

A Two-Step Hydroformylation of Alkynes

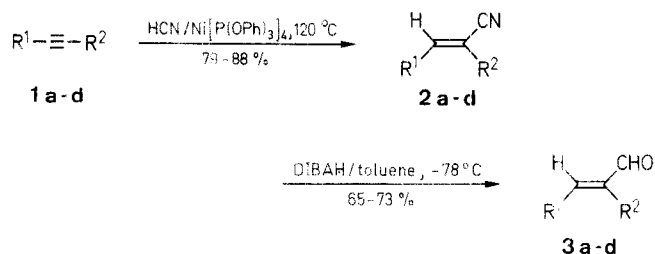
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A good-yielding, highly selective hydroformylation protocol for alkynes, involving nickel(0)-catalysed hydrocyanation, previously reported by us,^{4,5} followed by diisobutylaluminum hydride reduction, is presented.

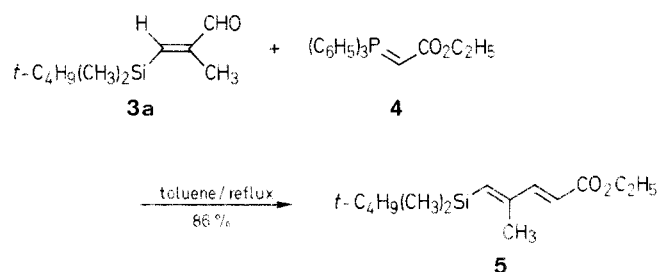
The hydroformylation (or oxo) reaction has found important applications in several commercial processes.^{1,2} The reaction involves transition metal-catalysed addition of the elements of H and CHO to a double bond. Many attempts to achieve a similar result with alkynes have been made but all have met with serious problems of low yields, lack of selectivity and over-reduction.³

Recently we demonstrated the hydrocyanation of alkynes **1** using nickel(0) catalyst to give the nitriles **2** in high-yield.⁴ Furthermore, with judicious choice of substituents, high degrees of regio- and stereochemical control can often be achieved.^{5,6,7} It seemed that these nitriles **2** were reasonable synthetic precursors to enals, the formal products of alkyne hydroformylation.



A few attempts to reduce α,β -unsaturated nitriles have been reported.⁸ Although diisobutylaluminum hydride (DIBAH) is often the reagent of choice in nitrile reductions,⁹ we found that the solvent plays a crucial role in the case of α,β -unsaturated systems. Thus, attempted reduction of compounds **2 a-d** with DIBAH in tetrahydrofuran under a variety of conditions gave complex mixtures of products. However switching to DIBAH in *toluene* gave reproducibly good yields of a single enal in each case (Table 1).⁸

Several of the enals do not keep well for any considerable length of time. However they may be isolated by vacuum distillation in pure form, suitable for further manipulation. For example **3a** reacts smoothly with phosphorane **4** in toluene¹⁰ to give the diene **5** in 86% yield.



Alternatively, the aldehydes could be characterized as 2,4-dinitrophenylhydrazone derivatives.¹¹

Boiling points are uncorrected and refer to oven temperature for Kugelrohr distillation and serve as a guide only. IR spectra were recorded on a Jasco IRA-1 spectrometer. ¹H-NMR spectra were recorded on a Varian EM-360A at 60 MHz and on a Bruker AM-300 at 300 MHz. Alkyne **1d** is a commercial product and alkynes **1a, b** and **c** were prepared as described previously.^{5,7} The α,β -unsaturated nitriles

Table 1. Yields of Nitriles **2** and Aldehydes **3**^a

Alkyne (1)	R ¹	R ²	Nitrile (2) ^b	Aldehyde (3)
a	<i>t</i> -C ₄ H ₉ (CH ₃) ₂ Si	CH ₃	88 ⁵	68
b	<i>t</i> -C ₄ H ₉ (CH ₃) ₂ Si	<i>n</i> -C ₄ H ₉	85 ⁵	72
c	H	CH ₂ CH ₂ OCH ₂ OCH ₃	79 ⁷	73
d	C ₆ H ₅	C ₆ H ₅	85 ⁴	65

^a Yields of distilled product.

