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A New Synthesis of α-Phenylhomoallylnitriles from β-Nitrostyrene and Allylic Silanes

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Synopsis. $TiCl_4$-catalyzed addition of allylic silanes to β-nitrostyrene affords γ,δ-unsaturated nitronates which, on treatment with low valent titanium in situ generated from Ti(IV) and zinc, are smoothly converted to γ,δ-unsaturated nitriles in moderate yields.

Michael-type additions of enol silyl ethers[1)] and allylic silanes[2)] to nitroalkenes have been used for the synthesis of 1,4-dicarbonyl compounds. In these reactions, an appropriate Lewis acid ($TiCl_4$, $SnCl_4$, or $AlCl_3$) is used as activator of nitroalkenes. Among the Lewis acids employed, $TiCl_4$ may be regarded as a potential reductant since, on treatment with zinc, it generates low valent titanium compound which can reduce carbonyl compounds to pinacols or olefins.[3)] Based on this dual role of titanium compound, we have developed a new method of preparing α-phenylhomoallylnitriles **4**[4)] from allylic silanes **1** and β-nitrostyrene (**2**).

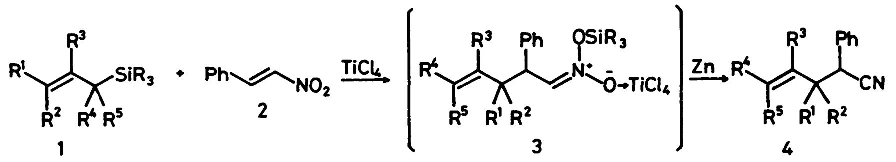
In the presence of $TiCl_4$, allylic silanes **1** react smoothly with β-nitrostyrene (**2**) to give γ,δ-unsaturated silyl nitronates **3**. Subsequent addition of zinc dust to the reaction mixture produces low valent titanium from $TiCl_4$, which then converts nitronates **3** to γ,δ-unsaturated nitriles **4**.[5)] Although the reaction is subject to extensive formation of phenylacetonitrile (**5**) as by-product, the yields of nitriles **4** are in most cases acceptable as shown in Table 1. In the absence of an allylic silane, β-nitrostyrene remained almost unaffected at low temperature, while by adding chlorodimethylphenylsilane or chlorotrimethylsilane instead of an allylic silane to the reaction system nitroolefin **2** was readily converted to nitrile **5** in good yield. Therefore, the formation of **5** as a common by-product would reasonably be attributed to the concurrent chlorinolysis of allylic silanes by $TiCl_4$.

Allylic groups usually entered into β-nitrostyrene (**2**) with allylic transposition (Entries 4—7).[6)] However, buten-3-ylsilane **1h** afforded a mixture of two regioisomers (**4h**:**4d**=32:13) (Entry 8), while 2-methyl-2-propenylsilane **1i** suffered hydrochlorination of double bond of the final product (Entry 9).

The present reaction not only offers a new synthetic route to γ,δ-unsaturated nitriles, but also demonstrates a successful use of titanium compound as Lewis acid and reductant in a simple one-pot procedure.[7)]

Experimental

Materials. Allylic silanes **1b** (bp 93 °C/2.27 kPa), **1h**[8)] (bp 106 °C/2.67 kPa), and **1i** (110 °C/3.07 kPa) were prepared from chlorodimethylphenylsilane and the Grignard reagents. Crotylsilane **1d** (bp 106 °C/2.67 kPa) and prenylsilane **1e** (bp 115—118 °C/2.00 kPa) were prepared from silyllithium and allylic halides according to the literature.[9)] Cinnamylsilane **1f** (bp 123 °C/27 Pa) was obtained by the reaction of a lithio derivative of allylbenzene with chlorodimethylphenylsilane. Allylic silane **1g** was prepared by our method.[10)] Titanium tetrachloride was used after distillation. Products were identified by mass, IR, and ^{1}H NMR spectra as well as by direct comparison with authentic specimens. Purification of the products was performed by a silica-gel column chromatography (Wakogel C-200; hexane–CH_2Cl_2



