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Synthesis of α-Alkoxyacrylonitriles Using Substituted Diethyl Cyanomethylphosphonates

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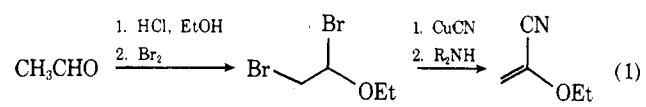
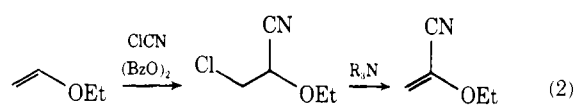
The synthesis of the thiophenoxy, methoxy, and *tert*-butoxy derivatives of diethyl cyanomethylphosphonates $(EtO)_2POCH(Z)CN$ **3** involved either the phenylsulfenylation of the anion of diethyl cyanomethylphosphonate (**4**) to afford **3a** (Z = SPh), the photolysis of the diazo derivative of **4** in methanol to afford **3b** (Z = OMe), or, preferably, the Arbusov reaction of methoxy- or *tert*-butoxybromoacetonitrile with triethyl phosphite to afford **3b** (Z = OMe) or **3c** (Z = O-*t*-Bu), respectively. The latter two phosphonate reagents **3b** and **3c** serve in the Horner–Emmons modification of the Wittig reaction to provide α-alkoxyacrylonitriles RR'C=C(OR")CN **1** from carbonyl compounds RR'C=O in excellent yield.

In connection with our interest in the chemistry of α,β-unsaturated nitriles,[1] we required a convenient synthesis of α-alkoxy- or α-thioalkoxyacrylonitriles. Cuvigny and Normant[2] have developed a substitution–elimination sequence for the conversion of aldehydes to α-alkoxyacrylonitriles which parallels a synthesis of α-ethoxyacrylonitrile reported earlier by Price[3] (eq 1). A more direct sequence developed by Vasil'eva[4] utilized the free-radical addition of cyanogen chloride to ethyl vinyl ether but suffered from low overall yields of α-ethoxyacrylonitrile (eq 2).

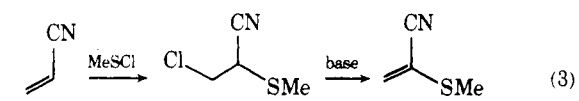


(1)

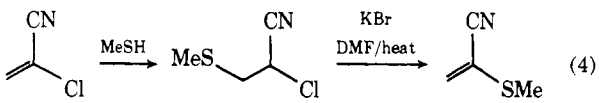


(2)

In contrast to the syntheses of α-alkoxyacrylonitriles in which the cyano group is introduced subsequent to the alkoxy group, the reported approaches to α-thioalkoxyacrylonitriles invert this order for the introduction of cyano and thioether groups. The addition of methylsulfenyl chloride to acrylonitrile and subsequent dehydrochlorination furnished α-thiomethoxyacrylonitrile[5] (eq 3). Alternatively, Gundermann[6] developed an interesting approach in which the 2-chloro-3-thiomethoxynitrile was dehydrochlorinated with concomitant migration of the thioether group to afford α-thiomethoxyacrylonitrile (eq 4).

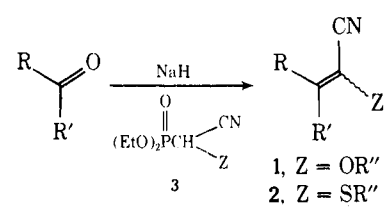


(3)



(4)

To develop a general synthesis of α-alkoxyacrylonitriles **1** and α-thioalkoxyacrylonitriles **2** which would avoid these multistep sequences, we required a Wittig reagent which could introduce the α-alkoxyacrylonitrile or α-thioalkoxyacrylonitrile synthon in a single operation. In particular, we desired the phosphonate Wittig reagents[7] **3** which offer the distinct advantage over phosphorane Wittig reagents of providing water-soluble, phosphate by-products. We now wish to report various synthetic approaches to these phosphonate reagents **3** and their application to the preparation of **1** and **2** (eq 5).

