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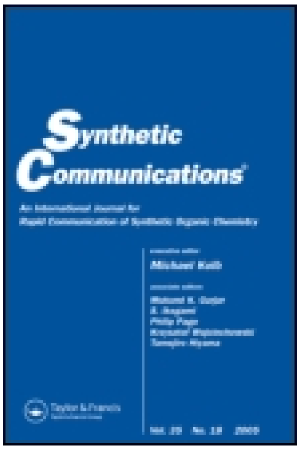

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APPLICATION OF TMSOTf IN THE BAYLIS-HILLMAN ADDUCTS

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APPLICATION OF TMSOTf IN THE BAYLIS-HILLMAN ADDUCTS

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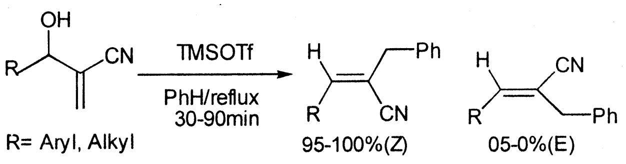
ABSTRACT

A simple and convenient methodology for the stereoselective construction of 2-benzyl substituted trisubstituted olefins[1,2] via TMSOTf catalyzed reaction of benzene with Baylis-Hillman adducts is described.

As part of our research program in Baylis-Hillman reaction,[3] I have undertaken the investigation of the reactions of benzene with representative 3-hydroxy-2-methylenealkanenitriles and methyl 3-hydroxy-2-methylene-alkanoates in the presence of trimethylsilyl trifluoromethanesulfonate[4] (**TMSOTf**).

First I have examined the reaction of benzene (5 ml) with 3-hydroxy-2-methylene-3-phenyl-propanenitrile (**1a**) (0.346 g, 2 mM) in the presence of TMSOTf (0.222 g, 1 mM) was refluxed for about 30 minutes. (2Z)-2-benzyl-3phenylprop-2-enenitrile (**2a**) was obtained in 86% yield (0.4371 g) after usual workup followed by column chromatography (2% ethyl acetate in hexane) in high stereoselectivity (97% (**Z**)-selectivity as evidenced by the ^{1}H NMR spectral analysis).

Encouraged by this observation, a variety of the Baylis-Hillman adducts (**1b–1f**) under the same conditions afforded the desired (2Z)-2-benzylalk-2-enenitriles (**2b–2f**) in high stereoselectivity (**Table 1**) (**eq. 1**).

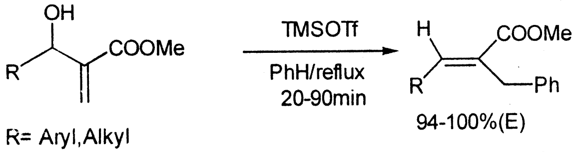


1a-1f **2a-2f**

To generalize this observation, a variety of 3-hydroxy-2-methylene alkanoates (**3a–3f**) on reaction with benzene in the presence of TMSOTf under reflux temperature afforded the desired (2E)-2-benzyl-3-phenylalk-2-enoates (**4a–4f**) in high (**E**)-stereoselectivity (**eq. 2**) (**Table 2**).

From these results, it is quite clear that nitriles (**2a–2f**) and esters (**4a–4f**) provide 2-benzyl substituted functionalized alkenes with opposite stereochemistry. This observation is consistent with our earlier results and may be explained by considering the difference in steric demands between the nitrile and ester groups.[5–7]

In conclusion, this methodology describes a simple stereoselective synthesis of (**Z**)- and (**E**)-2-benzyl substituted functionalized alkenes thus demonstrating the efficiency of trimethylsilyl trifluoromethane sulfonate.



3a-3f **4a-4f**

Table 1. TMSOTf Catalyzed Reaction of Benzene with 3-Hydroxy-2-methylene-alkanenitriles

Substrate	R	Reaction Time (minutes)	Product	Yield (%)	Z:E
1a	Phenyl	30	**2a**	86	97:03
1b	p-methylphenyl	30	**2b**	83	100:0
1c	p-chlorophenyl	30	**2c**	81	100:0
1d	p-isopropylphenyl	30	**2d**	83	100:0
1e	o-methylphenyl	45	**2e**	79	96:04
1f	n-pentyl	90	**2f**	64	95:5

Table 2. TMSOTf Catalyzed Reaction of Benzene with 3-Hydroxy-2-methylene-alkanoates

Substrate	R	Reaction Time (minutes)	Product	Yield (%)	Z:E
3a	Phenyl	20	**4a**	79	0:100
3b	p-methylphenyl	30	**4b**	81	0:100
3c	p-chlorophenyl	30	**4c**	83	05:95
3d	p-isopropylphenyl	30	**4d**	80	0:100
3e	o-methylphenyl	40	**4e**	78	04:96
3f	n-pentyl	90	**4f**	69	06:94

EXPERIMENTAL SECTION

Infrared spectra (**IR**) were recorded with a Perkin-Elmer 1310 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded at 200 and 50 MHz, respectively. Elemental analyses were recorded on Perkin-Elmer 240C-CHN analyzer.

