be used to prepare 3-alkenylfurans, in which the procedures for generating the required cuprate reagents are more complex. The alkenyllithium compounds necessary to produce the required cuprates were obtained via the corresponding alkenyltriphenyltin compounds.[14-16] After a model study with lithium diallylcuprate proved the feasibility of the approach [3-(1-butenyl)furan showed m/e 122 (M[+]), ^{1}H NMR δ 7.15 (m, 1 H), 7.0 (m, 1 H), 6.1 (m, 1 H), 5.5–5.65 (br m, 1 H), 4.78 (d, 1 H, J = 16 Hz), 4.75 (d, 1 H, J = 11 Hz), 2.2–2.5 (m, 4 H)], perillene was obtained in modest yield, using the previously unreported lithium bis(3-methyl-2-butenyl)cuprate.

Experimental Section

Melting points were obtained on a Thomas-Hoover apparatus and are uncorrected. NMR spectra (CDCl$_3$) were obtained on Varian T-60 and FT-80 spectrometers. Microanalyses were performed on a Hewlett-Packard CHN microanalyzer at the University of Kansas. Electron-impact mass spectrometry was carried out at 70 eV on a Nermag R-10-10 quadripole mass spectrometer.

3-Ethylfuran (2). 3-Furanmethanol (4.9 g, 0.05 mol) and p-toluenesulfonyl chloride (10.45 g, 0.055 mol) were dissolved in 125 mL of ether, and the solution was cooled to −20 °C. Freshly powdered sodium hydroxide (7.5 g, 0.1875 mol) was added portionwise to the solution over a 2-h period. The mixture was then stirred for 1 h and poured into ice–water. The ether layer was separated and washed twice more with cold water. The ether solution was then dried (Na$_2$SO$_4$) and filtered in the cold. Lithium dimethylcuprate was prepared by the method of Johnson[17] from 27.5 g (0.14 mol) of CuI and 200 mL of a 1.5 M solution of methyllithium. After addition of the methyllithium was complete, the mixture was stirred at −20 °C for 30 min, the ether solution of the 3-[[(p-tolylsulfonyl)oxy]methyl]furan (1) added dropwise, and the mixture stirred for 6 h at −20 °C. Saturated aqueous ammonium chloride (200 mL) was then added below 0 °C and the mixture stirred for 10 min. The ether solution was washed with saturated NaCl (2 × 100 mL). The ether was removed by distillation through a 6-in. Vigreux column. The crude product was distilled (25 mm, room temperature) in a Kugelrohr apparatus to yield 3.0 g of colorless liquid that contained 5% ether (60% yield). Pure 3-ethylfuran (1.87 g) was obtained by distillation in a spinning-band column, bp 92 °C. The compound was shown to be homogeneous by GLC (1% OV-17 column), NMR, and mass spectroscopy. 2: mass spectrum, m/e 96 (M[+]), 81 (M[+] − CH$_3$), 67 (M[+] − C$_2$H$_5$), 54 (M[+] − C$_2$H$_2$O); ^{1}H NMR δ 7.2 (m, 1 H), 7.1 (m, 1 H), 6.2 (m, 1 H), 2.4 (q, 2 H), 1.2 (t, 3 H, J = 8 Hz). Anal. Calcd for C$_6$H$_8$O: C, 74.97; H, 8.39. Found: C, 74.75; H, 8.12.

3-Pentylfuran (3). This was prepared as shown above, except that the addition of the cuprate was carried out at −50 °C, and the mixture was stirred for 4 h. Spinning-band distillation yielded first the coupling product octane (bp 125 °C) and then 3.1 g (45%) of 3-pentylfuran: bp 160 °C (lit.[18] bp 160 °C); mass spectrum,

m/e 138 (M[+]), 95 (M[+] − C$_3$H$_7$), 82 (M[+] − C$_4$H$_8$), 81 (M[+] − C$_4$H$_9$); ^{1}H NMR δ 7.2 (m, 1 H), 7.1 (m, 1 H), 6.2 (m, 1 H), 2.3 (t, 2 H, J = 6 Hz), 1.8–1.2 (m, 6 H), 0.9 (t, 3 H, J = 6 Hz). Anal. Calcd for C$_9$H$_{14}$O: C, 78.21; H, 10.21. Found: C, 78.30; H, 10.40.

