and washings were dried over anhydrous Na_2SO_4. After removal of the solvent the crude product was purified by distillation or flash chromatography. All products were identified by comparison of their ^1H NMR and IR spectra with those of authentic samples.

The polymer beads were recovered by filtration as described above, washed with ether (3 × 5 mL), acetonitrile (3 × 3 mL), and ether (3 × 3 mL), dried under vacuum, and reused for the next cycle of the reaction.

Electrolytic Oxidation of Diphenylmethane. Typical Procedure. Diphenylmethane (830 mg, 4.93 mmol), water (894 mg, 49.6 mmol), acetic acid (0.30 mL), and acetonitrile (2.70 mL), were placed in the cell, and then a mixture of PVP·HBr (522 mg) and PVP·H_2SO_4 (496 mg) was added. The electric current (20 mA) was passed with slow stirring at 40 °C. After 40 h the reaction mixture was filtered, the polymer beads were washed with ether (3 × 5 mL), and the combined filtrate and washings were dried over Na_2SO_4. After removal of the solvent, the crude product was purified by flash chromatography (hexane/ethyl acetate, 10:1) followed by bulb-to-bulb distillation to give 702 mg (78% yield) of benzophenone. The ^1H NMR and IR spectra were identical with those of an authentic material.

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Registry No. 1, 101-81-5; 2, 119-61-9; 3, 91-01-0; 4, 954-67-6; PVP·HBr, 82444-38-0; PVP·H_2SO_4, 91110-42-8; $C_6H_5CH_2CH_3$, 100-41-4; $C_6H_5CH_2CH_2CH_2CH_3$, 104-51-8; p-$CH_3OC_6H_4CH_2CH_3$, 1515-95-3; p-$CH_3COOC_6H_4CH_2CH_3$, 3245-23-6; $C_6H_5CH_3$, 108-88-3; p-$CH_3OC_6H_4CH_3$, 104-93-8; $C_6H_5COCH_3$, 98-86-2; $C_6H_5COCH_2CH_2CH_3$, 495-40-9; p-$CH_3OC_6H_4COCH_3$, 100-06-1; p-$CH_3COOC_6H_4COCH_3$, 13031-43-1; C_6H_5CHO, 100-52-7; p-$CH_3OC_6H_4CHO$, 123-11-5.

Nitrone Cycloadditions. An Efficient Method for the Homologation of Aldehydes to α,β-Unsaturated Aldehydes

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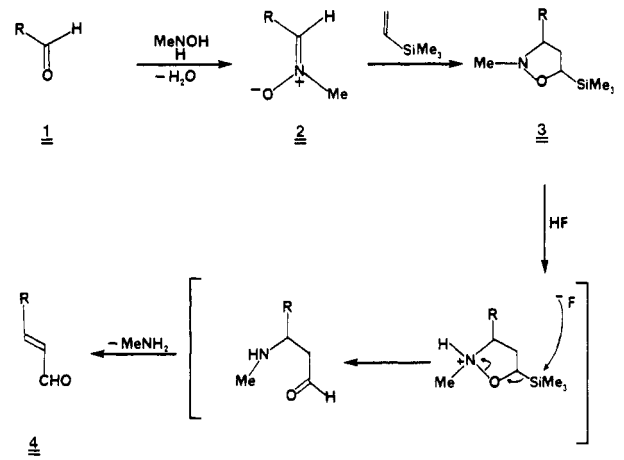
Homologation of an aldehyde into an α,β-unsaturated carbonyl compound with the introduction of two additional carbon atoms in the resulting chain is an important reaction in organic synthesis since the products are useful intermediates for further synthetic elaboration.[1] The Wittig reaction or the Emmons–Wadsworth–Horner modification of the Wittig reaction is most often employed to effect the transformation of an aldehyde into an olefinic ketone or ester derivative.[2] However, the direct conversion of an aldehyde to an α,β-unsaturated aldehyde cannot be performed by using Wittig methodology; therefore, alternative strategies have been developed to perform this conversion. Generally this involves the homologation of the aldehyde to the unsaturated ester followed by reduction with Dibal.