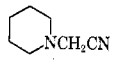


(5)

We have examined three different approaches to the phosphonates **3** (eq 6–8). Initially, we studied the sulfenylation of the anion of diethyl cyanomethylphosphonate (**4**) with phenylsulfenyl chloride and succeeded in obtaining the thiophenoxyphosphonate **3a** as the predominant product (eq 6). Our interest in exploring similarly substituted sulfur derivatives of **4** was dampened by the failure of the anion of **3a** to condense with carbonyl compounds other than nonenolizable aldehydes. For example, although benzaldehyde condensed with the anion of **3a** (1.0 equiv, 10% HMPA–DME, 81 °C, 24 h) to furnish (*E*)- and (*Z*)-2-thiophenoxycinnamonitriles in 68% yield, acetaldehyde failed to provide any of the desired product. The failure of the anion of **3a** to add to the carbonyl group of other aldehydes and ketones was attributed either to the steric bulk of the phosphonate or to the additional thioether stabilization[8] of the anion of **3a** relative to the anion of **4**. We consequently turned to the synthesis of the alkoxy derivatives of **4**.

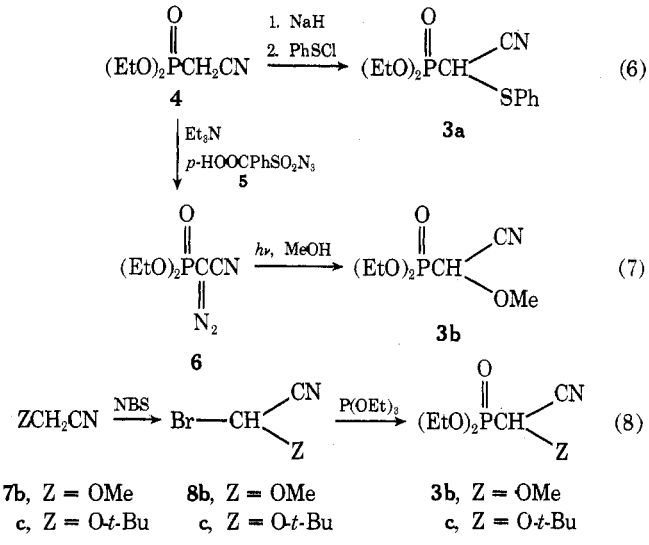
In a second effort to utilize **4** to secure the methoxyphosphonate **3b**, we investigated the reaction of the anion of **4** with *p*-toluenesulfonyl azide[9a] and *p*-carboxybenzenesulfonyl azide[9b] (**5**). Although the infrared spectrum of crude products displayed a signal at 4.74 μ which indicated successful diazo transfer, we were unable to obtain the azophosphonate **6** in

Table I. Substituted Acetonitriles 7

	Acetonitriles 7	Isolated yield, %	Reference to or method of synthesis of 7
a	$MeOC(CH_3)_2OCH_2CN$	57	*b*
b	$MeOCH_2CN$	70–77	*c*
c	$tBuOCH_2CN$	42	*a*
d	$PhCOOCH_2CN$	66	*a*
e	$tBuCOOCH_2CN$	74	*a*
f	$EtOCOOCH_2CN$	48	*a*
g	$EtOCSSCH_2CN$	75	*a*
h	$PhCOSCH_2CN$	66	*a*
i	$MeCOSCH_2CN$	64	*a*
j	$(i\text{-}Pr)_2NCH_2CN$	69	*d*
k		80	*d*

[a] This work. [b] N. B. Lorette and W. L. Howard, *J. Org. Chem.*, **25**, 521 (1960). [c] J. A. Scarrow and C. F. H. Allen, "Organic Syntheses", Collect. Vol. II, Wiley, New York, N.Y., 1943, p 387. [d] D. B. Luten, Jr., *J. Org. Chem.*, **3**, 588 (1939).

yields greater than 30%. We demonstrated, nevertheless, that the photolysis of **6** in methanol provided **3b** (eq 7). The unsatisfactory overall yield of **3b** from **4** led us to examine an alternative approach.



7b, Z = OMe **8b**, Z = OMe **3b**, Z = OMe
c, Z = O-*t*-Bu **c**, Z = O-*t*-Bu **c**, Z = O-*t*-Bu

Dawson and Burger[10] first demonstrated that the Arbusov reaction[11] of chloroacetonitrile and triethyl phosphite would furnish diethyl cyanomethylphosphonate (**4**). To utilize this same approach in the synthesis of phosphonates **3**, we required the substituted haloacetonitriles **8**. The NBS bromination of methoxyacetonitrile (**7b**) or *tert*-butoxyacetonitrile (**7c**) furnished the desired monobromination products **8b** and **8c**, respectively. The Arbusov reaction of **8b** or **8c** with triethyl phosphite afforded the phosphonates **3b** and **3c** in ca. 60% yield from the acetonitriles **7** (eq 8). The success of this approach prompted a survey of the NBS bromination of other oxygen, sulfur, and nitrogen substituted acetonitriles **7**. With the exception of **7b, 7c,** and **7h,** the substituted acetonitriles shown in Table I afforded intractable mixtures on exposure to NBS. The monobromination product **8h** of cyanomethyl thiolbenzoate (**7h**) failed to participate in the Arbusov reaction with triethyl phosphite.

