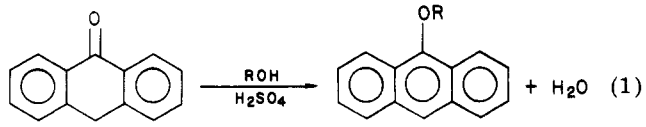
Table I. Synthesis of 9-Anthryl Ethers and Sulfides

1	R	method[a]	% yield	mp, °C	2	R	% yield	mp, °C
a	CH_2CH_2Br	A	74	119–120	a	n-C_4H_9	85	
b	CH_3	B	90	88–89[6]	b	phenyl	74	99–100[9]
c	C_2H_5	B	74	66–67[6]	c	p-tolyl	63	108–109[9]
d	CH_2CH_2OH	A	70	110–113	d	i-C_3H_7	23	ref 9

[a] In method A, water is removed as the benzene azeotrope; in method B, the appropriate ortho ester is added to the reaction.

tions), the two-step procedure may be preferred. Alkyl or aryl thiols may similarly be used to afford 9-anthryl alkyl or aryl sulfides. These reactions are rather slow, however, and the anthryl sulfides can be obtained more readily by a variation of Barnett and Needham's trans-etherification reaction.[3] Alkyl or aryl thiols undergo methanesulfonic acid catalyzed methanol–thiol exchange with 9-methoxyanthracene to afford 9-anthryl alkyl or aryl sulfides. Methanol removal is unnecessary for completion of these exchanges. Equations 1 and 2 illustrate the preceding reactions.



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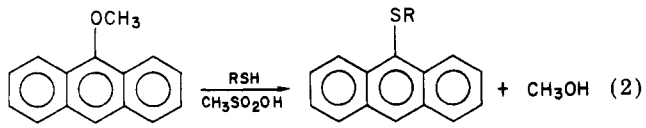

1b 2

Table I provides representative examples of each type of reaction. The indicated yields pertain to purified products. These examples are offered not necessarily as the best procedure for making any given compound but rather to illustrate simple, convenient procedures amenable to large-scale operation.

Experimental Section

All compounds described in this paper were adequately characterized in terms of spectral measurement, melting points (when reported) and elemental composition. Representative synthetic procedures are described. Varian EM-390 and Nicolet 7000 FT IR spectrometers were used to obtain NMR and infrared spectra. A Büchi apparatus was used to determine melting points (uncorrected). Mass spectra were obtained on a Varian MAT CH-5 or MAT 311A spectrometer. Microanalyses were performed by J. Nemeth and Associates, University of Illinois.

9-(2-Bromoethoxy)anthracene (1a). Method A. A stirred solution of anthrone (1.94 g, 10 mmol), 2-bromoethanol (12.5 g, 100 mmol), and sulfuric acid (0.5 mL) in 40 mL of benzene was heated to reflux; water being azeotropically removed by a Dean–Stark trap. After 48 h, when NMR analysis showed the absence of anthrone (δ 4.31 (s, 2 H)), the reaction was cooled to room temperature, poured into 100 mL of saturated $NaHCO_3$ solution, and extracted with ether (3 × 50 mL). The organic extracts were washed with brine (2 × 100 mL) and dried over $MgSO_4$, and the solvent was removed in vacuo, affording a brown syrup. Recrystallization from ethanol afforded yellow 9-(2-bromoethoxy)anthracene: 2.24 g (74%); mp 119–120 °C; NMR ($CDCl_3$) δ 3.75 (t, 2 H), 4.92 (t, 2 H), 7.20–7.48 (m, 4 H), 7.70–7.92 (m, 2 H), 8.12–8.38 (m, 2 H); IR (KBr) 3300–2917, 1628, 1433, 1415, 1248 (s), 1277, 1222, 1168, 1098 (vs) 997 cm^{-1}; MS (70 eV), m/e (relative intensity) 302 (9, M^+), 300 (9, M^+), 193 (49), 178 (15), 178 (100), 176 (17), 165 (10), 89 (15), 76 (17). Anal. Calcd for $C_{16}H_{13}BrO$: C, 63.81; H, 4.32; Br, 26.55. Found: C, 64.69; H, 4.26; Br, 26.35.