(3-Methyl-2-butenyl)triphenyltin. A small amount of 1-bromo-3-methyl-2-butene[19] and iodomethane was added to a suspension of Mg (10 g, 0.42 mol) in ether (120 mL). After reaction was initiated, the mixture was heated to reflux and a solution of the remainder of 29.8 g (0.2 mol) 1-bromo-3-methyl-2-butene and triphenyltin chloride (50 g, 0.13 mol) in tetrahydrofuran (120 mL) was added over 4 h, the temperature being allowed to rise to 50 °C. Benzene (120 mL) was then added and the mixture heated under reflux overnight. The cooled mixture was then treated with saturated aqueous ammonium chloride (100 mL), the liquid was decanted, and the salts were washed twice with ether. The combined organic solutions were dried (Na$_2$SO$_4$) and the solvents evaporated in vacuo to yield the solid product. This was recrystallized from petroleum ether to afford colorless crystals (39.7 g, 73%): mp 73–74 °C; ^{1}H NMR δ 7.3 (m, 15 H), 5.3 (t, 1 H), 2.3 (d, 2 H, J = 8 Hz), 1.6 (s, 3 H), 1.4 (s, 3 H). Anal. Calcd for C$_{23}$H$_{24}$Sn: C, 65.91; H, 5.77. Found: C, 66.08; H, 5.61.

3-(4-Methyl-3-pentenyl)furan (Perillene, 4). (3-Methyl-2-butenyl)triphenyltin (25.1 g, 0.06 mol) was dissolved in ether (100 mL). Phenyllithium (42 mL of 1.6 M solution, 0.067 mol) was added slowly with stirring. After 1 h of stirring at 25 °C, the white precipitate was removed by centrifugation and the supernatant used for further reaction. This was slowly added at −78 °C to a suspension of cuprous iodide (2.66 g, 0.014 mol) in ether. This red mixture was stirred for 30 min, after which a solution of 3-[[(p-tolylsulfonyl)oxy]methyl]furan, prepared from 0.98 g of 3-furanmethanol as described under 3-ethylfuran above, was slowly added at −78 °C, and the mixture was stirred for 4 h at −78 °C. The mixture was treated with saturated aqueous ammonium chloride (50 mL) at 0 °C, washed with saturated NaCl (2 × 25 mL), and dried (Na$_2$SO$_4$), and the solvents were evaporated. This material was purified by column chromatography on silica gel followed by medium-pressure chromatography, using hexane as eluant. A colorless liquid, 0.23 g (15%), was obtained: mass spectrum, m/e 150 (M[+]), 135 (M[+] − CH$_3$), 81 (M[+] − C$_5$H$_9$), 69 (M[+] − C$_5$H$_5$O); ^{1}H NMR δ 7.2 (m, 1 H), 7.1 (m, 1 H), 6.2 (m, 1 H), 5.1 (t, 1 H), 2.5–2.0 (m, 4 H), 1.8 (s, 3 H), 1.6 (s, 3 H). Anal. Calcd for C$_{10}$H$_{14}$O: C, 79.96; H, 9.39. Found: C, 79.68; H, 9.19.

Registry No. 1, 84802-88-0; 2, 67363-95-5; 3, 6177-84-0; 4, 539-52-6; (CH$_3$)$_2$CuLi, 15681-48-8; (C$_4$H$_9$)$_2$CuLi, 24406-16-4; ((CH$_3$)$_2$C=CHCH$_2$)$_2$CuLi, 84809-72-3; 3-furanmethanol, 4412-91-3; 1-bromo-3-methyl-2-butene, 870-63-3; (3-methyl-2-butenyl)triphenyltin, 65733-49-5.

