The Application of Lithium Reagents from (1-Methylthio)alkylphosphonate Esters to the Synthesis of Ketones

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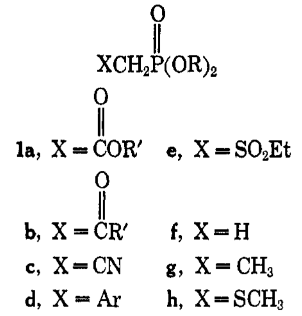
Diethyl methylthiomethylphosphonate can be alkylated by successive treatment with *n*-butyllithium and an *n*-alkyl iodide to give the corresponding (1-methylthio)alkylphosphonate esters (**4**). The lithio derivatives of the latter (**5**) react with carbonyl compounds to form β-alkoxy phosphonate adducts, which decompose upon heating to 50° (in tetrahydrofuran) to form substituted vinyl methyl sulfides (**7**). Ketones are obtained in good yield by mercury(II)-promoted hydrolysis of the vinyl sulfides **7**.

Phosphonate esters containing an electron-withdrawing substituent (**1a–d**) form stabilized carbanions which can effect the synthesis of certain olefins from aldehydes and ketones.[1,2] Very recently,[3] the scope of this reaction has been extended to include the synthesis of α,β-unsaturated sulfones *via* the phosphonate ester **1e**. It has also been shown[4] that the unstabilized carbanions from **1f** and **1g** can be formed as lithio derivatives and that these anions react with carbonyl compounds to produce β-hydroxy phosphonates, *e.g.*, the adducts **2a** and **2b** from benzophenone. However, even in cases most favorable for olefin formation such as **2a** and **2b**, Wittig elimination does not occur satisfactorily either from the β-hydroxy phosphonates or their conjugate bases. It was concluded[4] that the facile Wittig elimination of the β-alkoxy phosphonates requires the presence of an electron-withdrawing substituent on the carbon α to the phosphorus function.



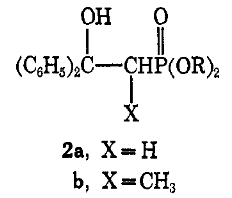
$XCH_2P(=O)(OR)_2$

1a, $X = C(=O)OR'$ **e**, $X = SO_2Et$

b, $X = C(=O)R'$ **f**, $X = H$

c, $X = CN$ **g**, $X = CH_3$

d, $X = Ar$ **h**, $X = SCH_3$



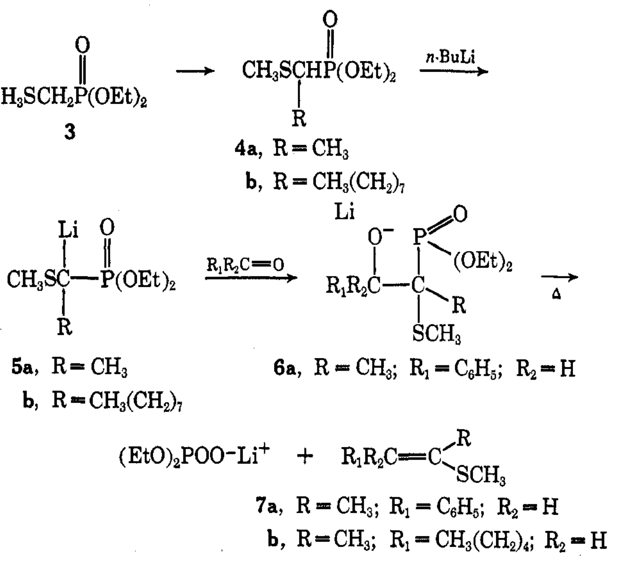
$(C_6H_5)_2C(OH)-CH(X)P(=O)(OR)_2$

2a, X = H

b, $X = CH_3$

The ability of bivalent sulfur to stabilize an adjacent carbanion[5] suggests the use of the thioalkyl moiety as an activating group X in the phosphonate olefin synthesis; the product of such a reaction would be a vinyl sulfide, a convenient precursor to aldehydes or ketones through hydrolysis.[6] Indeed, Green[7] has achieved limited success with a vinyl sulfide synthesis using **1h** as substrate, but his reaction conditions severely "limit the value of this reaction as a synthetic method."[7] We report herein the ready adaptation of the phosphonate olefin synthesis to the preparation of vinyl sulfides, and the subsequent hydrolysis of these compounds to unsymmetrical ketones.