In contrast to the anion of **3a,** the anions of the phosphonates **3b** or **3c** condensed with aldehydes or ketones to provide α-methoxyacrylonitriles **1b** or α-*tert*-butoxyacrylonitriles **1c,** respectively, in excellent yield (Table II). The success of **3b** and particularly **3c** in this reaction would suggest that the failure of **3a** to condense with carbonyl compounds can be attributed to sulfur stabilization and not to the steric bulk of the anion of **3a.** In summary, we have developed an effective synthesis of α-alkoxyacrylonitriles **1** which should supplant published procedures as the method of choice. Other research groups[2b,12] have demonstrated the synthetic versatility of α-alkoxyacrylonitriles **1,** and we hope to report on new applications of this synthon in future publications.

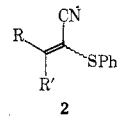
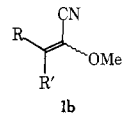
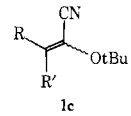
Experimental Section

Infrared spectra were determined on a Perkin-Elmer Model 337 spectrophotometer. NMR spectra were determined on a Varian A-60A spectrometer using tetramethylsilane as an internal standard. Mass spectra were determined on a Varian MAT CH5 mass spectrometer. Melting points were determined using a Thomas-Hoover apparatus and are uncorrected.

***tert*-Butoxyacetonitrile (7c).** A mixture of 16.5 g (0.183 mol) of paraformaldehyde, 42.6 g (45.7 ml, 0.500 mol) of acetone cyanohydrin, 1.2 g of anhydrous potassium carbonate, and 12 ml of methanol saturated with potassium carbonate was stirred at 25 °C for 1.5 h. Sufficient concentrated hydrochloric acid (ca. 3 ml) was added to obtain pH <6. The product was concentrated under reduced pressure, and the residue was diluted with 100 ml of ether, dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure (rotary evaporator) to afford 24.0 g of crude glycolonitrile[13] which was used *immediately* in the next step.

To 118 g (200 ml, 2.0 mol) of isobutylene liquefied in a 500-ml Parr shaker bottle at −78 °C was added 24.0 g of glycolonitrile, 100 ml of dichloromethane, and (slowly) 2 ml of concentrated sulfuric acid. The bottle was connected to the Parr shaker and shaken at 25 °C for 48 h or until the mixture was homogeneous. After releasing the pressure, the solution in the Parr bottle was stirred (caution: magnetic stirring bar was slowly lowered into the solution) in a hood at 25 °C until foaming ceased. To the yellow solution was added saturated aqueous sodium carbonate solution until pH 8. The product was extracted with 200 ml of ether. The ether solution was washed successively with two 100-ml portions of water and 100 ml of brine, and dried over anhydrous magnesium sulfate. The product was distilled to afford 23.8 g (42% based on acetone cyanohydrin) of **7c:** bp 50–54 °C (3 mm) [lit.[14] bp 44 °C (5.5 mm)]; ir (TF) shows no CN absorption, which is characteristic of α-alkoxyacetonitriles but has strong absorptions at 7.30, 8.40, and 9.18 μ; NMR ($CDCl_3$) δ 1.28 [s, 9, $C(CH_3)_3$] and 4.18 (s, 2, OCH_2CN); mass spectrum (70 eV) *m/e* (rel intensity) 113 (1), 98 (100), 57 (60), and 43 (61).

Table II. Synthesis of α-Thiophenoxy-, α-Methoxy-, or α-*tert*-Butoxyacrylonitriles

	Carbonyl compd RR′C=O		Isolated yields, %		
					
Registry no.	R	R′	2	1b	1c
100-52-7	Ph	H	68%	81	94
111-71-7	$(CH_2)_5CH_3$	H		71	99
108-94-1	$-(CH_2)_5-$		*a*	81	89
5396-91-8	$(CH_2)_2Ph$	$(CH_2)_2Ph$		96	84
98-86-2	Ph	CH_3	*a*	83	93
119-61-9	Ph	Ph		94	86

[a] No reaction.