(14) D. Seyferth and M. A. Weiner, *J. Org. Chem.*, **26**, 4797 (1961).
(15) G. M. Whitesides, W. F. Fischer, Jr., J. S. Filippo, Jr., R. W. Bashe, and H. O. House, *J. Am. Chem. Soc.*, **91**, 4871 (1969).
(16) J. Fried, H. C. Lin, J. C. Sih, P. Dalven, and G. F. Cooper, *J. Am. Chem. Soc.*, **94**, 4342 (1972).
(17) C. R. Johnson and G. A. Dutra, *J. Am. Chem. Soc.*, **95**, 7777 (1973).
(18) D. L. Dare, I. D. Entwistle, and R. A. W. Johnston, *J. Chem. Soc., Perkin Trans. 1*, 1130 (1973).
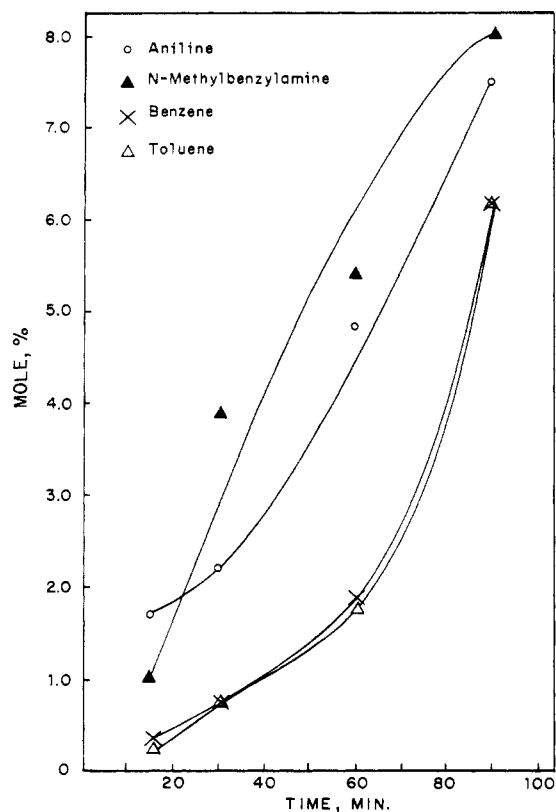
(19) H. Staudinger, W. Kreis, and W. Schilt, *Helv. Chem. Acta*, **5**, 743 (1922).

Denitrogenation. Novel High-Temperature Reactions of *N,N*-Dimethylaniline

Virgil I. Stenberg,* Vijay R. Srinivas, Richard J. Baltisberger, and N. F. Woolsey

Department of Chemistry, University of North Dakota, Grand Forks, North Dakota 58202

Introduction

Nitrogen removal studies are important for denitrogenation in petroleum and coal conversion technologies. *N,N*-Dimethylaniline was selected as an appropriate model for denitrogenation of aniline, pentylamine, indole, and carbazole moieties present in coal and petroleum because it contains two distinct C–N bond types. Heterocyclic

Figure 1.

compounds were found to be the major nitrogen-containing species in coal-derived products.[1-5] Small amounts of nonheterocyclic compounds such as amines and nitriles are also present.

Results

When N,N-dimethylaniline was heated with hydrogen at 425 °C for 90 min, benzene (6%), toluene (6%), aniline (7%), N-methylaniline (trace), and N-methylbenzylamine (8%) were formed as products. N-Methylaniline yielded aniline under similar conditions.

N-Methylbenzylamine is formed as an intermediate in the formation of benzene and toluene under the reaction conditions. Figure 1 illustrates the N,N-dimethylaniline reaction progress as a function of time and shows evidence for the transient presence of N-methylbenzylamine. N-Methylbenzylamine, under similar conditions, decomposes to form benzene and toluene. Figure 1 shows that these two products were formed during the latter stages of the reaction at the expense of N-methylbenzylamine.