We found that diethyl methylthiomethylphosphonate (**3**)[7] was metalated readily by 1 equiv of *n*-butyllithium in tetrahydrofuran at −70°. The alkylation of the lithio derivative was a facile reaction, affording good yields of diethyl (1-methylthio)ethylphosphonate (**4a**) or diethyl (1-methylthio)nonylphosphonate (**4b**). Sequential treatment of the phosphonates **4** with *n*-butyllithium and an aldehyde or ketone gave adducts **6**, which upon heating at 50° eliminated diethyl phosphate monoanion to give vinyl sulfides **7**. The lithio derivatives **5** could be formed either at −70° in tetrahydrofuran or at 0° in cyclohexane. The intermediacy of the hydroxyphosphonate anion **6** was demonstrated by the aqueous quenching of the reaction mixture from **5a** and benzaldehyde, whereupon protonated **6a** was obtained in 88% yield.



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4a, $R = CH_3$

b, $R = CH_3(CH_2)_7$

5a, $R = CH_3$

b, $R = CH_3(CH_2)_7$

6a, $R = CH_3$; $R_1 = C_6H_5$; $R_2 = H$

7a, $R = CH_3$; $R_1 = C_6H_5$; $R_2 = H$

b, $R = CH_3$; $R_1 = CH_3(CH_2)_4$; $R_2 = H$

The scope of the synthesis of vinyl sulfides *via* the Emmons–Horner phosphonate reaction can be seen from the data in Table I. In the two instances which afforded low yields of vinyl sulfides (*i.e.*, cyclopentanone and acetophenone), substantial amounts of base-catalyzed condensation products were obtained, indicating that for these ketones enolate formation by proton transfer is favored over attack at the carbonyl.

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[1] (a) W. S. Wadsworth, Jr., and W. D. Emmons, *J. Amer. Chem. Soc.*, **83**, 1733 (1961); (b) L. Horner, H. Hoffmann, and H. G. Wippel, *Chem. Ber.*, **91**, 61 (1958).

[2] For a recent review see A. V. Dombrovskii and V. A. Dombrovskii, *Russ. Chem. Rev.*, **35**, 733 (1966).

[3] I. C. Popoff, J. L. Dever, and G. R. Leader, *J. Org. Chem.*, **34**, 1128 (1969).

[4] E. J. Corey and G. T. Kwiatkowski, *J. Amer. Chem. Soc.*, **88**, 5654 (1966).

[5] G. Cilento, *Chem. Rev.*, **60**, 147 (1960).

[6] (a) B. S. Kupin and A. A. Petrov, *Zh. Org. Khim.*, **3**, 975 (1967); (b) J. H. S. Weiland and J. F. Arens, *Rec. Trav. Chim. Pays-Bas*, **79**, 1293 (1960); (c) T. Mukaiyama, S. Fukuyama, and T. Kumamoto, *Tetrahedron Lett.*, 3787 (1968).

[7] M. Green, *J. Chem. Soc.*, 1324 (1963).

TABLE I

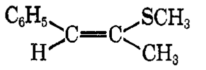
CONVERSION $R_1R_2C{=}O \rightarrow R_1R_2C{=}CR(SCH_3)$ USING DIETHYL (1-METHYLTHIO)ALKYLPHOSPHONATES

R	Carbonyl compd	Solvent^a	Yield of vinyl sulfide,^{b} %
CH_3	Benzaldehyde	T	80^c
CH_3	Benzophenone	T	84
CH_3	Hexanal	T	67^d
CH_3	Hexanal	C	67^e
CH_3	Cyclohexanone	T	82
$CH_3(CH_2)_7$	Cyclohexanone	T	72
CH_3	Acetophenone	T	Trace^{e,f}
CH_3	Acetophenone	C	Trace^e
CH_3	Cyclopentanone	T	7–10^g
CH_3	Cyclopentanone	C	7–10

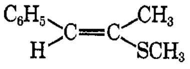
^{a} Solvents: T, tetrahydrofuran; C, cyclohexane. ^{b} After purification by preparative tlc. ^{c} Major isomer, E, 83%; minor isomer, Z, 17%. ^{d} Major isomer, E, 60%; minor isomer, Z, 40%. ^{e} Isomer ratio not determined. ^{f} A mixture of acetophenone and its base-catalyzed condensation product (α-methyl-β-benzoylstyrene) was recovered in *ca.* 60% yield. ^{g} 2-Cyclopentylidene cyclopentanone was also isolated in 35% yield.