Cyanomethyl Benzoate (7d). To 11.4 g (0.20 mol) of glycolonitrile (see preparation of **7c** for details) and 20.3 g (28 ml, 0.20 mol) of anhydrous triethylamine in 250 ml of anhydrous THF at 0 °C was added 28.4 g (22 ml, 0.20 mol) of benzoyl chloride dropwise over a 10-min period. The mixture was stirred for ca. 12 h at 25 °C, filtered to remove triethylamine hydrochloride, and evaporated to remove THF. The oil was dissolved in 100 ml of ether, washed successively with 50 ml of 1 M sodium hydroxide solution, two 100-ml portions of water, and 50 ml of brine, and dried over anhydrous magnesium sulfate. The product was distilled to afford 21.3 g (66%) of **7d:** bp 152–154 °C (11 mm); ir (TF) 5.78 (C=O), 6.25, and 6.31 μ (aromatic); NMR ($CDCl_3$) δ 4.96 (s, 2, OCH_2CN) and 7.25–8.20 (m, 5, aromatic); mass spectrum (70 eV) *m/e* (rel intensity) 161 (47), 117 (4), 105 (100), and 77 (55).

Cyanomethyl Pivalate (7e). The procedure described above was repeated using 12.9 g (0.23 mol) of glycolonitrile, 23.2 g (32 ml, 0.23 mol) of triethylamine, and 27.4 g (0.23 mol) of pivalyl chloride to afford 23.5 g (74%) of **7e:** bp 87.5–88.5 °C (16 mm); ir (TF) 5.76 μ (C=O); NMR ($CDCl_3$) δ 1.27 [s, 9, $C(CH_3)_3$] and 4.75 (s, 2, OCH_2CN); mass spectrum (70 eV) *m/e* (rel intensity) 141 (1), 98 (3), 85 (8), and 57 (100).

Cyanomethyl Ethylcarbonate (7f). The procedure described above was repeated using 13.2 g (0.23 mol) of glycolonitrile, 24.0 g (33 ml, 0.24 mol) of triethylamine, and 25.0 g (22 ml, 0.23 mol) of ethyl chloroformate to afford 14.3 g (48%) of **7f:** bp 110–114 °C (28 mm); ir (TF) 5.69 μ (C=O); NMR ($CDCl_3$) δ 1.36 (t, J = 7 Hz, 3, OCH_2CH_3), 4.33 (q, J = 7 Hz, 2, OCH_2CH_3), and 4.80 (s, 2, OCH_2CN); mass spectrum (70 eV) *m/e* (rel intensity) 129 (2), 102 (25), and 101 (40).

Cyanomethyl Ethylxanthate (7g). To 32 g (0.2 mol) of potassium ethylxanthate[15] in 200 ml of acetone at 0 °C under a nitrogen atmosphere was added 15.1 g (0.2 mol) of chloroacetonitrile in 100 ml of acetone dropwise over a 30-min period. The solution was stirred for an additional 6 h at 25 °C and filtered to remove potassium chloride. The filtrate was concentrated and distilled to afford 24.3 g (75%) of **7g:** bp 104.5–107 °C (0.7 mm); ir (TF) 4.45 μ (C≡N); NMR (CCl_4) δ 1.51 (t, J = 7 Hz, 3, OCH_2CH_3), 3.87 (s, 2, SCH_2CN), and 4.75 (q, J = 7 Hz, 2, OCH_2CH_3); mass spectrum (70 eV) *m/e* (rel intensity) 161 (43), 116 (10), 101 (6), 93 (5), 89 (6), 77 (7), 76 (23), and 73 (43).

Cyanomethyl Thiolbenzoate (7h). The procedure described for the preparation of **7g** was repeated using 16.0 g (0.1 mol) of sodium thiolbenzoate and 7.55 g (0.1 mol) of chloroacetonitrile to afford 12.7 g (66%) of **7h:** bp 136.5–140.5 °C (0.85 mm); ir (TF) 4.48 (C≡N), 6.00 (C=O), 6.30, and 6.35 μ (aromatic); NMR (CCl_4) δ 3.84 (s, 2, CH_2CN) and 7.25–8.05 (m, 5, aromatic); mass spectrum (70 eV) *m/e* (rel intensity) 177 (1), 161 (5), 122 (4), 105 (100), and 77 (50).

Cyanomethyl Thiolacetate (7i). The procedure described for the preparation of **7g** was repeated using 22.8 g (0.2 mol) of potassium thiolacetate and 15.1 g (0.2 mol) of chloroacetonitrile to afford 14.6 g (64%) of **7i:** bp 66–68 °C (0.7 mm); ir (TF) 4.48 (C≡N) and 5.90 μ (C=O); NMR (CCl_4) δ 2.45 (s, 3, CH_3) and 3.67 (s, 2, CH_2CN); mass spectrum (70 eV) *m/e* (rel intensity) 115 (2), 73 (4), and 43 (100).