The rearrangement of N,N-dimethylaniline into N-methylbenzylamine occurred intramolecularly. Similar reaction conditions were applied to N,N-diethylaniline, N,N-dimethyl-o-toluidine, N,N-dimethyl-m-toluidine, and N,N-dimethyl-p-toluidine. These amines yielded ethylbenzene, o-xylene, m-xylene, and p-xylene, respectively, with the exclusion of other isomers. In crossover experiments, a 1:1 mixture of N,N-dimethyl-p-toluidine and N,N-diethylaniline was allowed to react with H_2 at 425 °C for 1 h. Analysis of the product mixture by GLC indicated only trace quantities of p-ethyltoluene, a product that

Scheme I
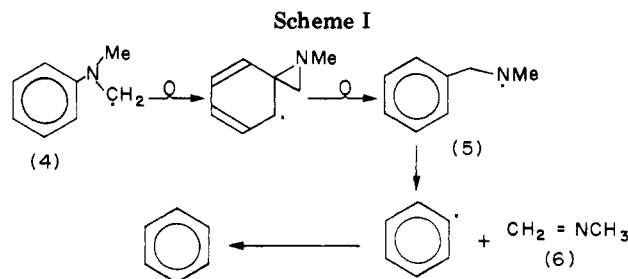
would be formed if the process were intermolecular.

Discussion

During studies on new methods of nitrogen removal from organic compounds, the 1,2-phenyl migration from nitrogen to carbon was observed. This rearrangement is related to the 1,2-phenyl migration that occurs when the neophyl radical (1) is converted into the 1-phenyl-2-methylprop-2-yl radical (3; eq 1).[6] From this and related
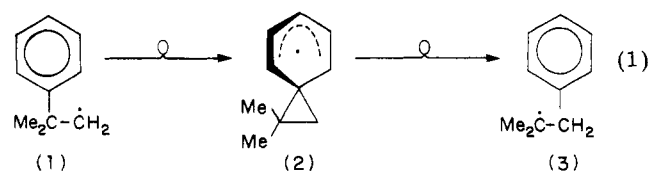
rearrangements, evidence exists of their intramolecular nature.[7] The spiro[2.5]octadienyl radical 2 has been implicated in the 2-phenylethyl rearrangement[8] as a short-lived intermediate. Between 366 and 400 °C, 1,2-diphenylethyl radical, readily formed from bibenzyl, was found to rearrange reversibly to give the 1,1-diphenylethyl radical.[9] Recently, the 1,2-migration of phenyl from oxygen to carbon in a free radical was reported.[10] At 400 °C, phenetole-β-^{14}C in tetralin yielded toluene containing a trace of ^{14}C, while the ethylbenzene formed was labeled. Crossover experiments performed with phenetole-α-^{14}C and ethyl p-tolyl ether confirmed the process to be an intramolecular one. In an attempt to find a neophyl-like rearrangement from nitrogen to carbon,[11] the peroxide initiated decarboxylation of 9-carbazolylacetaldehyde was studied at 140–170 °C. No phenyl migration was observed, and this was attributed to the inherent stability of the carbazole moiety.

On the basis of the products formed, the high-temperature reduction reaction of N,N-dimethylaniline appears to proceed down two reaction pathways: one to give rise to N-methylaniline and aniline, while the other along a competing route to give N-methylbenzylamine and its degradation products, benzene and toluene. Both observations are based on the data presented in Figure 1. N-Methylaniline and aniline are formed by reductive thermolysis of N,N-dimethylaniline followed by H abstraction.

N-Methylbenzylamine is formed from N,N-dimethylaniline via an intramolecular 1,2-phenyl shift from nitrogen

(1) Bratton, A. C.; Bailey, J. R. *J. Am. Chem. Soc.* **1937**, *59*, 175.