9-Methoxyanthracene (1b). Method B. A stirred solution of anthrone (1.94 g, 10 mmol), trimethyl orthoformate (1.06 g) and concentrated sulfuric acid (10 drops) in methanol (30 mL) and benzene (30 mL) was heated to reflux for 4 days. At this time, NMR analysis of the reaction mixture showed the absence of anthrone (δ 4.31 (s, 2 H)). The reaction was cooled to room temperature, poured onto 100 mL of a saturated $NaHCO_3$ solution, and extracted with ether (3 × 50 mL). The organic extracts were washed with brine, dried over $MgSO_4$, and filtered, and the solvent was removed in vacuo, leaving a brown solid. Recrystallization from ethanol afforded 9-methoxyanthracene: 1.85 g (89%); NMR ($CDCl_3$) δ 4.08 (s, 3 H), 7.22–7.42 (m, 4 H), 7.75–7.95 (m, 2 H), 8.07–8.30 (m, 3 H); IR (KBr) 2930 (w), 1348 (s), 1092, 972, 880, 842, 738 cm^{-1}.

***n*-Butyl 9-Anthryl Sulfide (2a).** A solution of 9-methoxyanthracene (1 g, 4.8 mmol), n-butyl mercaptan (2.5 mL), and 5 drops of methanesulfonic acid in benzene (20 mL) was heated to reflux for 15 h. After being allowed to cool to room temperature, the reaction mixture was poured into 5% NaOH and extracted with ether (50 mL). The organic extracts were washed with 5% NaOH and brine and dried over $MgSO_4$. Removal of the solvent and chromatography on silica (CH_2Cl_2/hexane elutent) afforded ***n*-butyl 9-anthryl sulfide**: 1.09 g (85%); yellow oil; NMR ($CDCl_3$) δ 0.79 (t, 3 H), 1.10–1.63 (m, 4 H), 2.78 (t, 2 H), 7.20–7.62 (m, 4 H), 7.73–8.03 (m, 2 H), 8.34 (s, 1 H), 8.72–8.98 (m, 2 H); IR (neat) 3010, 2900, 2850, 1440, 1310, 1270, 1015, 887, 845, 780, 735 cm^{-1}; MS (10 eV) m/e (relative intensity) 266 (100, M^+), 210 (59), 209 (38), 178 (10), 71 (10); calcd for $C_{18}H_{18}S$ mol wt 266.1129, found mol wt 266.1135 (HREIMS).

Acknowledgment. This work has been partially supported by a grant from the National Science Foundation.

Registry No. **1a**, 86129-58-0; **1b**, 2395-96-2; **1c**, 6487-28-1; **1d**, 86129-59-1; **2a**, 74851-72-2; **2b**, 74851-75-5; **2c**, 86129-60-4; **2d**, 86129-61-5; H_2SO_4, 7664-93-9; CH_3SO_2OH, 75-75-2; $HOCH_2CH_2OH$, 107-21-1; $HC(OEt)_3$, 122-51-0; PhSH, 108-98-5; 4-MeC_6H_4SH, 106-45-6; Me_2CHSH, 75-33-2; anthrone, 90-44-8; 2-bromoethanol, 540-51-2; trimethyl orthoformate, 149-73-5; n-butyl mercaptan, 109-79-5.

O-Trimethylsilyl Hydroxamoyl Chlorides as Nitrile Oxide Precursors

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Lately, a number of synthetic methodologies based on the manipulation of Δ^2-isoxazolines have appeared that point to a greatly expanded utility for this class of compounds.[1] Probably the most general synthetic approach to these species entails the cycloaddition of olefins to nitrile oxides generated by a variety of methods.[2] Of these, several have been employed extensively: the dehydro-

(1) (a) Curran, D. P. *J. Am. Chem. Soc.* **1982**, *104*, 4024 and references cited therein. (b) Grund, H.; Jäger, V. *Liebigs Ann. Chem.* **1980**, 80 and previous papers in the series. (c) Cunico, R. F. *J. Organomet. Chem.* **1981**, *212*, C51.

(2) Review: Grundmann, Ch.; Grünanger, P. "The Nitrile Oxides"; Springer-Verlag: New York, 1971.