Scheme I



During the course of a study in our laboratory we required a method to homologate an aldehyde to an α,β-unsaturated aldehyde utilizing conditions which avoided basic or reducing reagents. Based upon earlier findings,[3] we decided to investigate the nitrone route shown in Scheme I to accomplish our objective. A nitrone route was especially appealing since we had previously demonstrated that the nitrones of aldehydes are readily prepared by the reaction of a *N*-methylhydroxylamine and the respective aldehyde. Cycloaddition of nitrones **2** with a variety of electron-rich,[3] as well as electron-deficient, dipolarophiles[3,4] was documented and the reaction with vinyltrimethylsilane was expected to produce the 5-(trimethylsilyl)-substituted isoxazolidine **3** on the basis of the results of Cunico[5] and Padwa.[6] Treatment of the (trimethylsilyl)isoxazolidine with HF would result in the protonation–fragmentation of the isoxazolidine followed by elimination of the β-amino substituent to produce the desired unsaturated aldehyde. In this paper, we report the first example of a nitrone cycloaddition to a vinylsilane and that the resulting cycloadducts **3** serve as precursors of α,β-unsaturated aldehydes as outlined in Scheme I. This methodology is especially significant because it allows for the homologation of aldehydes by two carbons while avoiding strongly basic reaction conditions.

The results summarized in Table I show that the nitrone route in Scheme I is an excellent alternative to Wittig chemistry for the preparation of unsaturated aldehydes. Aldehydes are readily converted into the corresponding nitrones in excellent yield (see Experimental Section). In all but one instance, only the (*Z*)-nitrone was obtained.[7] The crude nitrones could be utilized in subsequent reactions without a decrease in the yield of cycloadduct. Cycloaddition of the nitrones and vinyltrimethylsilane in a benzene solution resulted in the formation of the 5-(trimethylsilyl)-substituted isoxazolidine in good yield. A mixture of stereoisomers was formed in the cycloaddition;

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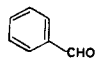
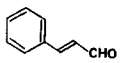
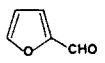
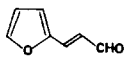
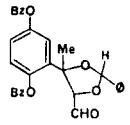
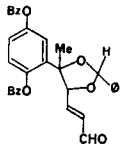
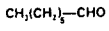
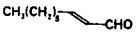
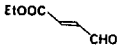
Table I. Conversion of Aldehydes to α,β-Unsaturated Aldehydes

aldehyde 1	yield of nitrone 2 (%)[b]	yield of (trimethylsilyl)-isoxazolidine 3 (%)[c]	yield of α,β-unsaturated aldehyde 4 (%)	overall[a] yield 1 → 4 (%)
 1a	95	94	 4a	95	81
 1b	89	63	 4b	77	43
 1c	79	84	 4c	75	50
 1d	78	62	 4d	59	29
 1e	85[d]	51	 4e[e]	72	31

[a] Unoptimized yield. [b] ^{1}H NMR analysis of the reaction mixture indicated that only the (*Z*)-nitrone was produced. [c] Yield of isolated, purified product. [d] 1.6:1.0 mixture of *Z* to *E*. [e] The aldehyde was extremely unstable and was converted to the hydrazone for analysis.

however, the stereoselectivity of the cycloaddition was not studied in detail since both stereocenters would be lost in the subsequent fragmentation of the isoxazolidine ring and expulsion of the amine. As predicted, treatment of the isoxazolidine **3** with HF/acetonitrile at room temperature for 1 min resulted in the formation of the α,β-unsaturated aldehyde. The resulting olefin always has the more stable *E* geometry, presumably due to postelimination isomerization of the double bond under the mildly acidic conditions. The presumed intermediate in the reaction—the β-amino aldehyde—was not detected in the reaction mixture.