Such behavior is especially characteristic of cyclopentanone in Wittig-type reactions.[8]

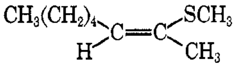
In those instances where the formation of isomeric vinyl sulfides was possible (**7a** and **7b**), the isomer ratios as given in Table I were determined by vpc. Stereochemistry was assigned from nmr data; in particular, the chemical shifts of the vinylic protons were diagnostic. Use of the tables of Pascual, Meier, and Simon,[9] which correlate chemical shifts of olefinic protons with their chemical environments, indicates that the vinylic proton in **7a**-E[10] will appear at δ 6.10, while the spectrum of **7a**-Z[10] will have this proton at δ 6.33. In fact, the nmr of **7a** revealed broad singlets at δ 6.12 and 6.40, with the former predominating (3:1 ratio). The major isomer is thus assigned the E stereochemistry. Likewise, the chemical shifts of the vinyl protons of **7b**-E and **7b**-Z are predicted to be δ 5.19 and 5.42, respectively. In fact, these protons appeared as broad triplets at δ 5.17 and 5.45 in a 3:2 ratio. The major isomer is therefore again assigned the E stereochemistry.



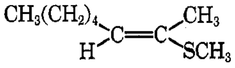
7a-Z



7a-E



7b-Z



7b-E

The hydrolysis of vinyl sulfides to ketones (or aldehydes) has usually been effected under rather drastic acidic conditions.[6] Seeking a milder hydrolysis procedure, we investigated the use of mercuric chloride in aqueous acetonitrile[11] and found that this medium afforded high yields of the pure ketones. Table II shows the results of these hydrolyses. To obtain optimum yields, the reaction mixtures were worked up soon after the disappearance of the vinyl sulfides (as determined by tlc). This avoided aldol condensation of the ketones, catalyzed by the acid formed along with the insoluble mercury mercaptide.

TABLE II

HYDROLYSIS OF VINYL SULFIDES TO KETONES

$$R_1R_2C{=}CR(SCH_3) \longrightarrow R_1R_2CHCOR$$

R	R_1	R_2	Temp, °C (hr)^a	Yield of ketone,^{b} %
CH_3	C_6H_5	H	50 (21)	84
CH_3	C_6H_5	C_6H_5	82 (41)	86
CH_3	$(CH_2)_5$		25 (20)	78
CH_3	$CH_3(CH_2)_4$	H	25 (6)	74^c
$CH_3(CH_2)_7$	$(CH_2)_5$		40 (26)	92

^{a} Aqueous acetonitrile, 2 equiv of mercuric chloride. ^{b} After purification by short-path distillation. ^{c} Purified by column chromatography.

The success of the vinyl sulfide formation and subsequent hydrolysis provides a convenient, efficient synthesis of ketones of the type RCOR′, where R originates from an alkylating agent and R′ embodies the carbon skeleton of a ketone or aldehyde. The utility of the synthesis is best seen in the case of cyclohexyl *n*-octyl ketone, derived from *n*-octyl iodide and cyclohexanone. This ketone has been prepared by (a) the glycidic ester synthesis[12] (overall yield, *ca.* 15%), and (b) the hydroboration of 1-octene with dicyclohexylborane and subsequent carbonylation and oxidation[13] (overall yield 71%, but contaminated with 19% dicyclohexyl ketone). In comparison, the present synthesis affords cyclohexyl *n*-octyl ketone of high purity in good overall yield (66%, two steps, purified intermediate).

Experimental Section

Melting points were taken in glass capillary tubes with a Büchi apparatus and are corrected; boiling points are uncorrected. Infrared spectra were recorded for neat liquid samples with a Perkin-Elmer Model 137 spectrophotometer, using the 6.24-μ band of polystyrene as standard. Refractive indices were obtained using a Bausch and Lomb Abbe-3L refractometer. Nuclear magnetic resonance data were determined for solutions in $CDCl_3$ (unless otherwise specified) at 60 Mcps using Varian Associates Model A-60 or T-60 instruments and are expressed in parts per million (ppm) downfield from internal tetramethylsilane. Tetrahydrofuran (THF) was dried before use by distillation from lithium aluminum hydride. Analytical gas chromatography was performed on the following columns: 6 ft × 0.125 in. 5% Carbowax 20M on Gas-Chrom Q, F & M Model 810 or 5750 instrument with flame ionization detection (column A); 10 ft × 0.25 in. 5% SE-30 silicon rubber on Diatoport S, F & M Model 300 instrument with thermal conductivity detection (column B); 10 ft × 0.25 in. 5% QF-1 fluorosilicon on Diatoport S, F & M Model 300 (column C). Flow rates were, for column A, 30 ml/min; for columns B and C, 60 ml/min. Elemental analyses were carried out by Scandinavian Microanalytical Laboratory, Herlev, Denmark, and by Elek Microanalytical Laboratory, Torrance, Calif.