0022-3263/83/1948-2780$01.50/0

Table I. Reaction of *O*-Trimethylsilyl Hydroxamoyl Chlorides with KF and Olefins[a]

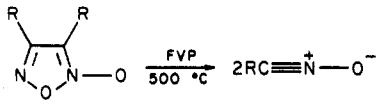
entry	substrate	olefin	product	yield,[b] %
1	3a	n-$C_6H_{13}CH{=}CH_2$	4a, R^1 = H, R^2 = n-C_6H_{13}	70
2		$Me_3SiCH{=}CH_2$	4a, R^1 = H, R^2 = $SiMe_3$	62
3		$PhCH{=}CH_2$	4a, R^1 = H, R^2 = Ph	76
4		$C_2H_5OCH{=}CH_2$	4a, R^1 = H, R^2 = OCH_2CH_3	70
5		$MeO_2CCH{=}CH_2$	4a, R^1 = H, R^2 = CO_2Me	88
6		$NCCH{=}CH_2$	4a, R^1 = H, R^2 = CN	70
7			4a, R^1, R^2 = 	71
8		c-$CH_3CH{=}CHCH_3$[c]	4a, R^1 = R^2 = CH_3 (cis)	44[d]
9		t-$CH_3CH{=}CHCH_3$[c]	4a, R^1 = R^2 = CH_3 (trans)	47[d]
10		 [c]	4a, R^1, R^2 = 	10[d]
11	3b	n-$C_6H_{13}CH{=}CH_2$	4b, R^1 = H, R^2 = n-C_6H_{13}	72
12		$C_2H_5OCH{=}CH_2$	4b, R^1 = H, R^2 = OCH_2CH_3	79
13		$NCCH{=}CH_2$	4b, R^1 = H, R^2 = CN	76

[a] All reactions were carried out at 25 °C for between 25 and 48 h, using equivalent amounts of substrate and olefin unless otherwise indicated. [b] Isolated yield from evaporative distillation or sublimation unless otherwise indicated; small amounts (<5%) of dimethylfuroxane were sometimes present in distilled samples originating from 3a. [c] Molar ratio of 3a/olefin was 1:4; butene runs were carried out in sealed pressure tubes. [d] Yields from quantative NMR analysis of distilled material; furoxane contamination was present.

halogenation of hydroxamoyl chlorides (eq 1) and the dehydration of primary nitroparaffins (eq 2).[3] Recently, another method that holds high promise for generality and utility has been reported that involves the flash vacuum pyrolysis (FVP) of furoxanes (2; eq 3).[4] Each of these methods possesses aspects that in certain circumstances may be manipulatively undesirable. Acetohydroxamoyl chloride (1a), for example, is thermally unstable[5] [although benzohydroxamoyl chloride (1b) is not]; attendant diphenylurea may pose separation problems in the approach of eq 2, and the nitrile oxide obtained from eq 3 must be used before the facile dimerization typical of these species returns it to furoxane.

$$\underset{\substack{\mathbf{1a},\ R = Me\\ \mathbf{b},\ R = Ph}}{RC(Cl){=}NOH} \xrightarrow{base} RC{\equiv}N^+O^- + base{\cdot}HCl \qquad (1)$$

$$RCH_2NO_2 \xrightarrow[Et_3N]{2PhNCO} RC{\equiv}N^+O^- + (PhNH)_2C{=}O \qquad (2)$$



2 (3)

$$RC(Cl){=}NOSiMe_3 + R^1CH{=}CHR^2 \xrightarrow[-Me_3SiF,\ KCl]{KF/CH_3CN} \underset{\substack{4a,\ R = Me\\ b,\ R = Ph}}{\text{4-isoxazoline}} \qquad (4)$$

3a, R = Me
b, R = Ph

We report a new approach to the in situ generation of nitrile oxides that employs shelf-stable precursors and that can be carried out under mild conditions. Chosen for examination as representative examples were the precursors *O*-(trimethylsilyl)benzohydroxamoyl chloride (**3b**), prepared from trimethylchlorosilane and a sample of benzonitrile oxide generated from **1b**, and *O*-(trimethylsilyl)acetohydroxamoyl chloride (**3a**), obtained from the reaction of trimethylchlorosilane with acetonitrile oxide generated from **2**.

Treatment of **3a,b** with potassium fluoride in acetonitrile containing various olefins resulted in the formation of Δ^2-isoxazolines **4a,b** (Table I). The yields of cycloadducts thus obtained, even on the small scale employed, compare favorably with those reported using other methodologies.[2] Preliminary experiments have also indicated that **3a** (but not **3b**) thermolyzes in refluxing toluene to afford nitrile oxide. Thus a 57% yield of 3-methyl-5-*n*-hexyl-Δ^2-isoxazoline was obtained from **3a** and 1-octene after 43 h.