It is noteworthy that the conditions of the HF-induced fragmentation are mild enough that even the acid-sensitive benzylidine group in **3c** withstands the reaction conditions. On the other hand, aldehyde **4e** was not stable under the reaction conditions and decomposed rapidly upon attempted chromatography. However, spectral data consistent with the proposed structure could be obtained. The structure of **4e** was confirmed by conversion of the aldehyde into the corresponding hydrazone.

The nitrone methodology developed above results in the homologation of an aldehyde to the α,β-unsaturated aldehyde in good overall yields (Table I). The advantage of the methodology is that it avoids the strongly basic conditions associated with Wittig chemistry and thus can be employed for the homologation of base-sensitive aldehydes.

Experimental Section

Melting points were taken in Kimax soft-glass capillary tubes by using a Thomas-Hoover Uni-Melt capillary melting point apparatus (Model 6406 K) equipped with a calibrated thermometer.

Proton magnetic resonance (NMR) spectra were recorded on Varian Associates analytical NMR spectrometers (Model EM-360) or a Bruker WP-200 or WP-360 Super Con spectrometer. Proton chemical shifts are reported in parts per million (δ) downfield from tetramethylsilane as an internal standard. Coupling constants (*J* values) are given in hertz and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Infrared spectra were recorded on a Perkin-Elmer Model 281B diffraction grating spectrophotometer. Peak positions are given in reciprocal centimeters and are listed as very strong (vs), strong (s), medium (m), or weak (w). Mass spectral data were obtained on a KRATOS MS-950 double-focusing high-resolution spectrometer or on a Finnigan 3200 twin EI and CI quadrapole mass spectrometer equipped with a Digital Equipment Corp. PDP 8/I computer. The chemical ionization carrier gas was methane.

Flash chromatography was performed by using thick-walled glass columns and medium-pressure silica (Merck, 32–63 μm) according to the method of Still.[8] All reported yields refer to isolated samples after treatment at high vacuum (0.1 torr) for 24 h to remove residual solvents.

Ether and benzene were distilled from sodium benzophenone ketyl. Acetonitrile was distilled from CaH_2.

General Method for Nitrone Formation. The aldehyde (1 mmol) dissolved in ether was added to a cooled (0 °C) solution of *N*-methylhydroxylamine hydrochloride, sodium bicarbonate (2 mmol), and calcium chloride (5 mmol) in ether. The mixture was stirred at 0 °C for 2 h and filtered. Evaporation in vacuo of the filtrates and flash chromatography of the residue provided pure (*Z*)-nitrone.

General Method for Formation of 5-(Trimethylsilyl)-isoxazolidines. A solution of the nitrone (1 mmol), freshly distilled vinyltrimethylsilane,[9] and benzene was stirred at reflux for 12–24 h. The reaction mixture was concentrated in vacuo, and flash chromatography of the residue provided a stereoisomeric mixture of 5-(trimethylsilyl)isoxazolidines.

General Method for Formation of α,β-Unsaturated Aldehydes. In a polyethylene reaction tube, the 5-(trimethylsilyl)isoxazolidine (1 mmol) was dissolved in acetonitrile (10 mL) to which 5 drops of a 50% HF (aq) solution was added. The solution was stirred for 0.5 h and then diluted with H_2O (5 mL). Solid K_2CO_3 was added until evidence of two layers was apparent. The top organic layer was drawn off while the aqueous layer was extracted (3 × 10 mL) with CH_2Cl_2. The organics were combined, dried (Na_2SO_4), and concentrated in vacuo. Flash chromatography of the residue provided the homologated α,β-unsaturated aldehyde.

α-Phenyl-*N*-methylnitrone (2a): mp 84–86 °C (lit.[10] mp 82–84 °C); NMR ($CDCl_3$) 3.81 (s, 3 H), 7.39 (m, 4 H), 8.22 (m,

(8) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
(9) Vinyltrimethylsilane purchased from Aldrich Chemical Co., Milwaukee, WI.
(10) Boyle, L.; Peagram, M.; Whitham, C. *J. Chem. Soc. B* **1971**, 1728.