Bromo(cyano)methyl Thiolbenzoate (8h). To 177 mg (1.0 mmol) of **7h** in 7.5 ml of anhydrous benzene was added 890 mg (5.0 mmol) of recrystallized[16] *N*-bromosuccinimide. The mixture was irradiated with a 250-W sun lamp for 24 h. The product was cooled, filtered, concentrated, and chromatographed on Merck silica gel F254 in 1:1 ether–hexane to afford 195 mg (76%) of **8h:** R_f 0.61; NMR (CCl_4) δ 6.18 (s, 1, CHBrCN) and 7.35–8.05 (m, 5, aromatic). The use of solvents other than benzene proved unsatisfactory. For example, using carbon tetrachloride (8-h irradiation time) instead of benzene provided none of **8h** and a 14% yield of dibromocyanomethyl thiolbenzoate: NMR (CCl_4) δ 7.25–8.25 (m, 5, aromatic).

Diethyl Cyano(thiophenoxy)methylphosphonate (3a). To 4.55 g (0.11 mol) of sodium hydride (washed with three 20-ml portions of anhydrous hexane to remove mineral oil) in 75 ml of anhydrous THF under a nitrogen atmosphere was added 17.7 g (0.10 mol) of diethyl cyanomethylphosphonate (**4**) in 25 ml of anhydrous THF. The mixture was stirred for 30 min at 25 °C at which time hydrogen gas evolution had ceased. To the solution was added 3.64 g (0.025 mol) of phenylsulfenyl chloride. After 1 h, the reaction mixture was quenched with water and extracted with ether. The ether solutions were washed repeatedly with water to remove 4 selectively, dried, concentrated, and distilled to afford 2.69 g (37% based on PhSCl[17]) of **3a:** bp 162–164 °C (0.2 mm); NMR ($CDCl_3$) δ 1.40 (t, J = 7 Hz, 6, OCH_2CH_3), 4.07 (d, J = 23 Hz, 1, PCH), 4.05–4.60 (two q, 4, OCH_2CH_3), and 7.30–7.85 (m, 5, aromatic); mass spectrum (70 eV) *m/e* 285. In a small-scale experiment, **3a** was conveniently isolated in 47% yield by chromatography on Merck silica gel F254 in 1:9 ether–hexane (R_f 0.6).

Diethyl Cyano(methoxy)methylphosphonate (3b). The procedure described below for the preparation of **3c** was repeated starting with 5.09 g (0.072 mol) of methoxyacetonitrile (**7b**) and 12.6 g (0.071 mol) of recrystallized[16] *N*-bromosuccinimide to afford 9.79 g of crude **8b** which displayed a characteristic NMR signal (CCl_4) at δ 6.30 (MeOCHBrCN). The Arbusov reaction of crude **8b** with 10.7 g (0.065 mol) of triethyl phosphite afforded 8.03 g (54% based on **7b**) of **3b:**[18] ir (TF) 7.87, 9.03, 9.53 (sh), and 9.80 μ; NMR ($CDCl_3$) δ 1.23 (t, J = 7 Hz, 6, OCH_2CH_3), 3.61 (s, 3, OCH_3), and 4.0–4.6 (m, 5, OCH_2CH_3 and PCH); mass spectrum (70 eV) *m/e* (rel intensity) 207 (7), 164 (6), 163 (8), 137 (27), and 109 (100).

In an alternate approach to the synthesis of **3b,** 384 mg (2.17 mmol) of **4** in 1 ml of anhydrous acetonitrile was added to a solution of 510 mg (2.25 mmol) of *p*-carboxybenzenesulfonyl azide[9b] and 464 mg (4.58 mmol) of triethylamine in 7 ml of anhydrous acetonitrile. The reaction mixture was stirred for 2 h at 25 °C, diluted with 25 ml of dichloromethane, washed with 20 ml of 5% sodium hydroxide solution and three 20-ml portions of water, and dried over anhydrous magnesium sulfate to afford 203 mg of red oil which contains 28% of **6** by NMR analysis. The crude **6** was photolyzed in methanol for 1 h using a high-pressure 450-W Hanovia lamp. The product (192 mg) was analyzed by GLC–mass spectrometry on a temperature programmed (90–120 °C) 6-ft OV-1 column to identify **3b.**

