were done according to the general procedure.

Crossover Experiment of *N,N*-Diethylaniline and *N,N*-Dimethyl-*p*-toluidine. The starting materials (2 mmol each) and water (16.7 mmol) were placed in a 12-mL stainless steel tube reactor and charged with 750 psig of H_2. The reactor was placed in a heater preheated to 425 °C and maintained at temperature for 1 h. After 1.5 min, the temperature of the tube stabilized at 425 °C. The general procedure for reactions was then followed. Gas chromatographic analysis, using authentic *p*-ethyltoluidine as one of the standards, demonstrated no more than 0.5% of *p*-ethyltoluidine was possibly present in the reaction mixture.

Reaction of *N*-Methylaniline. *N*-Methylaniline (17 mmol), water (60 mmol), and 750 psig of H_2 were introduced into a 250-mL Hastelloy C autoclave (Autoclave Engineers Inc., Erie, PA). The autoclave was then heated to 425 °C. Typical heat up times for this system was 1 h, 20 min. The reaction was run for 2 h, and the autoclave cooled overnight to room temperature. The workup and analysis were done according to the general procedure.

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Registry No. *N,N*-Dimethylaniline, 121-69-7; *N,N*-diethylaniline, 91-66-7; *N,N*-dimethyl-*o*-toluidine, 609-72-3; *N,N*-dimethyl-*m*-toluidine, 121-72-2; *N,N*-dimethyl-*p*-toluidine, 99-97-8; nitrogen, 7727-37-9.

A Convenient Synthesis of Dimethyl [(Alkylthio)methyl]phosphonates and Dimethyl [(Arylthio)methyl]phosphonates

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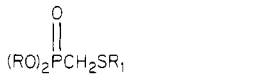
Dialkyl [(alkylthio)methyl]phosphonates **1a** and **1b** and dialkyl [(arylthio)methyl]phosphonates **1c** are useful reagents in organic synthesis. For example, **1a** and **1c**



1a, R_1 = alkyl
1b, R_1 = allyl
1c, R_1 = aryl

have been used as acyl anion equivalents to convert carbonyl compounds into vinyl sulfides that can be hydrolyzed to ketones and aldehydes.[1] Dialkyl [(allylthio)methyl]phosphonates such as **1b** have been used by Corey and Shulman to prepare allyl vinyl sulfides that have been used as substrates in the thio-Claisen rearrangement.[2]

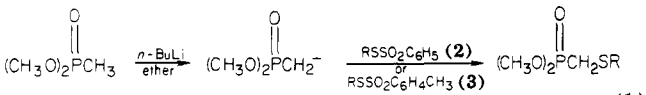
Several methods now exist for the synthesis of these (thiomethyl)phosphonate reagents.[1a,3] Unfortunately, none of these methods can be conveniently used to prepare all of the phosphonates **1a**–**1c**. The most well-known and widely used method to prepare phosphonates, the Arbuzov reaction of trialkyl phosphites with halides, requires the availability of a variety of chloromethyl alkyl (or aryl) sulfides in this case, and many α-halo sulfides are not readily available.[4] We report herein a general method to prepare a variety of phosphonate reagents **1** in moderate to good yield. This new method is especially applicable to the synthesis of various dimethyl [(*allyl*thio)methyl]-phosphonates **1b** that presently cannot be prepared in good yield by any other route.[6]

Table I. Conversion of Thiosulfonates 2 ($RSSO_2C_6H_5$) or 3 ($RSSO_2C_6H_4CH_3$) to Thiomethylphosphonates 4 ($(CH_3O)_2POCH_2SR$)

R	starting material	product	procedure[a]	% yield[b]
$CH_2CH=CH_2$	2a	4a	A	70
$CH_2C(CH_3)=CH_2$	2b	4b	A	63
$CH_2C(Cl)=CH_2$	2c	4c	A	50
$CH_2CH=CHCH_3$	2d	4d	A	55
CH_3	2e	4e	B	40
C_6H_5	2f	4f	B	70
$CH_2CH=CH_2$	3a	4a	A	63

[a] Procedures A and B are detailed in the Experimental Section. [b] All yields refer to isolated products purified by distillation or column chromatography.

The new approach to phosphonates **1** involves sulfenylation of dimethyl α-lithiomethylphosphonate with alkyl and aryl benzenethiosulfonates **2** or alkyl *p*-toluenethiosulfonates **3** (eq 1). The general procedure involves sequential treatment of commercially available dimethyl methylphosphonate with *n*-butyllithium at −78 °C in ether followed by **2** or **3**. The desired phosphonate **4** was isolated by an extraction procedure and purified by distillation or column chromatography. Using this procedure we have prepared a variety of phosphonates in moderate to good yield (Table I). The needed starting materials **2** and **3** are readily available in good yield by use of known methodology.[7]



4 (1)

Two comments should be made on this procedure. First, ether is a superior solvent to tetrahydrofuran in this sulfenylation reaction. With tetrahydrofuran as solvent, phosphonate **2a** was prepared in only 36% yield when all other experimental variables were held constant. Secondly, two different procedures were used to generate the desired phosphonates **4**. It was found that the yields of phosphonates that contained R = an allylic group (**4a**–**4d**) were highest when a slight excess of the dimethyl α-lithiomethylphosphonate was added to a solution of the alkyl benzenethiosulfonate (procedure A). In contrast, to obtain good yields of **4e** and **4f**, the alkyl (or aryl) benzenethiosulfonate was added to excess dimethyl α-lithiomethylphosphonate (procedure B).