2 H); IR (CCl_4) 3060 (m), 2950 (m), 1415 (vs) cm^{-1}.

***N*-Methyl-3-phenyl-5-(trimethylsilyl)isoxazolidine (3a)**: NMR ($CDCl_3$) 0.1 (s, 9 H), 1.8–2.9 (m, 2 H), 2.7 (s, 3 H), 3.2–3.9 (m, 2 H), 7.3 (m, 5 H); IR (neat) 3030 (m), 2960 (vs), 2840 (s), 1245 (vs) cm^{-1}.

α-Furyl-*N*-methylnitrone (2b): NMR ($CDCl_3$) 3.6 (s, 3 H), 6.3 (m, 1 H), 7.2 (m, 2 H), 7.5 (m, 1 H); IR (CCl_4) 3020 (w), 2940 (w), 1590 (w), 1410 (vs), 1145 (vs) cm^{-1}.

***N*-Methyl-3-furyl-5-(trimethylsilyl)isoxazolidine (3b)**: NMR ($CDCl_3$) 0.1 (s, 9 H), 1.9–2.6 (m, 2 H), 2.6 (s, 3 H), 3.1–3.8 (m, 2 H), 6.1 (m, 2 H), 7.2 (m, 1 H); IR (CCl_4) 2970 (m), 1255 (m), 1170 (vs) cm^{-1}; mass spectrum, *m/z* (relative intensity) 225 (M^+, 62), 210 (10), 73 (100).

β-Furylacrolein (4b): NMR ($CDCl_3$) 6.46 (dd, J = 1.8, 3.5, 1 H), 6.53 (dd, J = 7.9, 15.8, 1 H), 6.70 (d, J = 3.5, 1 H), 7.17 (d, J = 15.8, 1 H), 7.49 (d, J = 1.4, 1 H), 9.53 (d, J = 7.9, 1 H); IR (CCl_4) 3120 (w), 2805 (s), 2715 (s), 1685 (vs), 1630 (vs) cm^{-1}; mass spectrum, *m/z* (relative intensity) 122 (M^+, 100), 94 (45), 65 (40), 39 (31).

***N*-Methylnitrone 2c**: NMR ($CDCl_3$) 1.77 (s, 3 H), 3.19 (s, 3 H), 4.85 (A of AB q, J = 11.7, 1 H), 4.90 (B of AB q, J = 11.7, 1 H), 4.96 (A of AB q, J = 11.4, 1 H), 5.02 (B of AB q, J = 11.4, 1 H), 5.45 (d, J = 7.4, 1 H), 6.10 (s, 1 H), 6.74 (d, J = 7.4, 1 H), 6.8 (m, 2 H), 7.3 (m, 16 H); IR (CCl_4) 3030 (w), 2995 (m), 2830 (w), 1585 (m), 1490 (s) cm^{-1}; mass spectrum, *m/z* (relative intensity) 509 (M^+, 0.1), 280 (8), 91 (100).

***N*-Methyl-5-(trimethylsilyl)isoxazolidine 3c**: NMR ($CDCl_3$) 0.1 (s, 9 H), 1.8 (s, 3 H), 2.1–2.5 (m, 2 H), 2.3 (s, 3 H), 3.1 (m, 1 H), 3.3 (m, 1 H), 4.3 (m, 1 H), 5.1 (s, 2 H), 5.2 (s, 2 H), 5.9 (s, 1 H), 6.9 (m, 2 H), 7.3 (m, 16 H); IR (CCl_4) 3050 (m), 2970 (s), 2880 (s), 1480 (vs), 1200 (vs) cm^{-1}; mass spectrum, *m/z* (relative intensity), 609 (M^+, 0.1), 536 (2), 280 (14), 91 (100).