That potassium fluoride is crucial to the generation of nitrile oxide at ambient temperatures is not in doubt, as no isoxazoline product or consumption of **3a** was observed in a blank run omitting KF. However, at the present time we have insufficient data to choose between two possible mechanisms (whether concerted or stepwise) for the overall 1,3-dechlorosilylation of **3a,b**. These eliminations may be initiated either by direct fluoride ion attack at silicon or by a process entailing initial hydroxide ion attack at silicon, which is catalytic in trace water. It does appear that the transformation of **3a** to acetonitrile oxide under the conditions of eq 4 is irreversible. No peak attributable to *O*-(trimethylsilyl)acetohydroxamoyl fluoride was present in GLC traces of runs completed or in progress. Moreover, attempted reaction of FVP-generated acetonitrile oxide with trimethylfluorosilane afforded only the dimerization product (dimethylfuroxane) and no *O*-(trimethylsilyl)-acetohydroxamoyl fluoride, in marked contrast to the behavior of trimethylchlorosilane under identical conditions (vide supra).

We believe the current approach will be applicable to other *O*-silyl hydroxamoyl chlorides and may prove compatible with 1,3-dipolarophiles other than olefins.

Experimental Section

IR spectra were obtained on thin films with a Pye Unicam 3-200 spectrophotometer. ^1H NMR spectra were recorded in $CDCl_3$ solution with tetramethylsilane as internal standard, using a Varian A60A spectrometer. Unless indicated otherwise, reported "boiling points" are bath temperatures for evaporative distillations. GLC analyses were generally carried out with SE-30 or PMPE columns; the isomeric **4a** (R^1 = R^2 = CH_3) was collected with use of a 5-ft 15% FFAP column at 110 °C.

***O*-(Trimethylsilyl)acetohydroxamoyl Chloride (3a).** Acetonitrile oxide was prepared as described[4] by FVP of 3.00 g (26.3 mmol) dimethylfuroxane[3] and collected in a −78 °C trap.

(3) Mukaiyama, T.; Hoshino, T. *J. Am. Chem. Soc.* **1960**, *82*, 5339.
(4) Mitchell, W. R.; Paton, R. M. *Tetrahedron Lett.* **1979**, 2443.
(5) Piloty, O.; Steinbock, H. *Chem. Ber.* **1902**, *35*, 3101.

To this was added 40 mL of dry ether and 5.71 g (52.6 mmol) of trimethylchlorosilane and the mixture stored at -25 °C overnight. Ether was removed by rotary evaporation (to 0 °C) and the residue short-path distilled to give 5.33 g (61%) of water-white material: bp 34 °C (11 mm); NMR analysis indicated the presence of 3% hexamethyldisiloxane as the only significant contaminant; NMR δ 0.23 (s, 9 H), 2.24 (s, 3 H); IR 1617 (C=N), 1253 ($SiMe_3$) cm^{-1}. Anal. Calcd for $C_5H_{12}ClNOSi$: C, 36.24; H, 7.30. Found: C, 35.96; H, 7.49.

Conversion of 3a,b into Isoxazolines 4a,b. The generation of nitrile oxides from both **3a** and **3b**[6] is typified by the following procedure for the preparation of **4a** (R^1 = H, R^2 = n-C_6H_{13}). A flask with an open side arm was charged with a magnetic stirrer and 1.16 g (20 mmol) of potassium fluoride. KF was dried by heating the flask for several minutes with a flame while under nitrogen flow. After cooling, 6 mL of dry acetonitrile, 0.71 mL (0.51 g, 4.5 mmol) of 1-octene, and 0.75 g (4.5 mmol) of **3a** were added, the side arm was septum sealed and the flask stoppered and sealed with Parafilm. After stirring for 28 h at 25 °C, pentane and water were added, the pentane layer dried ($MgSO_4$) and concentrated, and the residue evaporatively distilled to give 0.53 g (70%) of 3-methyl-5-n-hexyl-Δ^2-isoxazoline: bp 50 °C (0.1 mm); NMR δ 0.68-1.83 (m, 13 H), 1.95 (t, 3 H, J = 1 Hz), 2.25-3.30 (m, 2 H), 4.2-4.8 (m, 1 H); IR 1613 cm^{-1}. Anal. Calcd for $C_{10}H_{19}NO$: C, 70.96; H, 11.31. Found: C, 71.09; H, 11.19.