(2) Nixon, A. C.; Thorpe, R. E. *J. Chem. Eng. Data* **1962**, *7*, 429.

(3) Jewell, D. M.; Hartung, G. K. *J. Chem. Eng. Data* **1964**, *9*, 297.

(4) Snyder, L. R. *Am. Chem. Soc., Div. Pet. Chem. Prepr.* **1970**, *15*(2), C44.

(5) Brandenburg, C. F.; Latham, D. R. *J. Chem. Eng. Data* **1968**, *13*, 391.

(6) Urry, W. H.; Kharasch, M. S. *J. Am. Chem. Soc.* **1944**, *66*, 1438.

(7) (a) Wilt, J. W. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, Chapter 8. (b) Beckwith, A. L. J.; Ingold, K. U. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, in press.

(8) Effio, A.; Griller, D.; Ingold, K. U.; Scaiano, J. C.; Sheng, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 6063.

(9) Poutsma, M. L. *Fuel* **1980**, *59*, 335.

(10) Collins, C. J.; Roark, W. J.; Raaen, V. F.; Benjamin, B. M. *J. Am. Chem. Soc.* **1979**, *101*, 1877.

(11) Vittimberga, B. M.; Herz, M. L. *J. Org. Chem.* **1970**, *35*, 3694.

Table I. Effect of Temperature on the
N,N-Dimethylaniline Reaction

temp, °C	products, mol %				
	PhH	PhCH₃	PhNH₂	PhCH₂NHCH₃	PhN(CH₃)₂
350	0	0	0	0	88
400	Tr	Tr	0.5	0.8	85.8
425	2.2	2.1	4.1	5.9	67.9
450	16.0	10.6	11.5	7.2	40.9

to carbon and readily cleaves under the conditions of the reaction to give benzene and toluene. The absence of the formation of mixed xylenes in the reactions of *N,N*-dimethyl-*p*-toluidine, *N,N*-dimethyl-*m*-toluidine, and *N,N*-dimethyl-*o*-toluidine followed by the absence of *p*-ethyltoluene in crossover experiments with *N,N*-diethylaniline and *N,N*-dimethyl-*p*-toluidine confirms the intramolecular, ipso nature of the process.

Scheme I outlines plausible mechanistic rationalizations consistent with the observed data. At 425 °C, it is reasonable to assume radical type reactions are occurring. A molecular fragment of the same mass as **6** is observed in the mass spectrum of *N*-methylbenzylamine.[12] This is indirect evidence for its formation in the *N,N*-dimethylaniline reaction mixture and suggests the route of benzene formation in the reaction solution.

The neophyl rearrangement is expected to be slightly exothermic due to a relief of steric compression and a primary radical conversion into a tertiary one in the course of the reaction. When the radical **4** rearranges into **5**, there is some relief of steric strain and the rearrangement involves little energy change. The bond energy of the phenyl–methyl bond is 100 kcal/mol and that of the phenyl–nitrogen about 104 kcal/mol.[13] The temperature dependence of the *N,N*-dimethylaniline–H₂ reaction as illustrated in Table I is more attributable to the rate of radical formation than the activation energy of rearrangement. However, as the temperature is increased, the rearrangement products, toluene and benzene, appear to better complete with demethylation.

In regard to denitrogenation of heavy crude oils and coal-derived liquids, the data herein demonstrate the rupture of the aromatic–nitrogen bond without first reducing the aromatic ring contrary some current thinking.[14,15]

Experimental Section

¹H NMR and ¹³C NMR spectra were recorded on a Varian Associates EM-390 and JEOL JNM-FX-60 spectrometer, respectively, with CDCl₃ as solvent and tetramethylsilane as internal standard; chemical shifts are given in δ units and refer to the center of the signal: s = singlet, d = doublet, and m = multiplet. The mass spectra were recorded on a Du Pont 21-491 mass spectrometer or GC-MS Hewlett Packard 5985B. Product analysis was done with a Varian Aerograph gas chromatograph Model 2100 equipped with a 0.64 cm × 183 cm OV-17 column. The temperature of the column was programmed to increase at a rate of 10 °C/min from 30 to 250 °C. Product identification was done by collection on a Varian Associates Model 90-P Aerograph gas chromatograph equipped with a 0.64 cm × 305 cm Carbowax column and obtainment of their mass spectra and ¹H NMR.