The present method makes readily available a variety of thiomethylphosphonate reagents that have not previ-

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(2) E. J. Corey and J. I. Shulman, *J. Am. Chem. Soc.*, **92**, 5522 (1970).

(3) (a) B. A. Arbuzov and N. P. Bogonostseva, *Zh. Obshch. Khim.*, **26**, 2419 (1956); **27**, 2360 (1957); (b) D. L. Comins, A. F. Jacobine, J. L. Marshall, and M. M. Turnbull, *Synthesis*, 309 (1978); (c) M. Mikolajczyk, S. Grzejszczak, A. Chefczynska, and A. Zatorski, *J. Org. Chem.*, **44**, 2967 (1979); (d) M. Mikolajczyk, P. Balczewsk, and S. Grzejszczak, *Synthesis*, 127 (1980).

(4) Several chloromethyl alkyl sulfides have been made by reaction of a mercaptan with gaseous HCl and formaldehyde (ref 5). Unfortunately, the reaction is inconvenient to carry out on a large scale and many α-chloro sulfides can be prepared in only moderate yields.

(5) L. A. Walter, L. H. Goodson, and R. J. Fosbinder, *J. Am. Chem. Soc.*, **67**, 655 (1945).

(6) Diethyl[(allylthio)methyl]phosphonate is the only known thiomethylphosphonate containing an *allylic* group. It has been prepared in two steps from allyl mercaptan in 38% yield: J. I. Shulman, Ph.D. Thesis, Harvard University, Cambridge, ref 2.

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ously been described. Most especially it allows for the convenient synthesis of phosphonate reagents **4a–4d** that can be used to prepare a variety of allyl vinyl sulfides.

Experimental Section

General Methods. ^{1}H NMR spectra were recorded on a Varian T-60 spectrometer. IR spectra were recorded with either a Perkin-Elmer 298 or 457 spectrometer. Alkyl benzenethiosulfonates **4a–4e** were prepared from an alkyl halide and sodium benzenethiosulfonate[7b] in 60–75% yield as previously described.[7] Allyl *p*-toluenethiosulfonate was prepared from allyl chloride and sodium *p*-toluenethiosulfonate in an analogous fashion. Phenyl benzenethiosulfonate was prepared by known methods.[8]

General Procedure A. To a stirred solution of dimethyl methylphosphonate (1.4 mmol) in 3 mL of anhydrous ether at −65 °C under argon was added *n*-butyllithium (1.4 mmol) dropwise. The milky white reaction mixture was stirred 10 min at −65 °C, cooled to −78 °C, and then transferred via syringe to a second flask containing the alkyl benzenethiosulfonate **2** (1 mmol) in 2 mL of ether at −78 °C. The anion was added to **2** over a 5-min interval. The reaction mixture was stirred 10 min at −78 °C and then the reaction was quenched by addition of 1 mL of methanol. The crude phosphonate **4** was isolated by an extractive workup with ether-saturated ammonium chloride solution. Crude products were purified by silica gel column chromatography or distillation at reduced pressure.

General Procedure B. To a stirred solution of dimethyl methylphosphonate (5.0 mmol) in 5 mL of anhydrous ether at −65 °C under argon was added *n*-butyllithium (5.0 mmol) dropwise. The milky white reaction mixture was stirred 10 min at −65 °C and then cooled to −78 °C, and the alkyl or aryl benzenethiosulfonate **2** (1.0 mmol) was added in 1 mL of ether dropwise over 5 min. After the mixture was stirred 10 min at −78 °C, the reaction was quenched with 1 mL of methanol and the phosphonate **4** was isolated and purified as in procedure A.

Dimethyl [(allylthio)methyl]phosphonate (4a): colorless liquid; ^{1}H NMR ($CDCl_3$) δ 2.75 (d, 2 H, PCH_2S, J = 13 Hz), 3.38 (d, 2 H, SCH_2, J = 7 Hz), 3.88 (d, 6 H, CH_3, J = 11 Hz), 5.05–6.20 (m, 3 H, $CH{=}CH_2$); IR (film) 3040, 2920, 2820, 1610, 1430, 1240, 1170, 1030, 910, 870, 830, 810 cm^{-1}; mass spectrum, m/e 196 (M^+), 155, 124 (base), 94, 79; exact mass calcd for $C_6H_{13}O_3PS$ 196.0323, found 196.0337.