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(8) D. R. Coulson [*Tetrahedron Lett.*, 3323 (1964)] found only 2-cyclopentylidene cyclopentanone (50% yield) upon reaction of cyclopentanone with $(C_6H_5)_3P{=}C(CH_3)OCH_3$. G. Wittig, W. Böll, and K.-H. Krück [*Chem. Ber.*, **95**, 2514 (1962)] could isolate the desired vinyl ether from the reaction of cyclopentanone with $(C_6H_5)_3P{=}CHOCH_3$ in only 14% yield; a large amount of aldol condensation product was also formed.

(9) C. Pascual, J. Meier, and W. Simon, *Helv. Chim. Acta*, **49**, 164 (1966).

(10) See J. E. Blackwood, C. L. Gladys, K. L. Loening, A. E. Petrarca, and J. E. Rush, *J. Amer. Chem. Soc.*, **90**, 509 (1968), for the use of the Entgegen–Zusammen priority nomenclature to specify configuration about a double bond.

(11) See E. J. Corey and D. Crouse, *J. Org. Chem.*, **33**, 298 (1968), for the use of this system for the hydrolysis of dithianes.

(12) H. H. Morris and M. L. Lusth, *J. Amer. Chem. Soc.*, **76**, 1237 (1954). These authors also prepared some of the ketone for comparison by an alkylcadmium-type Grignard reaction. No yield was given.

(13) H. C. Brown and M. W. Rathke, *ibid.*, **89**, 4528 (1967); H. C. Brown, G. W. Kabalka, and M. W. Rathke, *ibid.*, **89**, 4530 (1967).

Diethyl (1-Methylthio)ethylphosphonate (4a).—A solution of 11.88 g (60 mmol) of diethyl methylthiomethylphosphonate[7] in 200 ml of dry THF under argon and cooled to −70° was treated with 51 ml (62 mmol) of 1.22 *M* *n*-butyllithium in pentane. Stirring of the yellow solution was continued for 5 hr at −70°, after which time 4.4 ml (10.0 g, 70 mmol) of methyl iodide was added. After an additional 30 min at −70°, the solution was allowed to warm to room temperature. The bulk of the solvents were removed on a rotary evaporator, and the remaining yellow oil was treated with 75 ml of water and extracted with two 75-ml portions of ether. The combined extracts were washed with brine, dried over anhydrous magnesium sulfate, and distilled. Three fractions were collected, total 9.75 g (77%), at temperatures of 55–70° (0.20 mm); all were shown by nmr to be sufficiently pure for further use. Most of the product boiled at 68–70° (0.20 mm): purity >95% by vpc (column A at 150°, retention time 2.7 min); $n^{23}\text{D}$ 1.4620; nmr δ 1.35 (triplet, 6 H, $J_{\text{HH}} = 7$ cps, methyl groups on the ethyl ester), 1.48 (doublet of doublets, 3 H, $J_{\text{HH}} = 7$ cps, $J_{\text{PH}} = 16$ cps, methyl adjacent to phosphorus), 2.29 (singlet, 3 H, methylthio), 2.70 (symmetrical multiplet, 1 H, methine), and 4.20 (symmetrical multiplet, 4 H, methylene on ethyl ester). The infrared spectrum was characterized by a strong P═O stretching absorption at 8.00 μ and a CH_2OP stretching vibration at 8.58 μ.

Anal. Calcd for $C_7H_{17}PSO_3$: C, 39.60; H, 8.08; S, 14.60. Found: C, 39.44; H, 8.10; S, 14.67.