Diethyl *tert*-Butoxy(cyano)methylphosphonate (3c). To 50 g (0.442 mol) of *tert*-butoxyacetonitrile (**7c**) in 1.5 l. of benzene was added 78.7 g (0.442 mol) of recrystallized[16] *N*-bromosuccinimide. The mixture was irradiated with a 250-W sun lamp for 30 min at which time the orange color had discharged. The product was cooled in an ice bath until the benzene solution just started to solidify and then filtered to remove the precipitated succinimide. The filtrate was evaporated to afford a pale orange oil which was again filtered to afford 76.6 g of crude **8c** which displayed a characteristic NMR signal ($CDCl_3$) at δ 6.35 (*t*-BuOCHBrCN). The crude **8c** was used immediately in the next step.

A mixture of 76.6 g of crude **8c** and 66.4 g (69 ml, 0.40 mol) of triethyl phosphite[21] in a 500-ml three-necked flask equipped with a large-bore, efficient condenser was heated to initiate an exothermic Arbusov reaction. An ice bath was occassionally applied to moderate the reaction. When the reaction subsided (<5 min), the solution was again heated for 15 min at reflux. The condenser was removed, and the flask was connected to a dry ice–acetone trap. Heating was continued (using a 110 °C oil bath) for an additional 15 min under a stream of nitrogen to entrain the ethyl bromide generated in the reaction. The product was distilled through a short-path distillation head to afford 63.3 g (57% based on **7c**) of **3c** as a viscous, pale yellow oil: bp 116–118 °C (0.5 mm); ir (TF) 7.18, 7.31, 7.88, and 9.90 μ; NMR ($CDCl_3$) δ 1.32 [s, 9, $C(CH_3)_3$], 1.40 (t, J = 7 Hz, 6, OCH_2CH_3), 4.08–4.73 (m, 5, OCH_2CH_3 and PCH); mass spectrum (70 eV) *m/e* (rel intensity) 234 (10), 193 (22), 138 (78), and 57 (100).

The following is a typical experimental procedure for the preparation of α-alkoxyacrylonitriles **1.**

(*E*)- and (*Z*)-α-*tert*-Butoxycinnamonitrile (1c, R = Ph; R′ = H). To 93 mg of 57% sodium hydride (washed with three 5-ml portions of anhydrous hexane) in 3 ml of anhydrous THF under a nitrogen atmosphere was added 499 mg (2.0 mmol)[22] of **3c** in 1 ml of anhydrous THF. After the evolution of hydrogen gas had subsided, the solution was refluxed for 15 min to complete the generation of the anion of **3c.** To this solution was added 106 mg (1.0 mmol) of distilled benzaldehyde in 1.0 ml of anhydrous THF. The mixture was refluxed for 3 h, cooled, poured into 50 ml of water and 2 ml of brine, and extracted with three 20-ml portions of ether. The combined ether solutions were washed successively with two 25-ml portions of water and 25 ml of brine and dried over anhydrous magnesium sulfate. The solvent was evaporated to afford 356 mg of oil which was chromatographed on Merck silica gel F254 in 1:3 ether–hexane to afford 188 mg (94%) of **1c** (R = Ph; R′ = H): R_f 0.61; ir (TF) 4.53 (C≡N), 6.18 (C=C), and 6.37 μ (aromatic); NMR (CCl_4) δ 1.41 and 1.49 [two s, 9, $C(CH_3)_3$ of *E* and *Z* isomers], 6.28 and 6.72 (two s, 1, vinyl H of *E* and *Z* isomers), and 7.17–7.75 (m, 5, aromatic H); mass spectrum (70 eV) *m/e* 201, 91, 77, and 57.

1c [R = $(CH_2)_5CH_3$; R′ = H]: ir (TF) 4.52 (C≡N) and 6.10 μ (C=C); NMR ($CDCl_3$) δ 0.72–1.08 [m, 3, $(CH_2)_4CH_3$], 1.08–1.60 [m, 8, $(CH_2)_4CH_3$], 1.32 and 1.41 [two s, 9, $C(CH_3)_3$ of *E* and *Z* isomers], 1.80–2.50 (m, 2, C=CHCH_2), 5.80 and 5.93 (two t, J = 8 Hz, 1, C=CHCH_2 of *E* and *Z* isomers); mass spectrum (70 eV) *m/e* (rel intensity) 209 (<1) and 57 (100).