α,β-Unsaturated aldehyde 4c: NMR ($CDCl_3$) 1.46 (s, 3 H), 4.99 (dd, J = 1.1, 2.5, 1 H), 5.07 (s, 4 H), 5.74 (s, 1 H), 6.3 (m, 2 H), 6.9 (m, 2 H), 7.4 (m, 16 H), 8.86 (d, J = 7.5, 1 H); IR (CCl_4) 3050 (w), 2880 (w), 2730 (w), 1695 (vs) cm^{-1}; mass spectrum, *m/z* (relative intensity) 506 (M^+, 0.1), 332 (7), 91 (100). Anal. Calcd[11] for $C_{33}H_{30}O_5$: C, 78.22; H, 5.97. Found: C, 78.03; H, 6.12.

α-*n*-Hexyl-*N*-methylnitrone (2d): NMR ($CDCl_3$) 0.8–1.5 (m, 11 H), 2.3–2.7 (m, 2 H), 3.6 (s, 3 H), 6.7 (t, J = 7, 1 H); IR (neat) 3050 (w), 2930 (vs), 1605 (s), 1410 (vs) cm^{-1}; mass spectrum, *m/z* (relative intensity) 144 (M^+ + 1, 25), 86 (50), 73 (100).

***N*-Methyl-3-*n*-hexyl-5-(trimethylsilyl)isoxazolidine (3d)**: NMR ($CDCl_3$) 0.1 (s, 9 H), 0.8–1.0 (m, 3 H), 1.2–1.6 (m, 10 H), 1.8–2.4 (m, 3 H), 2.6 (s, 3 H), 3.1–3.9 (m, 1 H); IR (neat) 2960 (vs), 2860 (s), 1250 (s), 825 (vs), cm^{-1}; mass spectrum, *m/z* (relative intensity) 243 (M^+, 15) 227 (41), 170 (39), 158 (25), 140 (67), 73 (100).

2-Nonenal (4d): NMR ($CDCl_3$) 0.89 (m, 3 H), 1.29–1.57 (m, 8 H), 2.36 (ddt, J = 1.5, 6.8, 5.0, 2 H), 6.12 (ddt, J = 1.5, 7.9, 15.6, 1 H), 6.86 (dt, J = 6.8, 15.6, 1 H), 9.50 (d, J = 7.9, 1 H); IR (neat) 2940 (vs), 2740 (w), 1690 (vs), 890 (vs), 715 (vs) cm^{-1}; mass spectrum, *m/z* (relative intensity) 140 (M^+, 100).

α-Carbethoxy-*N*-benzylnitrone (2e) (E and Z mixture): NMR ($CDCl_3$) 1.3 (t, 3 H), 4.3 (q, 2 H), 5.5 (m, 2 H), 7.1 (s, 1 H), 7.4 (m, 5 H); IR (CCl_4) 3030 (w), 2980 (m), 1745 (s), 1140 (vs) cm^{-1}.

***N*-Benzyl-3-carbethoxy-5-(trimethylsilyl)isoxazolidine (3e)**: NMR ($CDCl_3$) 0.1 (s, 9 H), 1.1 (t, 3 H), 2.0–2.6 (m, 2 H), 3.3–4.2 (m, 6 H), 7.2 (s, 5 H); IR (neat) 3040 (m), 2960 (s), 2840 (m), 1745 (vs), 1185 (vs) cm^{-1}; mass spectrum, *m/z* (relative intensity) 307 (M^+, 15), 234 (22), 91 (100).

***p*-Nitrophenylhydrazone of 4e**: mp 158–162 °C; NMR (Me_2SO-d_6) 1.23 (t, J = 7.1, 3 H), 4.15 (q, J = 7.1, 2 H), 6.35 (d, J = 15.6, 1 H), 7.15 (A of AB q, J = 9.2, 2 H), 7.25 (dd, J = 15.6, 9.7, 1 H), 7.84 (d, J = 9.7, 1 H), 8.14 (B of AB q, J = 9.2, 2 H); IR (CCl_4) 3050 (w), 2940 (m), 1735 (m), 1610 (m), 1340 (vs) cm^{-1}.