Dimethyl [(methallylthio)methyl]phosphonate (4b): colorless liquid; ^{1}H NMR ($CDCl_3$) δ 1.85 (br s, 3 H, CH_3), 2.70 (d, 2 H, PCH_2S, J = 14 Hz), 3.32 (br s, 2 H, SCH_2), 3.85 (d, 6 H, CH_3, J = 11 Hz), 4.95 (br s, 2 H, $=CH_2$); IR (film) 3040, 2920, 2880, 2820, 1625, 1435, 1360, 1240, 1170, 1020, 890, 830, 810 cm^{-1}; mass spectrum, m/e 210 (M^+), 155, 124 (base), 109, 94, 79; exact mass calcd for $C_7H_{15}O_3PS$ 210.0480, found 210.0457.

Dimethyl [[(2-chloroallyl)thio]methyl]phosphonate (4c): pale-yellow liquid; ^{1}H NMR ($CDCl_3$) δ 2.70 (d, 2 H, PCH_2S, J = 13 Hz), 3.63 (s, 2 H, SCH_2), 3.80 (d, 6 H, CH_3, J = 11 Hz), 5.27–5.58 (m, 2 H, $=CH_2$); IR (film) 2950, 2850, 1625, 1255, 1055, 1030, 840, 815, 620 cm^{-1}; mass spectrum, m/e 230 (M^+), 232 (M^+ + 2), 195, 124 (base), 109, 94, 79, 58, 45, 43.

Dimethyl [(crotylthio)methyl]phosphonate (4d): colorless liquid; ^{1}H NMR ($CDCl_3$) δ 1.75 (d, 3 H, CH_3, J = 4 Hz), 2.70 (d, 2 H, PCH_2S, J = 14 Hz), 3.32 (d, 2 H, SCH_2, J = 6 Hz), 3.85 (d, 6 H, CH_3, J = 11 Hz), 5.50–5.75 (m, 2 H, $CH{=}CH$); IR (film) 3010, 2975, 2850, 1650, 1450, 1370, 1250, 1180, 1050, 1025, 835, 820 cm^{-1}; mass spectrum, m/e 210 (M^+), 156, 124 (base), 110, 94, 79, 55; exact mass calcd for $C_7H_{15}O_3PS$ 210.0479, found 210.0482.

Dimethyl [(methylthio)methyl]phosphonate (4e): colorless liquid; ^{1}H NMR ($CDCl_3$) δ 2.35 (s, 3 H, CH_3), 2.78 (d, 2 H, PCH_2S, J = 12 Hz), 3.82 (d, 6 H, CH_3, J = 11 Hz); IR (film) 2950, 2850, 1700, 1630, 1450, 1370 cm^{-1}; mass spectrum, m/e 170 (M^+), 124 (base), 109, 94, 79, 61, 45.

Dimethyl [(phenylthio)methyl]phosphonate (4f): colorless liquid; ^{1}H NMR ($CDCl_3$) δ 3.23 (d, 2 H, PCH_2S, J = 14 Hz), 3.82 (d, 6 H, CH_3, J = 12 Hz), 7.14–7.70 (m, 5 H, C_6H_5); IR (film) 3050, 2950, 2840, 1580, 1480, 1435, 1250, 1180, 1050, 1025, 840, 815, 740, 690 cm^{-1}; mass spectrum, m/e 232 (M^+), 231 (base), 123, 121, 110, 109, 93, 77; exact mass calcd for $C_9H_{12}O_3PS$ (M^+ − H) 231.0245, found 231.0233.

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Registry No. 2a, 69530-64-9; **2b**, 69530-65-0; **2c**, 69567-85-7; **2d**, 69530-66-1; **2e**, 1125-25-3; **2f**, 1212-08-4; **3a**, 52713-51-6; **4a**, 84836-03-3; **4b**, 84836-04-4; **4c**, 84836-05-5; **4d**, 84836-06-6; **4e**, 25508-32-1; **4f**, 70369-42-5; $(CH_3O)_2P(O)CH_3$, 756-79-6.

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(8) B. M. Trost and G. S. Massiot, *J. Am. Chem. Soc.*, **99**, 4405 (1977).

HMPA Dehydro Dimer: A Remarkable Complexing Agent of Lithium Cation

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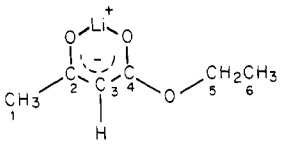
Lithiated enolates are particularly stable. Thus, the Li enolate of ethyl acetoacetate **1** does not react with diethyl



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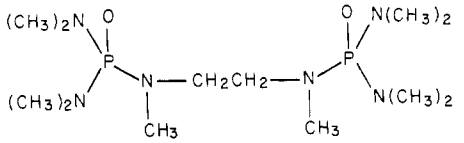

2

sulfate at room temperature while the K enolate does.[2] However, in the presence of solvents capable of coordinating cations such as HMPA[2,3] or of macrocyclic coordinates,[4] the anion–cation interaction is weakened so that alkylation does take place.

We decided to examine to what extent HMPA dehydro dimer ("diHMPA") **2**, obtained by radical coupling of HMPA,[5] should present stronger complexing properties of alkali cations, due to chelate formation. In this paper, we examine the behavior of **1**, as well as the K analogue of **1**, in the presence of "diHMPA" (**2**).

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0022-3263/83/1948-1111$01.50/0