1c [R, R′ = $-(CH_2)_5-$]: ir (TF) 4.53 (C≡N) and 6.12 μ (C=C); NMR ($CDCl_3$) δ 1.37 [s, 9, $C(CH_3)_3$], 1.43–1.76 (m, 6, CH_2), and 2.03–2.55 (m, 4, C=C–CH_2); mass spectrum (70 eV) *m/e* (rel intensity) 193 (3), 178 (9), 137 (16), 110 (20), 68 (19), and 57 (100).

1c (R = R′ = CH_2CH_2Ph): ir (TF) 4.54 (C≡N), 6.18 (C=C), 6.25 and 6.32 μ (aromatic); NMR ($CDCl_3$) δ 1.29 [s, 9, $C(CH_3)_3$], 2.28–2.95 (m, 8, CH_2), and 7.23 (s, 10, aromatic H); mass spectrum (70 eV) *m/e*

(rel intensity) 318 (1), 176 (18), 159 (35), 133 (39), 120 (67), and 57 (100).

1c (R = Ph; R′ = CH_3): ir (TF) 4.54 (C≡N), 6.21 (C=C), and 6.36 μ (aromatic); NMR ($CDCl_3$) δ 1.22 and 1.49 [two s, 9, $C(CH_3)_3$ of *E* and *Z* isomers], 2.15 and 2.31 (two s, 3, C=C–CH_3 of *E* and *Z* isomers), and 7.40 (s, 5, aromatic H); mass spectrum (70 eV) *m/e* (rel intensity) 215 (3), 200 (7), 159 (56), 132 (100), and 57 (90).

1c (R = R′ = Ph): mp 96–96.5 °C; ir (KBr) 4.53 (C≡N), 6.28 (C=C), and 6.38 μ (aromatic); NMR ($CDCl_3$) 1.32 [s, 9, $C(CH_3)_3$] and 7.34 (s, 10, aromatic H); mass spectrum (70 eV) *m/e* (rel intensity) 277 (3), 194 (100), 77 (5), and 57 (59).

1b (R = Ph; R′ = H): ir (TF) 4.47 (C≡N), 6.02 (C=C), and 6.33 μ (aromatic); NMR ($CDCl_3$) δ 3.78 and 3.93 (two s, 3, OCH_3 of *E* and *Z* isomers), 6.18 and 6.56 (two s, 1, vinyl H of *E* and *Z* isomers), and 7.22–7.76 (m, 5, aromatic H); mass spectrum (70 eV) *m/e* (rel intensity) 159 (100), 144 (82), 116 (75), and 89 (45).

1b (R = $(CH_2)_5CH_3$; R′ = H): ir (TF) 4.49 and 4.53 (C≡N of *E* and *Z* isomers) and 6.11 μ (C=C); NMR ($CDCl_3$) δ 0.65–1.72 [m, 11, $(CH_2)_4CH_3$], 1.72–2.48 (m, 2, C=CHCH_2), 3.63 and 3.73 (two s, 3, OCH_3 of *E* and *Z* isomers), and 5.55 (t, *J* = 8 Hz, 1, C=CHCH_2 of *E* and *Z* isomers); mass spectrum (70 eV) *m/e* (rel intensity) 167 (20) and 43 (100).

1b [R, R′ = $-(CH_2)_5-$]: ir (TF) 4.54 (C≡N) and 6.02 μ (C=C); NMR ($CDCl_3$) δ 1.35–1.82 (m, 6, CH_2), 2.10–2.56 (m, 4, C=C–CH_2), and 3.67 (s, 3, OCH_3); mass spectrum (70 eV) *m/e* (rel intensity) 151 (25), 108 (16), 81 (23), and 68 (100).

1b (R = R′ = CH_2CH_2Ph): ir (TF) 4.53 (C≡N), 6.09 (C=C), and 6.24 μ (aromatic); NMR ($CDCl_3$) δ 2.30–2.98 (m, 8, CH_2), 3.47 (s, 3, OCH_3), and 7.21 (s, 10, aromatic H); mass spectrum (70 eV) *m/e* (rel intensity) 291 (3), 221 (14), 200 (16), 168 (13), and 91 (100).

1b (R = Ph; R′ = CH_3): ir (TF) 4.56 (C≡N), 6.18 (C=C), and 6.33 μ (aromatic); NMR ($CDCl_3$) δ 2.14 and 2.28 (two s, 3, vinyl CH_3 of *E* and *Z* isomers), 3.69 and 3.81 (two s, 3, OCH_3 of *E* and *Z* isomers), and 7.39 (s, 5, aromatic H); mass spectrum (70 eV) *m/e* (rel intensity) 173 (100), 158 (85), 130 (33), and 103 (71).