(12) Golden, D. M.; Solly, R. K.; Gac, N. A.; Benson, S. W. *J. Am. Chem. Soc.* **1972**, *94*, 363.

(13) Weast, R. C., Ed.; "Handbook of Chemistry and Physics", 55th ed.; CRC Press: Cleveland, OH, 1974-1975; p F-220.

(14) Katzer, J. R.; Gates, B. C.; Olson, J. H.; Kwart, H.; Stiles, A. B., Ninth Quarterly Report, prepared for Fossil Energy, May 1978, Department of Energy, Washington, DC.

(15) Katzer, J. R.; Gates, B. C.; Kwart, H.; Olson, J. H.; Stiles, A. B., Tenth Quarterly Report, prepared for Fossil Energy, Jan 1978, Department of Energy, Washington, DC.

Structural proof of compounds from their spectra were deduced from comparisons to spectra of authentic pure compounds.

Materials. The following compounds were used as starting materials in the autoclave reactions: *N,N*-dimethylaniline, *N,N*-diethylaniline, *N,N*-dimethyl-*o*-toluidine (Eastman); *N,N*-dimethyl-*p*-toluidine, *N,N*-dimethyl-*m*-toluidine, *N*-methylbenzylamine, and *N*-methylaniline (Pfaltz and Bauer).

General Procedure for Reactions. The starting material (4.5 mmol) and water (16.7 mmol) were placed in a 12-mL stainless steel tube reactor[16] equipped with a high-pressure valve, and 750 psig of H₂ gas was introduced into the reactor. The reactor was placed in a heater preheated to 450 °C. After 2 min the temperature of the tube stabilized at 425 °C. The shaker was then turned on for the designated length of time. The times cited in Figure 1 refer to the time at the designated temperature. The reactor was then taken out of the heater, plunged into water, and cooled to -78 °C by use of a dry ice–acetone bath. The cool down time was 0.5 min. After the gases were vented out, the reactor was then dismantled, a specific weight of an internal standard was added, and the mixture was taken up in ether. The ether solution of the products was directly used for product analysis. When the product to be collected by preparative gas chromatography was a neutral compound, the ether solution of the product mixture was first extracted with hydrochloric acid to remove all basic compounds.

Time Study of the *N,N*-Dimethylaniline Reaction. The 12-mL stainless steel microreactor was used.[16] The reactor was charged with 0.5 g of *N,N*-dimethylaniline and 750 psig of H₂. The reaction was kept at temperature for the designated times. The internal standard was diphenylmethane.

Analysis. Gas chromatographic analyses were done with (i) 3% OV-17 on Suppelcoport A (column A), (ii) 7% Carbowax 20M on Chromosorb W (column B), and (iii) 7% Carbowax 20M and 4% KOH on Chromosorb W (column C).

Product Identification. *o*-Xylene was identified by its GLC spiked with an authentic sample on columns A and B; its mass spectrum and ¹H NMR compared favorably to that reported.[17] *m*-Xylene and *p*-xylene were identified by their GLC retention times and spiking with authentic samples. Aniline was identified by its GLC spike, retention time on columns A and C, and its ¹H NMR and ¹³C NMR. Its mass spectrum was comparable to those reported for aniline[17] and an authentic sample. *N*-Methylaniline was identified by its GLC retention time on column C as compared with that of an authentic sample. Its mass and ¹H NMR spectra were comparable to those reported for *N*-methylaniline[17] and an authentic sample. *N*-Methylbenzylamine was identified by its GLC retention time on columns A and B as compared to that of an authentic sample. Its mass spectrum was comparable to that reported.[17] Ethylbenzene was identified by retention time on column A and its mass spectrum was comparable to that reported.[17] Benzene was identified by its GLC spike retention time on columns A and C; its mass spectrum was comparable to that of an authentic sample. Toluene was identified by its GLC spike retention time on columns A and C; its mass spectrum was comparable to that reported.[17]

