0.5): ^{1}H NMR ($CDCl_3$) δ 1.1 (t, 6 H), 0.9–1.5 (m, 8 H), 2.3 (m, 4 H), 5.9 (t, 1 H), and 7.2 ppm (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 11.6 (t), 14.1 (t), 22.2 (d), 22.9 (d), 32.9 (d), 35.6 (d), 43.5 (d), 125.8 (d), 128.8 (d), 129.3 (d), 127.0 (s), and 154.0 ppm (s); IR (neat) 3100, 2980, 1465, 1450, 1375, and 660 cm^{-1}; mass spectrum (*m/z*, rel intensity) 248 (10, P), 246 (100), 203 (25), 189 (30), 147 (30), 136 (20), 97 (80), 79 (75), and 41 (80). Anal. Calcd for $C_{16}H_{24}S$ *m/z* 248.1600, obsd *m/z* 248.1606 (±1.2 mmu).

Capillary GC/MS analysis revealed **5a** to be a 53:47 mixture of *E*:*Z* isomers.

4-(Phenylthio)-3-heptene (5b). Reaction of 0.3 g (1.0 mmol) of **4a** and the lithium dimethylcuprate slurry gave 0.12 g (0.6 mmol, 55%) of **5b** as a 70:30 mixture of *E*:*Z* isomers (R_f, 0.5): ^{1}H NMR ($CDCl_3$) δ 1.1 (t, 6 H), 1.0–2.7 (m, 4 H), 5.9 (t, 1 H), and 7.0–7.2 ppm (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 11.5 (q), 18.0 (q), 22.9 (t), 30.7 (t), 125.8 (d), 127.6, 128.0 (d), 128.9 (d), 129.0 (d), 132.0 (s), and 153 ppm (s); IR (neat) 3100, 2950, 2810, 1600, 1495, 1450, 1375, 700, and 650 cm^{-1}; mass spectrum (*m/z*, rel intensity) 206 (20, P), 204 (60), 189 (21), 175 (32), 134 (35), 110 (70), 79 (85), and 67 (100). Anal. Calcd for $C_{13}H_{18}S$ *m/z* 206.1129, obsd *m/z* 206.1121 (±1.0 mmu).

3-Phenyl-4-(phenylthio)-3-hexene (5c). Reaction of 0.7 g (2.5 mmol) of **4a** and the lithium diphenylcuprate slurry gave 0.38 g (1.4 mmol, 57%) of **5c** as a 55:45 mixture of *E*:*Z* isomers (R_f, 0.5): ^{1}H NMR ($CDCl_3$) δ 1.0 (t, 3 H), 2.0–3.2 (m, 4 H), 4.1 (m, 2 H), 5.7 (t, 1 H), and 6.9–7.5 ppm (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 13.7 (q), 31.2 (t), 37.5 (t), 48.0 (t), 97.0 (d), 126.0 (d), 127.1 (d), 127.5 (d), 128.4 (d), 129.4 (d), 140.0 (s), 140.0 (s), and 155.0 ppm (s); IR (neat) 3150, 2900, 1600, 1500, 1450, 1370, and 710 cm^{-1}; mass spectrum (*m/z*, rel intensity) 268 (3, P), 266 (25), 237 (27), 159 (50), 128 (100), 116 (50), 91 (40), 77 (50), and 51 (20). Anal. Calcd for $C_{18}H_{20}S$ *m/z* 268.1281, obsd *m/z* 268.1277 (±1.3 mmu).

7,7-Dimethyl-4-(phenylthio)-3-octene (5d). Reaction of 0.3 g (1.1 mmol) of **4a** and the lithium di-*tert*-butylcuprate slurry gave 0.13 g (0.5 mmol, 48%) of **5d** as a 60:40 *E*:*Z* mixture of isomers (R_f, 0.5): ^{1}H NMR ($CDCl_3$) δ 0.9–1.5 (m, 12 H), 2.3 (m, 4 H), 5.8 (t, 1 H), and 7.0–7.5 ppm (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 11.6 (q), 22.6 (d), 26.3 (q), 32.6 (s), 35.6 (t), 123.0 (d), 125.1 (d), 128.0 (d), 129.2 (d), 139.1 (s), and 155.0 ppm (s); IR (neat) 3150, 2950, 1600, 1500, 1470, 1350, and 700 cm^{-1}; mass spectrum (*m/z*, rel intensity) 248 (7, P), 246 (60), 231 (8), 217 (7), 191 (11), 137 (15), 121 (90), and 57 (100). Anal. Calcd for $C_{16}H_{24}S$ *m/z* 248.1599, obsd *m/z* 248.1590 (±1.2 mmu).