Scheme

Table 1. Homoallylnitriles Obtained from Allylic Silanes and β-Nitrostyrene

Entry		Allylic silane 1						Homoallylnitrile 4	Phenylacetonitrile 5	Other product
		SiR_3	R^1	R^2	R^3	R^4	R^5	Yield/%[a)]	Yield/%[a)]	Yield/%[a)]
1	a	$SiMe_3$	H	H	H	H	H	55	30	—
2	b	$SiMe_2Ph$	H	H	H	H	H	61	23	—
3	c	$SiPh_3$	H	H	H	H	H	69	15	—
4	d	$SiMe_2Ph$	Me	H	H	H	H	65[b)]	21	—
5	e	$SiMe_2Ph$	Me	Me	H	H	H	33	21	—
6	f	$SiMe_2Ph$	Ph	H	H	H	H	41[c)]	19	—
7	g	$SiMe_2Ph$	H	H	H	Me	CO_2Me	46	20	—
8	h	$SiMe_2Ph$	H	H	H	Me	H	32[d)]	22	13[e)]
9	i	$SiMe_2Ph$	H	H	Me	H	H	—	11	19[f)]

a) Isolated yields. b) Diastereomeric mixture (75:25 estimated by 400 MHz ^{1}H NMR). c) Diastereomeric mixture (67:33 estimated by 400 MHz ^{1}H NMR). d) Stereoisomeric mixture (*E*-**4h**:*Z*-**4h**=ca. 1:1). e) 3-Methyl-2-phenyl-4-pentenenitrile **4d**. f) 4-Chloro-4-methyl-2-phenylpentanenitrile.

as eluent) and/or preparative GPC (Japan Analytical Industry, LC-08; JAI-1H (20 mmIDX60 cm)+JAI-2H (20 mmIDX60 cm)).

General Procedure. To a stirred solution of β-nitrostyrene (**2**, 164 mg, 1.1 mmol) and an allylic silane (**1**, 1 mmol) in CH_2Cl_2 (10 ml) was added $TiCl_4$ (1 M** CH_2Cl_2 solution, 1.5 ml) at −15 °C under argon. After disappearance of **2** (ca. 2 h), dry THF and zinc dust (200 mg, 3 mmol) were added successively and the resulting dark purple mixture was stirred for another hour. The reaction was quenched by adding aqueous $NaHCO_3$ and ether. The suspension was then filtered through a Celite pad. The filtrate was separated and the aqueous layer was extracted twice with ether. The combined extracts were washed with brine and dried over Na_2SO_4. Evaporation of the solvent gave an oily material which was chromatographed on silica gel.

2-Phenyl-4-pentenenitrile 4a. 60 MHz ^1H NMR (CCl_4) δ= 2.58 (2H, t, J=7 Hz), 3.78 (1H, t, J=7 Hz), 5.12 (2H, m), 5.68 (1H, ddt, J=16, 10, and 7 Hz), and 7.30 (5H,m); IR (NaCl) 3047 (m), 3010 (m), 2975 (m), 2960 (m), 2900 (m), 2225 (m), 1635 (s), 1450 (s), 990 (m), 920 (s), 750 (vs), and 690 cm^{-1} (vs); MS m/z (rel intensity) 157 (M^+, 63), 117 (37), 116 (100), and 90 (98).

3-Methyl-2-phenyl-4-pentenenitrile 4d. 400 MHz ^1H NMR ($CDCl_3$) (major isomer) δ=1.12 (3H, d, J=6.7 Hz), 2.66 (1H, m), 3.82 (1H, d, J=11.6 Hz), 5.15 (2H, m), 5.75 (1H, m), and 7.30 (5H, m); (minor isomer) δ=1.14 (3H, d, J=7.6 Hz), 2.66 (1H, m), 3.73 (1H, d, J=6.4 Hz), 5.05 (2H, m), 5.75 (1H, m), and 7.30 (5H, m); IR (NaCl) 3080 (m), 3055 (m), 2960 (vs), 2925 (m), 2230 (m), 1640 (m), 1490 (s), 1455 (vs), 995 (s), 925 (vs), 750 (s), and 700 cm^{-1} (vs); MS m/z (rel intensity) 171 (M^+, 24), 117 (59), 116 (100), 115 (100), and 90 (21).