Runs that generated isoxazolines of possibly significant water solubility (Table I, entries 4-6, 8, and 9) were worked up by filtration of the crude reaction mixture, followed by distillation.

The thermal generation of acetonitrile oxide from **3a** was shown to occur by refluxing a mixture of 0.51 g (4.5 mmol) of 1-octene, 0.75 g (4.5 mmol) of **3a**, and 6 mL of dry toluene under nitrogen for 43 h. Distillation afforded 0.44 g (57%) of the isoxazoline.

Other new isoxazolines (**4a,b**) reported here are listed in the following entries of Table I.

Entry 7: bp 90 °C (0.6 mm); NMR δ 0.9-1.7 (m, 6 H), 1.89 (t, 3 H, J = 1 Hz), 2.35 (br s, 1 H), 2.49 (br s, 1 H), 2.96 (d, 1 H, J = 8 Hz), 4.40 (d, 1 H, J = 8 Hz); IR 1620 cm^{-1}. Anal. Calcd for $C_9H_{13}NO$: C, 71.49; H, 8.67. Found: C, 71.26; H, 8.99.

Entry 8: bp 45 °C (0.5 mm); NMR δ 1.04 (d, 3 H, J = 7 Hz), 1.23 (d, 3 H, J = 6.5 Hz), 1.93 (s, 3 H), 3.04 (m, 1 H), 4.62 (AB q, 1 H, J = 6.5, 9.5 Hz); IR 1627 (w), 1462 (sh), 1445 (s), 1387 (s), 1324 (m), 1310 (sh), 1060 (m), 1025 (m), 985 (m), 890 (s), 863 (s), 770 (w), 729 (w), 636 (m) cm^{-1}. Anal. Calcd for $C_6H_{11}NO$: C, 63.69; H, 9.80. Found: C, 63.47; H, 9.79.

Entry 9: bp 45 °C (0.25 mm); NMR δ 1.16 (d, 3 H, J = 7 Hz), 1.32 (d, 3 H, J = 6 Hz), 1.90 (d, 3 H, J = 1 Hz), 2.74 (m, 1 H), 4.12 (AB q, 1 H, J = 6, 9 Hz); IR 1624 (s), 1460 (sh), 1440 (s), 1385 (s), 1328 (m), 1090 (w), 1056 (m), 1010 (m), 978 (w), 890 (s), 870 (s), 843 (m), 788 (w), 717 (w) cm^{-1}. Anal. Calcd for $C_6H_{11}NO$: C, 63.69; H, 9.80. Found: C, 63.26; H, 9.97.

Entry 11: mp 51.6-52.0 °C (from hexane-ether); NMR δ 0.65-2.1 (m, 13 H), 2.90 (*ABX* pattern, 1 H, J = 8.5, 16.5 Hz), 3.38 (*ABX* pattern, 1 H, J = 10, 16.5 Hz), 4.43-5.0 (m, 1 H), 7.22-7.90 (m, 5 H); IR 1690 (w), 1660 (w), 855 (s), 790 (s) cm^{-1}. Anal. Calcd for $C_{10}H_{11}NO$: C, 77.88; H, 9.15. Found: C, 77.70; H, 8.90.

Registry No. **3a**, 86260-81-3; **3b**, 69054-15-5; **4a** (R^1 = H; R^2 = n-C_6H_{13}), 83670-86-4; **4a** (R^1 = H; R^2 = $SiMe_3$), 78847-14-0; **4a** (R^1 = H; R^2 = Ph), 7064-06-4; **4a** (R^1 = H; R^2 = OCH_2CH_3), 86260-82-4; **4a** (R^1 = H; R^2 = CO_2Me), 55134-82-2; **4a** (R^1 = H; R^2 = CN), 86260-83-5; **4a** (R^1, R^2 = bicyclo[2.2.1]heptane-2,3-diyl, 83670-87-5; *cis*-**4a** (R^1 = R^2 = CH_3), 82150-07-0; *trans*-**4a** (R^1 = R^2 = CH_3), 82150-02-5; **4a** (R^1, R^2 = cyclohexane-1,2-diyl), 24010-91-1; **4b** (R^1 = H; R^2 = n-C_6H_{13}), 84965-95-7; **4b** (R^1 = H; R^2 = OCH_2CH_3), 86260-84-6; **4b** (R^1 = H; R^2 = CN), 1011-38-7; n-$C_6H_{13}CH{=}CH_2$, 111-66-0; $Me_3SiCH{=}CH_2$, 754-05-2; $PhCH{=}CH_2$, 100-42-5; $C_2H_5OCH{=}CH_2$, 109-92-2; $MeO_2CCH{=}CH_2$, 96-33-3; $NCCH{=}CH_2$, 107-13-1; *c*-$CH_3CH{=}CHCH_3$, 590-18-1; *t*-$CH_3CH{=}CHCH_3$, 624-64-6; acetonitrile oxide, 7063-95-8; trimethylchlorosilane, 75-77-4; norbornene, 498-66-8; cyclohexene, 110-83-8; benzonitrile oxide, 873-67-6.