^b The nitriles were separated from a small amount of a regioisomer by radial chromatography.

Table 2. Physical and Spectroscopic Data for Aldehydes **3**

Aldehyde	b.p. (°C)/mbar or m.p. (°C)	Molecular Formula ^a or Lit. m.p. (°C)	IR (Film) ν (cm ⁻¹)	¹ H-NMR (C ₆ D ₆) δ, J (Hz)	MS (70 eV) m/e (%)
3a	100/0.4	C ₁₀ H ₂₀ OSi (168.1)	see experimental		
3b	100/0.4	C ₁₃ H ₂₆ OSi (226.2)	1690, 1600	0.20 [s, 6H, Si(CH ₃) ₂]; 0.92 (m, 3H, CH ₃); 0.94 (s, 9H, <i>t</i> -C ₄ H ₉); 1.33 [m, 4H, (CH ₂) ₂ CH ₃]; 2.31 (t, 2H, CH ₂ C=, <i>J</i> = 7.5); 6.65 (s, 1H, =CH); 9.4 (s, 1H, CHO)	226 (M ⁺ , 1), 185 (20), 169 (20), 75 (100)
3c	130/20	C ₇ H ₁₂ O ₃ (144.2)	1680, 1595	2.56 (t, 2H, CH ₂ C=, <i>J</i> = 6.6); 3.34 (s, 3H, OCH ₃); 3.65 (t, 2H, CH ₂ O, <i>J</i> = 6.6); 4.60 (s, 2H, OCH ₂ O); 6.08 (s, 1H, (Z)-HC=); 6.38 (s, 1H, (E)-HC=); 9.54 (s, 1H, CHO)	—
3c	— ^c	C ₁₃ H ₁₆ N ₄ O ₆ (324.1)	—	2.79 (t, 2H, CH ₂ =C, <i>J</i> = 6.8); 3.38 (s, 3H, OCH ₃); 3.81 (t, 2H, CH ₂ O, <i>J</i> = 6.8); 4.67 (s, 2H, OCH ₂ O); 5.58 [s, 1H, (E)-HC=]; 5.70 [s, 1H, (Z)-HC=]; 7.81 (s, 1H, HC=N); 7.94 (d, 1H, H-6', <i>J</i> = 9.6); 8.32 (dd, 1H, H-5', <i>J</i> = 9.6, 2.3); 9.13 (d, 1H, H-3', <i>J</i> = 2.3); 11.15 (s, 1H, NH)	324 (M ⁺ , 1)
3d	93.5-94	95 ¹²	1690, 1600 ^d	7.15-7.5 (m, 11H, C ₆ H ₅ and =CH); 9.8 (s, 1H, CHO)	208 (M ⁺ , 100), 179 (80), 178 (25), 165 (28), 152 (20), 105 (50), 102 (35), 91 (35), 77 (30), 51 (20)

^a Satisfactory microanalyses obtained: C ± 0.3, H ± 0.3.

^b Recorded at 300 MHz, except for **3d**.

^c M.p. of the 2,4-DNP derivative: 112°C.

^d In CHCl₃.

2a–d were prepared as described in the literature.^{4,5,7} DIBAH is available commercially as a 1.5 M solution in toluene. All reactions were carried out under an atmosphere of N₂ using degassed solvents.