All the required starting materials were obtained as follows:

Molecules **1a–1f** and **3a–3f** were prepared by the reaction of the corresponding aldehydes with acrylonitrile and methyl acrylate in presence of a catalytic amount of DABCO according to the literature procedure.[8–10]

General Procedure for the Preparation of 2a–2f and 4a–4f

To a stirred solution of alcohol (**1a–1f, 3a–3f**) (2 mM) in dry benzene (5 mL), was added TMSOTf (0.222 g, 1 mM) at room temperature and heated under reflux for the time specified in the Table. Then the reaction mixture was cooled and diluted with ether (20 mL), and washed successively with water and aqueous K_2CO_3 solution. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated. The crude product thus obtained was purified by column chromatography (silicagel, 2% ethyl acetate in hexane) to afford the desired product (**2a–2f**, **4a–4f**) as colourless liquid. All compounds gave satisfactory spectral data (1R, ^{1}H NMR and ^{13}C NMR) and elemental analysis. Stereochemical assignment and isomeric purities were based on difference in chemical shifts and integration ratios of isomeric β-allylic protons in ^{1}H NMR analysis.

(2Z)-2-Benzyl-3-phenylprop-2-enenitrile(2a): ^{1}H NMR: δ 3.73 (s, 2H), 6.94 (s, 1H), 7.22–7.45 (m, 8H), 7.63–7.76 (m, 2H); ^{13}C NMR: δ 35.46, 42.08, 110.67, 118.63, 127.29, 128.64, 128.72, 128.83, 130.05, 133.52, 136.45, 143.98. IR (neat): 2210, 1622 cm^{-1}; Elemental Analysis calculated for $C_{16}H_{13}N$: C, 87.63; H, 5.97; N, 6.38 and found C, 87.92; H, 5.95; N, 6.42.

(2Z)-2-Benzyl-3-(4-methylphenyl)prop-2-enenitrile(2b): ^{1}H NMR (200 MHz) ($CDCl_3$): δ 2.35 (s, 3H), 3.66 (s, 2H), 6.91 (s, 1H), 7.17–7.45 (m, 7H), 7.61 (d, 2H, J = 8 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.13, 41.82, 109.18, 118.68, 126.91, 128.57, 129.27, 130.61, 136.58, 140.21, 143.78; IR (neat); 2210, 1610 cm^{-1}; Elemental Analysis calculated for $C_{17}H_{15}N$: C, 87.51; H, 6.48; N, 6.00 and found C, 87.48; H, 6.50; N, 5.97.

(2Z)-2-Benzyl-3-(4-chlorophenyl)prop-2-enenitrile(2c): ^{1}H NMR: δ 3.60 (s, 2H), 6.81 (s, 1H), 7.14–7.39 (m, 7H), 7.59 (d, 2H, J = 8.0 Hz). ^{13}C NMR: δ 41.91, 111.43, 118.33, 127.37, 128.85, 128.91, 129.87, 131.91, 135.87, 136.17, 142.49. IR (neat): 2212, 1624 cm^{-1}; Elemental Analysis calculated for $C_{16}H_{12}NCl$: C, 75.74; H, 4.76; N, 5.52 and found C, 75.54; H, 4.76; N, 5.57.

(2Z)-2-Benzyl-3-(4-isopropylphenyl)prop-2-enenitrile(2d): ^{1}H NMR: δ 1.32 (d, 6H, J = 6.8 Hz), 2.92 (sept, 1H, J = 6.8 Hz), 3.74 (s, 2H), 6.91 (s, 1H), 7.23–7.42 (m, 7H), 7.71 (d, 2H, J=8.3 Hz); ^{13}C NMR: δ 23.67, 34.00, 42.15, 109.49, 118.89, 126.87, 127.27, 128.82, 131.23, 136.67, 144.01, 151.36; IR (neat): 2210, 1606 cm^{-1}; Elemental Analysis calculated for $C_{19}H_{19}N$: C, 87.31; H, 7.33; N, 5.36 and found C, 87.56; H, 7.30; N, 5.37.

(2Z)-2-Benzyl-3-(2-methylphenyl)prop-2-enenitrile(2e): ^{1}H NMR (200 MHz) ($CDCl_3$): δ 2.32 (s, 3H), 3.68 (s, 2H), 6.98 (s, 1H), 7.13–7.44 (m, 7H), 7.63 (d, 2H, J = 8 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.12, 41.80, 109.12, 118.69, 126.89, 128.54, 129.23, 130.64, 136.51, 140.22, 143.72; IR (neat): 2214, 1613 cm^{-1}; Elemental Analysis calculated for $C_{17}H_{15}N$: C, 87.51; H, 6.48; N, 6.00 and found C, 87.46; H, 6.53; N, 6.02.