Temperature Effect. *N,N*-Dimethylaniline (0.0042 mol), 0.0167 mol of H₂O, and 750 psi of H₂ were held for 1 h at the desired temperatures in the 12-mL tube reactors according to the general procedure.

Reactor Cleaning Procedure. After reaction, the tubes were rinsed with water, treated with concentrated HNO₃ for 30 min, rinsed with water, scrubbed with a wire brush, treated with aqueous NaHCO₃ for 30 min, rinsed with water and then with acetone, and dried at 110 °C. The valves were rinsed several times with acetone.

Reduction of *N*-Methylbenzylamine and *N,N*-Diethylaniline. *N*-Methylbenzylamine (4 mmol), 16.7 mmol of H₂O, and 750 psig of H₂ were put in the 12-mL stainless steel autoclave and heated to 425 °C for 32 min. The reaction with *N,N*-diethylaniline was done similarly but for 1 h. The workup and product analysis

(16) Stenberg, V. I.; VanBuren, R. L. *Chem. Ind.* (*London*) **1980**, *14*, 569.

(17) Grasselli, J. G.; Ritchey, W. M. "Atlas of Spectral Data and Physical Constants for Organic Compounds", 2nd ed.; CRC Press: Cleveland, OH, 1975; Vol. 1–5.

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.

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

Janice Gorzynski Smith,* M. S. Finck, B. D. Kontoleon, M. A. Trecoske, L. A. Giordano, and L. A. Renzulli

Carr Laboratory, Mount Holyoke College, South Hadley, Massachusetts 01075

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

$$\underset{\substack{|| \\ (RO)_2PCH_2SR_1}}{O}$$
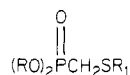
1a, R_1 = alkyl
1b, R_1 = allyl
1c, R_1 = aryl

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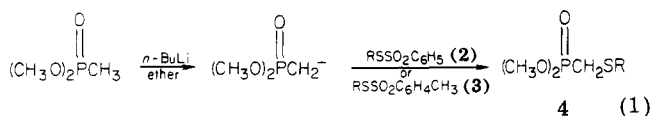
Table I. Conversion of Thiosulfonates 2 ($RSSO_2C_6H_5$) or 3 ($RSSO_2C_6H_4CH_3$) to Thiomethylphosphonates 4 (($CH_3O)_2POCH_2SR$)

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.

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 [(allylthio)methyl]phosphonates **1b** that presently cannot be prepared in good yield by any other route.[6]

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 se-

$$(CH_3O)_2PCH_3 \xrightarrow[\text{ether}]{n\text{-BuLi}} (CH_3O)_2PCH_2^- \xrightarrow[\substack{\text{RSSO}_2C_6H_5 \,(2) \\ \text{or} \\ \text{RSSO}_2C_6H_4CH_3 \,(3)}]{} (CH_3O)_2PCH_2SR$$

$$\mathbf{4} \qquad (1)$$

quential 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]

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-

(1) (a) M. Green, *J. Chem. Soc.*, 1324 (1963); (b) M. Mikolajczyk, S. Grzejszczak, W. Midura, and A. Zatorski, *Synthesis*, 278 (1975); (c) I. Shahak and J. Almog, *Synthesis*, 145 (1976); (d) E. J. Corey and J. I. Shulman, *J. Org. Chem.*, **35**, 777 (1970).
(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.