3,3-Dimethyl-2-phenyl-4-pentenenitrile 4e. 60 MHz ^1H NMR (CCl_4) δ=1.16 (6H, s), 3.50 (1H, s), 5.02 (2H, m), 5.80 (1H, dd, J=16 and 10 Hz), and 7.20 (5H, m); IR (NaCl) 2955 (vs), 2920 (m), 2235 (w), 1490 (s), 1450 (s), 1000 (m), 730 (vs), and 700 cm^{-1} (vs); MS m/z (rel intensity) 185 (M^+, 15), 117 (100), 116 (80), 115 (22), and 90 (16).

2,3-Diphenyl-4-pentenenitrile 4f. Colorless solids; mp 116—117 °C; 400 MHz ^1H NMR ($CDCl_3$) (major isomer) δ=3.72 (1H, t, J=7 Hz), 4.07 (1H, d, J=7 Hz), 5.17 (2H, m), 6.05 (1H, ddd, J=16, 10, and 7 Hz), and 7.20 (10H, m); (minor isomer) δ=3.68 (1H, t, J=7 Hz), 4.15 (1H, d, J=7 Hz), 5.17 (2H, m), 6.23 (1H, ddd, J=16, 10, and 7 Hz), and 7.20 (10H, m); IR (NaCl) 3050 (m), 3000 (m), 2945 (s), 2910 (s), 2195 (vw), 1450 (m), 1110 (vs), 790 (vs), 745 (m), and 695 cm^{-1} (vs); MS m/z (rel intensity) 234 (M^+, 4), 207 (3), 119 (84), 118 (100), and 117 (100); Anal. Found: C, 87.25; H, 6.53; N, 5.85%. Calcd for $C_{17}H_{15}N$: C, 87.51; H, 6.48; N, 6.00%.

Methyl 5-Cyano-2-methyl-5-phenyl-2-pentenoate 4g. 60 MHz ^1H NMR ($CDCl_3$) δ=1.76 (3H, broad s), 2.72 (2H, t, J=7 Hz), 3.70 (3H, s), 3.86 (1H, t, J=7 Hz), 6.64 (1H, m), and 7.29 (5H, m); IR (NaCl) 2930 (m), 2910 (m), 2225 (m), 1710 (vs), 1450 (s), 1120 (vs), 740 (s), and 690 cm^{-1} (vs); MS m/z (rel intensity) 229 (M^+, 26), 143 (14), 128 (15), and 117 (100).

2-Phenyl-4-hexenenitrile 4h. 400 MHz ^1H NMR ($CDCl_3$) (cis isomer) δ=1.55 (3H, d, J=7.0 Hz), 2.67 (2H, m), 3.80 (1H, m), 5.43 (1H, m), 5.65 (1H, dq, J=10.1 and 7.0 Hz), and 7.32 (5H, m); (trans isomer) δ=1.70 (3H, d, J=6.1 Hz), 2.56 (2H, m), 3.80 (1H, m), 5.43 (1H, m), 6.59 (1H, dq, J=15.6 and 6.1 Hz), and 7.32 (5H, m); IR (NaCl) 3020 (m), 2960 (m), 2910 (m), 2245 (m), 1600 (m), 1495 (s), 1455 (vs), 970 (s), 760 (s), and 700 cm^{-1} (vs); MS m/z (rel intensity) 171 (M^+, 39), 117 (100), 116 (96), and 90 (49).

4-Chloro-4-methyl-2-phenylpentanenitrile. 400 MHz ^1H NMR ($CDCl_3$) δ=1.63 (3H, s), 1.78 (3H, s), 2.22 (1H, dd, J=15.0 and 3.1 Hz), 2.47 (1H, dd, J=15.0 and 9.8 Hz), 4.18 (1H, dd, J=9.8 and 3.1 Hz), and 7.40 (5H, m); IR (NaCl) 3010 (m), 2230 (m), 1600 (m), 1490 (s), 1450 (s), 1115 (s), 750 (s), and 700 cm^{-1} (vs); MS m/z (rel intensity) 209 (M^++2, 4), 207 (M^+, 9), 172 (18), 157 (7), 131 (100), 130 (13), 129 (40), 128 (14), 117 (57), and 116 (81).

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**1M=1mol dm^{-3}.