Diethyl (1-Methylthio)nonylphosphonate (4b).—To a solution of 11.88 g (60 mmol) of diethyl methylthiomethylphosphonate[7] in 200 ml of dry THF under argon and at −70° was added 55 ml (67 mmol) of 1.22 *M* *n*-butyllithium in pentane. After 4 hr of stirring, the solution was treated with 18.0 g (75 mmol) of *n*-octyl iodide, resulting in the formation of a precipitate. The mixture was stirred at −70° for 45 min, then at room temperature for 15 hr. Removal of the bulk of the solvents with a rotary evaporator and work-up as above afforded, after distillation, 6.46 g, bp 123–132° (0.12 mm), and 6.42 g, bp 132–133° (0.12 mm). That these fractions were identical was shown by nmr. The total yield was 12.89 g (69%): $n^{23}\text{D}$ 1.4620; nmr δ 0.89 (collapsed triplet, 3 H, terminus of alkyl chain), 1.1–2.0 including 1.34 (triplet, $J_{\text{HH}} = 7$ cps) and a broad envelope peaking at 1.28 (20 H, methyl groups on ethyl esters, and methylene protons on alkyl chain), 2.18 (singlet, 3 H, methylthio), 2.60 (broad multiplet, 1 H, methine), and 4.20 (symmetrical multiplet, 4 H, methylenes on ethyl esters). The infrared spectrum contained a strong P═O stretching band at 8.00 μ and a CH_2OP stretching vibration at 8.60 μ.

Anal. Calcd for $C_{14}H_{31}PSO_3$: C, 54.17; H, 10.07; S, 10.33. Found: C, 54.41; H, 10.00; S, 10.28.

Preparation of Diethyl (1-Methyl-1-methylthio-2-hydroxy-2-phenyl)ethylphosphonate (Protonated 6a) from Diethyl (1-Methylthio)ethylphosphonate and Benzaldehyde.—To a solution of 212 mg (1.0 mmol) of diethyl (1-methylthio)ethylphosphonate in 10 ml of dry THF under argon and at −70° was added 0.85 ml (1.1 mmol) of 1.3 *M* *n*-butyllithium in pentane. After 3.75 hr the solution was treated with 1.0 ml (1.05 g, 10.0 mmol) of benzaldehyde. Following stirring at −70 and 0° for 15 min each, the reaction mixture was poured into 10 ml of water and extracted with 10 ml of ether. The extract was washed with successive 10-ml portions of saturated aqueous ammonium chloride, sodium bicarbonate, and sodium chloride. Evacuation at 1 mm for 17 hr left 280 mg (88%) of the hydroxyphosphonate. The nmr spectrum showed peaks at δ 1.20 (complex envelope, 9 H, methyl groups on ethyl esters and adjacent to phosphorus), 1.90 and 2.20 (singlets, 3 H, methylthio in *threo* and *erythro* isomers), 4.20 (multiplet, 4 H, methylene protons on ethyl esters), 4.56 (singlet, 1 H, hydroxyl), 5.09 and 5.18 (pair of doublets, 1 H, $J_{\text{PH}} = 11$ and 6 cps, methine, *threo* and *erythro*), and 7.41 (multiplet, 5 H, aromatic).

General Procedure for the Formation of Vinyl Sulfides.—To 510 mg (2.4 mmol) of diethyl (1-methylthio)ethylphosphonate or 744 mg (2.4 mmol) of diethyl (1-methylthio)nonylphosphonate in 12 ml of dry THF at −70° or cyclohexane at 0° and under argon was added 1.6 ml (2.0 mmol) of 1.25 *M* *n*-butyllithium in pentane. The resulting solution was stirred at low temperature (−70 or 0°, depending upon the solvent) for 4–6 hr. The carbonyl compound (1.8 mmol) was added, neat or in 4 ml of THF or cyclohexane, and stirring was continued at low temperature for 30–60 min. The clear solution was next heated at 50° under argon for 15–20 hr to effect elimination of the diethyl phosphate anion. The resulting mixture, now yellow (various intensities of brown for reactions that gave poor yields of vinyl sulfides), was treated with 10 ml of water and 10 ml of saturated aqueous ammonium chloride, and then extracted with 10 ml of ether. The ether extract was successively washed with 10-ml portions of saturated aqueous sodium bicarbonate and brine; all aqueous phases were back-washed with 10 ml of ether. The combined ether extracts were dried over anhydrous magnesium sulfate and concentrated on a rotary evaporator. Isolation of the pure vinyl sulfide was readily accomplished by preparative tlc on silica gel PF_{254}, using 1:1 methylene chloride–cyclohexane as eluent. The vinyl sulfides were all active in the uv, with R_f values of *ca.* 0.7.