Acknowledgment. We acknowledge the generous financial support of the Public Health Service (GM 30743-01). We thank Dr. Robert Minard and Mr. Greg Hancock for help in obtaining mass spectra and Mr. Alan Freyer and Dr. V. Elango for FT-NMR spectra.

(11) Elemental analyses were performed by Micro-Tech Laboratories, Skokie IL.

Registry No. **1a**, 100-52-7; **1b**, 98-01-1; **1c**, 91328-45-9; **1d**, 111-71-7; **1e**, 924-44-7; (*Z*)-**2a**, 7372-59-0; (*Z*)-**2b**, 91328-46-0; **2c**, 91328-47-1; (*Z*)-**2d**, 91328-48-2; (*E*)-**2e**, 81206-60-2; (*Z*)-**2e**, 81206-61-3; *cis*-**3a**, 91328-49-3; *trans*-**3a**, 91328-56-2; *cis*-**3b**, 91328-50-6; *trans*-**3b**, 91328-57-3; **3c**, 91328-51-7; *cis*-**3d**, 91328-52-8; *trans*-**3d**, 91328-58-4; *cis*-**3e**, 91328-53-9; *trans*-**3e**, 91328-59-5; (*E*)-**4a**, 14371-10-9; (*E*)-**4b**, 39511-08-5; **4c**, 91328-54-0; (*E*)-**4d**, 18829-56-6; (*E*)-**4e**, 2960-66-9; (*E*)-**4e** (*p*-nitrophenylhydrazone), 91328-55-1; MeNHOH·HCl, 4229-44-1; CH_2=$CHSiMe_3$, 754-05-2.

Reduction of 4-Cyanoisoxazoles with Lithium Aluminum Hydride. Synthesis of 5-Aminoisoxazoles

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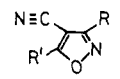
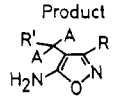
In the course of our investigations of the reduction of isoxazole derivatives with complex metal hydrides, 2-, 3-, and 4-isoxazolines have been selectively synthesized in good yields.[1-3] In order to obtain adequate reactivity of the isoxazole ring toward reduction, activation of the nucleus by quaternization of the nitrogen[1] or introduction of electron-accepting groups at C-4[2] is necessary. In particular, 3,5-dimethylisoxazoles with electron-withdrawing groups at C-4 on reaction with sodium borohydride are reduced to 2-isoxazolines regiospecifically.[2] Although the reduction of 4-cyano-3,5-dimethylisoxazole with sodium borohydride leads to the expected 4-cyano-2-isoxazoline,[2] surprisingly, we found that reduction of 4-cyano-3,5-dimethylisoxazole with lithium aluminum hydride leads to 5-amino-4-ethyl-3-methylisoxazole resulting from an unusual rearrangement.

The interest in 5-aminoisoxazoles as intermediates for the synthesis of derivatives with antihistaminic,[4] analgesic,[5] antibactericidal,[6] and insecticidal[7] activity led us to study

Table I. Reduction of 3,5-Disubstituted-4-cyanoisoxazoles 1a-c with Lithium Aluminum Hydride (1 Equiv) at 0 °C in Ether for 6 h

	Metal Complex Hydride	Product 	Yield %
1a, R=R'=CH_3	$LiAlH_4$	2a, R=R'=CH_3, A=H	55
1a, R=R'=CH_3	$LiAlD_4$	2b, R=R'=CH_3, A=D	55
1b, R=Ph, R'=CH_3	$LiAlH_4$	2c, R=Ph, R'=CH_3, A=H	75
1b, R=Ph, R'=CH_3	$LiAlD_4$	2d, R=Ph, R'=CH_3, A=D	75
1c, R=R'=Ph	$LiAlH_4$	2e, R=R'=Ph, A=H	45

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