2-Methyl-4-(phenylthio)-3-decene (5e). Reaction of 0.5 g (1.6 mmol) of **4b** and the lithium di-*n*-butylcuprate slurry gave 0.28 g (1.1 mmol, 71%) of **5e** as a 70:30 mixture of *E*:*Z* isomers (R_f, 0.5): ^{1}H NMR ($CDCl_3$) δ 0.95 (t, 3 H), 1.0 (d, 6 H), 1.0–2.6 (m, 10 H), 2.7 (m, 1 H), 5.7 (d, 1 H), and 7.2 ppm (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 20.5 (q), 20.7 (q), 22.8 (q), 28.2 (d), 29.4 (d), 32.9 (d), 33.5 (d), 42.7 (d), 123.4 (d), 125.8 (d), 128.8 (d), 129.3 (d), 132.0 (s), and 154.0 ppm (s); IR (neat) 3150, 2950, 2800, 1600, 1450, 1350, and 700 cm^{-1}; mass spectrum (*m/z*, rel intensity) 262 (5, P), 260 (55), 217 (15), 183 (16), 161 (14), 147 (5), 109 (80), and 95 (100). Anal. Calcd for $C_{17}H_{26}S$ *m/z* 262.1757, obsd *m/z* 262.1747 (±1.3 mmu).

2-Methyl-4-(phenylthio)-3-heptene (5f). Reaction of 0.3 g (0.9 mmol) of **4b** and the lithium dimethylcuprate slurry gave 0.09 g (0.4 mmol, 50%) of **5f** as an 80:20 mixture of *E*:*Z* isomers (R_f, 0.5): ^{1}H NMR ($CDCl_3$) δ 0.9–1.0 (t, 6 H), 1.1 (t, 3 H), 1.8–3.0 (m, 5 H), 5.6 (d, 1 H), and 7.1–7.5 ppm (7, 5 H); ^{13}C NMR ($CDCl_3$) δ 13.7 (q), 18.5 (q), 19.8 (q), 22.6 (t), 29.4 (t), 29.5 (d), 125.1 (d), 126.3 (d), 129.1 (d), 133.0 (s), and 153.2 (s); IR (neat) 3100, 2950, 1600, 1500, 1470, 1350, 700, and 650 cm^{-1}; mass spectrum (*m/z*, rel intensity) 220 (3, P), 218 (80), 208 (10), 189 (5), 161 (20), 141 (50), 109 (100), 98 (80), 77 (50), and 67 (95). Anal. Calcd for $C_{14}H_{20}S$ *m/z* 220.1287, obsd *m/z* 220.1287 (±1.1 mmu).

2-Methyl-6-phenyl-4-(phenylthio)-3-hexene (5g). Reaction of 0.4 g (1.2 mmol) of **4b** and the lithium diphenylcuprate slurry gave 0.2 g (0.76 mmol, 64%) of **5g** as a 95:5 mixture of *E*:*Z* isomers (R_f, 0.5): ^{1}H NMR ($CDCl_3$) δ 1.2 (t, 6 H), 2.2 (m, 2 H), 2.4 (m, 1 H), 2.6 (t, 2 H), 5.8 (d, 1 H), and 7.0–7.5 ppm (m, 10 H). ^{13}C NMR ($CDCl_3$) δ 21.9 (q), 22.0 (q), 29.4 (d), 125.3 (d), 125.6 (d), 126.0 (d)8, 127.1 (d), 125.5 (d), 128.0 (d), 128.5 (d), 129.3 (d), 139.0 (s), 141.2 (s), and 154.1 ppm (s); IR (neat) 3150, 2900, 2850, 1600, 1500, 1450, 1370, and 700 cm^{-1}; mass spectrum (*m/z*, rel intensity) 282 (7, P), 280 (60), 237 (100), 204 (10), 189 (9), 159 (90), 128 (95), 91 (40), and 77 (30). Anal. Calcd for $C_{19}H_{22}S$ *m/z* 282.1446, obsd *m/z* 282.1440 (±1.4 mmu).

4-(Phenylthio)-2,7,7-trimethyl-3-octene (5h). Reaction of 0.3 g (1.2 mmol) of **4b** with the lithium di-*tert*-butylcuprate slurry gave 0.2 g (0.8 mmol, 66%) of **5h** as a 90:10 mixture of *E*:*Z* isomers (R_f, 0.5): ^{1}H NMR ($CDCl_3$) δ 0.9–2.8 (m, 19 H), 5.7 (d, 1 H), and 7.1–7.5 ppm (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 18.9 (q), 19.0 (q), 26.1 (q), 26.2 (q), 26.3 (q), 28.8 (d), 29.4 (t), 29.5 (t), 125.8 (d), 126.5 (d), 128.0 (d), 129.1 (d), 132.1 (s), and 152.0 (s); IR (neat) 3150, 2950, 1650, 1600, 1500, 1450, 1370, and 700 cm^{-1}; mass spectrum (*m/z*, rel intensity) 262 (3, P), 260 (58), 203 (10), 161 (10), 151 (45), 135 (100), 109 (70), 95 (50), and 57 (80). Anal. Calcd for $C_{17}H_{26}S$ *m/z* 262.1757, obsd *m/z* 262.1744 (±1.3 mmu).

Convenient Approaches to Ketals from Phthalide: Monosubstituted Isobenzofurans

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Two new methods for the formation of ketals from phthalide are described. The ketals are readily converted to monosubstituted isobenzofurans (IBFs),[1] making these among the most easily prepared members of this family of reactive dienes.

The use of phthalide (**1**) for the preparation of the parent IBF was developed in this laboratory some time ago.[2] Procedural improvements[3] and modifications have

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