1b (R = R′ = Ph): mp 69.5–70.5 °C; ir (KBr) 4.53 (C≡N), 6.21 (C=C), and 6.38 δ (aromatic); NMR (CCl_4) δ 3.75 (s, 3, OCH_3), 7.25 and 7.32 (two s, 10, aromatic H); mass spectrum (70 eV) *m/e* (rel intensity) 235 (100), 165 (84), and 77 (10).

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Registry No.—*E*-**1b** (R = Ph; R = H), 59463-29-5; *Z*-**1b** (R = Ph; R′ = H), 59463-30-8; *E*-**1b** (R = $(CH_2)_5CH_3$; R′ = H), 59463-31-9; *Z*-**1b** (R = $(CH_2)_5CH_3$; R′ = H), 59463-32-0; **1b** (R, R′ = $-(CH_2)_5-$), 59463-33-1; **1b** (R = R′ = CH_2CH_2Ph), 59463-34-2; *E*-**1b** (R = Ph; R′ = CH_3), 59463-35-3; *Z*-**1b** (R = Ph; R′ = CH_3), 59463-36-4; **1b** (R = R′ = Ph), 59463-37-5; *E*-**1c** (R = Ph; R′ = H), 59463-38-6; *Z*-**1c** (R = Ph; R′ = H), 59463-39-7; *E*-**1c** (R = $(CH_2)_5CH_3$; R′ = H), 59463-40-0; *Z*-**1c** (R = $(CH_2)_5CH_3$; R′ = H), 59463-41-1; **1c** (R, R′ = $-(CH_2)_5-$), 59463-42-2; **1c** (R = R′ = CH_2CH_2Ph), 59463-43-3; *E*-**1c** (R = Ph; R′ = CH_3), 59463-44-4; *Z*-**1c** (R = Ph; R′ = CH_3), 59463-45-5; **1c** (R = R′ = Ph), 59463-46-6; **3a**, 59463-47-7; **3b**, 59463-48-8; **3c**, 59463-49-9; **4**, 2537-48-6; **6**, 59463-50-2; **7b**, 1738-36-9; **7c**, 59463-51-3; **7d**, 939-56-0; **7e**, 59463-52-4; **7f**, 59463-53-5; **7g**, 59463-54-6; **7h**, 59463-55-7; **7i**, 59463-56-8; **8b**, 59463-57-9; **8c**, 59463-58-0; **8h**, 59463-59-1; acetone cyanohydrin, 75-86-5; glycolonitrile, 107-16-4; isobutylene, 115-11-7; benzoyl chloride, 98-88-4; pivalyl chloride, 3282-30-2; potassium ethylxanthate, 140-89-6; chloroacetonitrile, 107-14-2; sodium thiolbenzoate, 51066-54-7; potassium thiolacetate, 10387-40-3; dibromocyanomethyl thiolbenzoate, 59463-60-4; phenylsulfenyl chloride, 931-59-9; triethyl phosphite, 122-52-1; acetonitrile, 75-05-8.

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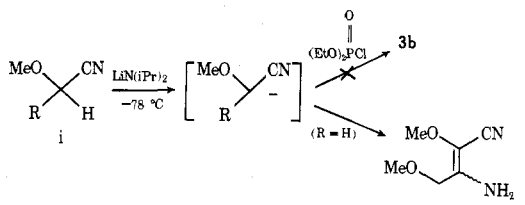
(17) All efforts to secure **3a** using 1:1 molar ratios of PhSCl and the anion of **4** led to $(EtO)_2POC(SPh)_2CN$ as the predominant product. For example, the addition of the anion of **4** to an equimolar amount of PhSCl in THF gave a 30% yield of $(EtO)_2POC(SPh)_2CN$ and a 2% yield of **3a**.
(18) Yet another approach to the synthesis of **3b** involves the reaction of the anion of methoxyacetonitrile (**7b**) with diethyl chlorophosphate. We were not surprised at the failure of this reaction to furnish **3b**. We have investigated the alkylation of a series (shown in Table I) of substituted acetonitriles such as i (R = H) and have observed the rapid self-condensation of the



i ii

anions of i to give the β-aminoacrylonitriles ii. In sharp contrast, Stork[19] has reported the efficient alkylation of substituted acetonitriles (R = alkyl or aryl group). Recently however, Büchi[20] reported on the successful alkylation of dimethylaminoacetonitrile with an allylic bromide, but we have been unable to generalize this reaction to other systems.
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(22) Only 1.5 equiv of the anion of **3b** was required to secure the yields of α-methoxyacrylonitriles **1b** shown in Table II.