(2Z)-2-Benzyloct-2-enenitrile(2f): ^{1}H NMR: δ 0.91 (dist. t, 3H), 1.14–1.58 (m, 6H), 2.32–2.53 (m, 2H), 3.52 (s, 2H), 6.22 (t, 1H, 7.6 Hz), 7.16–7.44 (m, 5H); ^{13}C NMR: δ 13.78, 22.24, 28.10, 31.12, 31.36, 40.23, 114.09, 117.38, 126.98, 128.62, 136.68, 148.64 IR (neat): 2212, 1624 cm^{-1} Elemental Analysis calculated for $C_{15}H_{19}N$: C, 84.45; H, 8.98; N, 6.56 and found C, 84.16; H, 6.92; N, 6.57.

Methyl(2E)-2-benzyl-3-phenylprop-2-enoate(4a): ^{1}H NMR: δ 3.74 (s, 3H), 3.93 (s, 2H), 7.92 (s, 1H), 7.12–7.49 (m, 10H). ^{13}C NMR: δ 33.15, 51.97, 126.09, 127.83, 128.54, 128.67, 129.17, 130.74, 134.96, 135.37, 139.41, 140.83, 168.52. IR (neat): 1714, 1631 cm^{-1}; Elemental Analysis calculated for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39 and found C, 80.76; H, 6.42.

Methyl (2E)-2-benzyl-3-(4-methylphenyl)prop-2-enoate(4b): ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.32 (s, 3H), 3.74 (s, 3H), 3.97 (s, 2H), 7.13–7.36 (m, 9H), 7.91 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.05, 33.07, 51.74, 125.95, 127.71, 128.07, 128.35, 129.14, 19.68, 132.30, 138.73, 139.33, 140.77, 168.42; IR (neat): 1713, 1632 cm^{-1}; Elemental Analysis calculated for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81 and found C, 81.08; H, 6.80.

Methyl(2E)-2-benzyl-3-(4-chlorophenyl)prop-2-enoate(4c): ^{1}H NMR: δ 3.76 (s, 3H), 3.93 (s, 2H), 7.86 (s, 1H), 7.12–7.41 (m, 9H); ^{13}C NMR: δ 33.13, 51.57, 52.16, 126.27, 127.84, 128.23, 128.65, 128.83, 129.57, 130.51, 131.38, 133.75, 134.71, 139.07, 139.52, 168.38. IR (neat): 1712, 1631 cm^{-1}; Elemental Analysis calculated for $C_{17}H_{15}O_2Cl$: C, 71.20; H, 5.27 and found C, 71.48; H, 5.28.

Methyl(2E)-2-benzyl-3-(4-isopropylphenyl)prop-2-enoate(4d): ^{1}H NMR: δ 1.26 (d, 6H, J=6.8 Hz), 2.93 (sept, 1H, J=6.8 Hz), 3.73 (s, 1H), 4.21 (s, 2H), 7.09–7.43 (m, 9H), 7.89 (s, 1H); ^{13}C NMR: δ 23.79, 33.21, 33.97, 51.97, 126.04, 126.71, 127.91, 128.55, 129.49, 129.77, 132.87, 139.52, 141.06, 149.87, 168.77; IR (neat): 1712, 1630 cm^{-1}; Elemental Analysis calculated for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53 and found C, 81.88; H, 7.52.

Methyl(2E)-2-benzyl-3-(2-methylphenyl)prop-2-enoate(4e): ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.38 (s, 3H), 3.72 (s, 3H), 3.84 (s, 2H), 7.12–7.38 (m, 9H), 7.92 (s, 1H); ^{13}C NMR (50 MHz), $CDCl_3$): 21.08, 33.02, 51.76, 125.92, 127.74, 128.05, 128.38, 129.12, 19.66, 132.30, 138.71, 139.30, 140.72, 168.41; IR (neat): 1714, 1631 cm^{-1}; Elemental Analysis calculated for $C_{18}H_{18}O_2$; C, 81.17; H, 6.81 and found C, 81.04; H, 6.83.

2-Benzyloct-2-enoate(4f): ^{1}H NMR: δ 0.92 (dist.t, 3H), 1.121.56 (m, 6H), 2.48 (q, 2H), 3.52 (s, 2H), 6.22 (t, 1H, 7.6 Hz), 7.16–7.44 (m, 5H); ^{13}C NMR: δ 13.78, 22.24, 28.10, 31.12, 31.36, 40.23, 114.09, 117.38, 126.98, 128.62, 136.68, 148.64; IR (neat): 2212, 1624 cm^{-1}; Elemental Analysis calculated for $C_{16}H_{22}O_2$: C, 78.00; H, 9.00 and found C, 77.74; H, 8.93.

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