Methyl α-methylstyryl sulfide (7a) was obtained in 80% yield by the addition of neat benzaldehyde to the anion **5a**, formed in THF. Vpc (column A, 100°) showed the liquid product to be homogeneous. The two possible isomers (**7a**-E, retention time 5.3 min; **7a**-Z, retention time 6.2 min) were present in a 5:1 ratio: nmr δ 2.09 and 2.13 (doublets, 3 H, $J = 1.5$ cps, E and Z vinylic methyl groups, respectively), 2.20 and 2.26 (singlets, 3 H, Z and E methylthio groups, respectively), 6.12 and 6.40 (broad singlets, 1 H, E and Z vinylic protons, respectively), and 7.20 (broad singlet, 5 H, aromatic). The infrared spectrum contained bands at 6.20 and 6.38 μ, owing to a double bond conjugated with an aromatic ring. Both infrared and nmr spectra were virtually identical with those reported[6a] for the vinyl sulfide. The Russian workers did not report the isomer ratio of their vinyl sulfide (formed by the reaction of $C_6H_5C{\equiv}CCH_3$ with CH_3SH), but the ratio of the olefinic protons in the nmr of their product seemed to be nearly the same as in the present case. The product had $n^{24}\text{D}$ 1.6085 (lit.[6a] $n^{20}\text{D}$ 1.6125).

Methyl 1-methyl-1-heptenyl sulfide (7b) was prepared in 67% yield by the addition of hexanal (neat or in solution) to the anion **5a**, formed in either THF or cyclohexane. Vpc (column A, 100°) showed the oil to be homogeneous and a 3:2 mixture of E and Z isomers (retention times 2.1 and 1.8 min, respectively). The nmr spectrum contained peaks at δ 0.89 (collapsed triplet, 3 H, methyl at terminus of alkyl chain), 1.30 (multiplet, 6 H, methylenes), 1.87 and 1.99 (doublets, 3 H, $J = ca.$ 1.5 cps, vinylic methyls on E and Z isomers, respectively), 2.1–2.3 (multiplet, 2 H, allylic protons), 2.20 (singlet, 3 H, methylthio), and 5.17 and 5.45 (broad triplets, 1 H, vinyl protons of E and Z isomers, respectively). The infrared spectrum showed a C═C stretching frequency at 6.14 μ.

Anal. Calcd for $C_9H_{18}S$: C, 68.28; H, 11.46; S, 20.26. Found: C, 68.30; H, 11.45; S, 20.22.

Methyl α-methyl-β-phenylstyryl sulfide was prepared in 84% yield by the addition of a THF solution of benzophenone to the anion **5a** in THF. The product, a vaguely yellow solid, mp 36–38°, was homogeneous by vpc (column B at 190°, retention time 5.8 min): nmr δ 2.10 (singlet, 3 H), 2.16 (singlet, 3 H), and 7.20 (multiplet, 10 H). The infrared spectrum displayed C═C stretching vibrations at 6.28 and 6.39 μ.

Anal. Calcd for $C_{16}H_{16}S$: C, 79.94; H, 6.71; S, 13.34. Found: C, 79.94; H, 6.61; S, 13.23.

Methyl (1-cyclohexylidene)ethyl sulfide was obtained in 82% yield by the addition of a solution of freshly distilled[14] cyclohexanone in THF to the anion **5a**, formed in THF. The oily product was shown to be homogeneous by vpc (column C at 100°, retention time 6.6 min): nmr δ 1.45 (multiplet, 6 H, alicyclic), 1.98 (singlet), 2.19 (singlet), and 2.0–2.5 (multiplet, 10 H, vinylic methyl, methylthio, and allylic protons, respectively). The infrared spectrum contained a weak C═C stretching absorption at 6.16 μ.

Anal. Calcd for $C_9H_{16}S$: C, 69.16; H, 10.32; S, 20.52. Found: C, 68.94; H, 10.24; S, 20.06.

Methyl (1-cyclohexylidene)nonyl sulfide was prepared in 72% yield by the addition of a solution of freshly distilled cyclohexanone in THF to the anion **5b**, also in THF. Vpc (column B at 190°, retention time 6.2 min) proved the homogeneity of the oil: nmr δ 0.89 (poorly resolved triplet, 3 H, terminal methyl on the alkyl chain), 1.30 (broad band, 12 H, aliphatic methylenes), 1.53 (broad singlet, 6 H, alicyclic methylenes), 2.13 (sharp singlet, 3 H, methylthio), and 2.0–2.7 (multiplet, 6 H, allylic). The infrared spectrum contained a weak C═C stretching frequency at 6.18 μ.