(6) Akimova, G. S.; Petrukhno, L. A. *Zh. Obshch. Khim.* **1978**, *48*, 2385.

Synthesis of Trisubstituted Vinyl Chlorides[1]

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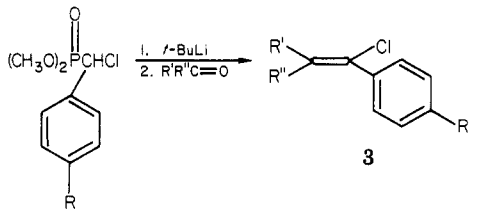
We have previously shown that 1,2-diarylvinyl chlorides can be synthesized from diphenyl (1-chlorobenzyl)-phosphonates, base, and aryl aldehydes in a Horner-Emmons type fashion.[2] Savignac et al.[3] have since devised an appealing method for the synthesis of 1-chlorobenzylphosphonates and obtained greater yields of the vinyl chlorides. Trisubstituted vinyl chlorides have eluded this synthetic procedure since success with a ketone in a reaction with the α-heterosubstituted phosphonate carbanion has been achieved only with cyclohexanone.[3]

We now report the expansion of this method to include more sterically hindered ketones such as benzophenone. By decreasing the bulk of the phosphonate moiety by using methyl instead of phenyl esters and utilizing more vigorous reaction conditions, good yields of trisubstituted vinyl chlorides were obtained. Thus, lithium dimethyl (1-chlorobenzyl)phosphonate was refluxed in THF for 24-48 h with the appropriate ketone to yield the corresponding 1-chloro-2,2-disubstituted-1-phenylethene (**3**; Table I; eq 1).



(1)

3

2a, R = H
b, R = OCH_3

The position of the olefinic double bond and the chlorine atom are not in doubt; various functional groups are not affected by this reaction; and the carbonyl compound may contain a double or triple bond.[2] ^{13}C NMR spectra were taken of a representative number of the trisubstituted vinyl chlorides from asymmetric ketones including those of **3f** and **3h**. In Figures 1 and 2 the peaks of the methyl groups of the ^{13}C NMR spectra of **3f** and **3h** are given. The larger of the two peaks is assigned to the least hindered E isomers. The ratio between the two peaks indicates the E/Z ratio. The exhibited spectra were in full agreement with the proposed structures for those compounds. The stereochemistry of the products seems to be readily explainable on the basis of steric hinderance. In all these compounds, **3e**, **3f**, and **3h**, practically only one isomer, the one with the large (in comparison to the alkyl groups) phenyl groups on opposite sides of the double bond, was obtained. With groups of comparable sizes, e.g., **3c**, the E and Z isomers were formed in virtually the same amounts. In addition to the stereochemistry the yields of the vinyl chlorides also seem to be governed by steric effects. The readily available starting materials and the ease of this reaction make this a simple and general method for the

(1) This paper is part 13 of the series Synthesis with α-Heterosubstituted Phosphonates. Part 12: Crenshaw, M. D.; Schmolka, S. J.; Zimmer, H.; Whittle, R.; Elder, R. C. *J. Org. Chem.* **1982**, *47*, 101.

(2) (a) Zimmer, H.; Bercz, P. J.; Maltenieks, O. J.; Moore, M. W. *J. Am. Chem. Soc.* **1965**, *87*, 2777. (b) Zimmer, H.; Hickey, K. R.; Schumacher, R. J. *Chimia* **1974**, *28*, 656.

(3) Petrova, J.; Coutrot, P.; Dreux, M.; Savignac, P. *Synthesis* **1975**, 658.

0022-3263/83/1948-2782$01.50/0