(E)-2-Methyl-3-(*t*-butyldimethylsilyl)propenal (3a); Typical Procedure:

To a solution of the nitrile **2a** (0.55 g, 3 mmol) in dry toluene (5 mL) cooled to -78°C is added a 1.5 M solution of DIBAH in toluene (2.4 mL). The solution is stirred at -78°C for 3 h and then poured onto a mixture of cold 5% H₂SO₄ (20 mL) and ether (20 mL). After stirring for 30 min at 0°C , the ether layer is separated, washed with saturated brine (20 mL), dried (MgSO₄), filtered and evaporated. The crude aldehyde is purified by distillation (Kugelrohr), **3a**; yield: 0.4 g (72%); b.p. $100^{\circ}\text{C}/0.4\text{ mbar}$.

C₁₀H₂₀OSi calc. C 65.2 H 10.9

(168.1) found 65.4 10.9

IR (Film): $\nu = 1695, 1600\text{ cm}^{-1}$.

¹H-NMR (CDCl₃): $\delta = 0.22$ [s, 6H, Si(CH₃)₂]; 0.96 (s, 9H, *t*-C₄H₉); 1.92 (s, 3H, CH₃); 6.75 (s, 1H, =CH); 9.45 (s, 1H, CHO).

MS: m/e (%) = 168 (M⁺, 1), 141(43), 138(45), 127(50), 125(27), 124(56), 111(28), 97(25), 84(29), 75(100), 73(43), 59(44), 57(22), 43(27).

2,4-Dinitrophenylhydrazone of 3a: m.p. 199°C (benzene/light petroleum).

MS: $m/e = 364.159 \pm 0.003$ (M⁺, C₁₆H₂₄N₄O₄Si requires 364.157).

¹H-NMR (CDCl₃): $\delta = 0.20$ [s, 6H, Si(CH₃)₂]; 0.94 (s, 9H, *t*-C₄H₉); 2.11 (s, 3H, CH₃); 6.12 (s, 1H); 7.78 (s, 1H, CH=N); 7.97 (d, 1H, H-6', $J = 9.5\text{ Hz}$); 8.3 (dd, 1H, H-5', $J = 9.5, 2\text{ Hz}$); 9.13 (d, 1H, H-3', $J = 2\text{ Hz}$); 11.13 (s, 1H, NH).

MS: m/e (%) = 364 (M⁺, 2), 307(100), 98(25), 75(28).

Physical and spectroscopic data for aldehydes **3b–d** are summarized in Table 2.

(E,E)-Ethyl 4-methyl-5-*tert*-butyldimethylsilylpent-2,4-dienoate (5):

To a solution of the phosphorane **4** (0.28 g, 0.81 mmol) in toluene (4 mL) is added dropwise a solution of the aldehyde **3a** (0.1 g, 0.54 mmol) in toluene (4 mL). The solution is heated under reflux for 18 h after which the solvent is removed under reduced pressure. The crude oil is purified by radial chromatography on silica gel (eluent: ether/pentane, 1:10) to afford **6a**; yield: 0.12 g (86%); b.p. $120^{\circ}\text{C}/2.7\text{ mbar}$.

C₁₄H₂₆O₂Si calc. C 66.1 H 10.3

(254.2) found 66.1 10.0

IR (film): $\nu = 1720, 1620\text{ cm}^{-1}$.

¹H-NMR (CDCl₃): $\delta = 0.12$ [s, 6H, Si(CH₃)₂]; 0.89 (s, 9H, *t*-C₄H₉); 1.29 (t, 3H, CH₂CH₃, $J = 7.1\text{ Hz}$); 1.91 (d, 3H, CH₃, $J = 0.7\text{ Hz}$); 4.20 (q, 2H, CH₂CH₃, $J = 7.1\text{ Hz}$); 5.81 (d, 1H, H-2, $J = 15.8\text{ Hz}$); 5.99 (s, 1H, H-5); 7.29 (dd, 1H, H-3, $J = 15.8, 0.7\text{ Hz}$).

MS: m/e (%) = M⁺ not observed, 197(56), 169(28), 149(50), 131(18), 119(20), 109(18), 103(28), 97(30), 95(27), 85(28), 83(28), 75(100), 73(75), 73(40), 69(50), 57(80), 55(48).

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