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[14] It was observed that the use of cyclohexanone which had been distilled and stored under nitrogen in a serum-stoppered flask for 5 days gave drastically reduced yields of vinyl sulfide.

Anal. Calcd for $C_{16}H_{30}S$: C, 75.51; H, 11.88; S, 12.60. Found: C, 75.77; H, 11.86; S, 12.44.

Reaction of the Anion 5a with Cyclopentanone.—When the general procedure for the formation of vinyl sulfides was carried out, adding a solution of freshly distilled cyclopentanone in THF or cyclohexane to the anion **5a** in the same solvent, only 7–10% of the desired methyl (1-cyclopentylidene)ethyl sulfide could be isolated. Homogeneity of the product was proven by vpc (column B at 100°, retention time 4.5 min): nmr δ 1.69 (multiplet, 4 H, alicyclic), 1.96 (triplet,[15] 3 H, J = 1.5 cps, allylic methyl), 2.25 (singlet), and 2.1–2.6 (multiplet, 7 H, methylthio and allylic methylenes). The infrared spectrum contained a weak C=C stretching absorption at 6.10 μ.

Anal. Calcd for $C_8H_{14}S$: C, 67.53; H, 9.92; S, 22.54. Found: C, 67.59; H, 9.85; S, 21.90.

In addition, a 35% yield of 2-cyclopentylidene cyclopentanone was isolated by preparative tlc (R_f 0.40, silica gel, 1:1 methylene chloride–cyclohexane). The nmr spectrum contained only a complex envelope of peaks at δ 1.3–3.0. The infrared spectrum contained strong bands at 5.82 and 6.09 μ.[16]

Reaction of the Anion 5a with Acetophenone.—The general vinyl sulfide procedure was carried out with **5a** and acetophenone in either THF or cyclohexane; only 3 mg (~1%) of material with the correct R_f value for a vinyl sulfide (0.75) could be isolated; this material was not further characterized. In addition, a 60% yield of a mixture of acetophenone and its aldol condensation product was recovered. The condensation product had an nmr spectrum containing a vinylic methyl at δ 2.17 and an olefinic proton at δ 6.18, in addition to aromatic protons.

Phenylacetone.—To a solution of 90 mg (0.55 mmol) of methyl α-methylstyryl sufide in 4 ml of 3:1 acetonitrile–water was added a solution of 300 mg (1.1 mmol) of mercuric chloride in 4 ml of the same solvent system. The cloudy mixture was stirred at 50° for 21 hr and then filtered through Hyflo Super Cel, with thorough ether washing. The filtrate was washed with aqueous sodium bicarbonate and then with brine and dried over anhydrous magnesium sulfate. Concentration on the rotary evaporator and short-path distillation afforded 62 mg (84%) of the ketone as a colorless oil, which gave a single spot on tlc:[17] $n^{24}\mathrm{D}$ 1.5155 (lit.[18] $n^{20}\mathrm{D}$ 1.5168); nmr δ 2.13 (singlet, 3 H, methyl), 3.69 (singlet, 2 H, methylene), and 7.28 (singlet, 5 H, aromatic). The infrared spectrum contained a C=O stretching frequency at 5.81 μ.

1,1-Diphenylacetone.—To a solution of 96 mg (0.40 mmol) of methyl α-methyl-β-phenylstyryl sulfide in 4 ml of 3:1 acetonitrile–water was added 217 mg (0.80 mmol) of mercuric chloride in 4 ml of the same solvent mixture. The homogeneous solution was refluxed (*ca.* 82°) for 41 hr, during which time the colorless mercury mercaptide precipitated. Work-up as above and short-path distillation afforded 72 mg (86%) of a colorless liquid, which solidified upon cooling, mp 43.5–45.0° (lit.[19] mp 45–46°). The product gave a single spot on tlc:[17] nmr δ 2.23 (singlet, 3 H, methyl), 5.15 (singlet, 1 H, methine), and 7.31 (singlet, 10 H, aromatic). The infrared spectrum contained a C=O band at 5.82 μ.

2-Octanone.—To 111 mg (0.70 mmol) of methyl 1-methyl-1-heptenyl sulfide in 4 ml of 3:1 acetonitrile–water was added 380 mg (1.40 mmol) of mercuric chloride in 3 ml of the same solvent system. A colorless precipitate appeared immediately on mixing. After 6 hr of stirring at room temperature, the milky mixture was filtered through Hyflo Super Cel, with thorough ether washing. The filtrate was washed with aqueous sodium bicarbonate and then with brine, dried over anhydrous magnesium sulfate, and concentrated on the rotary evaporator. The resulting oil was passed through a short silica gel column (methylene chloride eluent) to remove mercuric salts, affording, after removal of solvent, 67 mg (74%) of liquid whose infrared and nmr spectra were identical with those of authentic 2-octanone, $n^{25}\mathrm{D}$ 1.4145 (lit.[20] $n^{20}\mathrm{D}$ 1.4161). The ketone gave a single spot on tlc.[17]

Cyclohexyl Methyl Ketone.—To 195 mg (1.25 mmol) of methyl (1-cyclohexylidene)ethyl sulfide in 8 ml of 3:1 acetonitrile–water was added a solution of 678 mg (2.5 mmol) of mercuric chloride in 5 ml of the same solvent system. After 20 hr of stirring at room temperature, the mixture (a colorless precipitate with a pink supernatent liquid) was filtered through Hyflo Super Cel, with generous ether washing. The filtrate was washed with aqueous sodium bicarbonate and then brine and dried over anhydrous magnesium sulfate. Concentration by rotary evaporator and short-path distillation afforded 123 mg (78%) of the clear, colorless liquid ketone, $n^{25}\mathrm{D}$ 1.4513 (lit.[21] $n^{20}\mathrm{D}$ 1.4530). The product gave a single spot on tlc:[17] nmr (CCl_4) δ 1.5 (broad multiplet, 10 H, alicyclic), 2.03 (singlet, 3 H, methyl), and 2.18 (multiplet, 1 H, methine)' The infrared spectrum contained a C=O band at 5.83 μ.

Cyclohexyl *n*-Octyl Ketone.—A nonhomogeneous mixture of 102 mg (0.40 mmol) of methyl (1-cyclohexylidene)nonyl sulfide in 6 ml of 5:1 acetonitrile–water was treated with 217 mg (0.80 mmol) of mercuric chloride in 3 ml of the same solvent system. The cloudy reaction mixture was heated at 50° for 26 hr, giving a colorless precipitate and a pink, supernatent liquid. Work-up as above and short-path distillation gave 83 mg (92%) of the ketone as a colorless liquid, $n^{25}\mathrm{D}$ 1.4575 (lit. $n^{20}\mathrm{D}$ 1.4585,[12] 1.4600[13]). A single spot was observed on tlc:[17] nmr δ 0.8–2.0, including a poorly resolved triplet at 0.93 and a broad band at 1.27 (25 H), and 2.37 (multiplet, 3 H, protons α to carbonyl). The infrared spectrum contained a C=O band at 5.82 μ.

Registry No.—**4a**, 22966-40-1; **4b**, 22966-41-2; protonated **6a**, 22966-42-3; **7a-E**, 22951-18-4; **7b-E**, 22951-19-5; **7a-Z**, 22966-52-5; **7b-Z**, 22966-53-6; methyl α-methyl-β-phenylstyryl sulfide, 22966-43-4; methyl (1-cyclohexylidene)ethyl sulfide, 22966-44-5; methyl (1-cyclohexylidene)nonyl sulfide, 22966-45-6; methyl (1-cyclopentylidene)ethyl sulfide, 22929-24-4.

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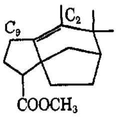
(15) Such homoallylic coupling to *cis*-oriented protons has precedent; for example, G. A. Neville and I. G. Nigam [*Tetrahedron Lett.*, 837 (1969)] have noted that the methyl group at C_2 of compound i is a triplet, J = 1.0 cps, due to coupling to the C_9 protons.



i

(16) See K. Nakanishi, "Practical Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p 165.

(17) Silica gel, 1:1 methylene chloride–cyclohexane eluent.

(18) O. Wallach, *Ann. Chem.*, **332**, 305 (1904).

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(21) N. D. Zelinsky and E. M. Tarassowa, *Ann. Chem.*, **508**, 115 (1934).