

Methanolic trimethylamine mediated Baylis–Hillman reaction

Deevi Basavaiah,* Anumolu Jagannathan Rao, and Marimganti Krishnamacharyulu

School of Chemistry, University of Hyderabad, Hyderabad - 500 046, India

E-mail: dbsc@uohyd.ernet.in

Dedicated to Professor S. V. Kessar on his 70th birthday

(received 03 Jun 02; accepted 14 Aug 02; published on the web 22 Aug 02)

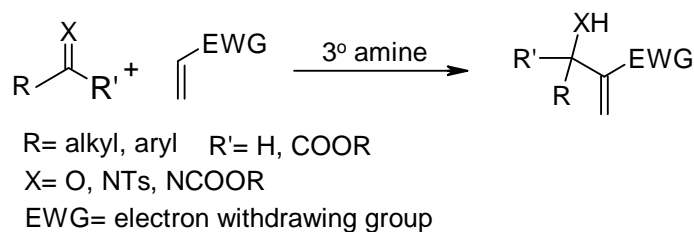
Abstract

Application of methanolic trimethylamine, the tertiary amine containing minimum number of carbon atoms with lowest possible molecular weight, for mediating the Baylis–Hillman coupling of various aldehydes with activated olefins *viz.* methyl acrylate, acrylonitrile and acrolein is described.

Keywords: Baylis–Hillman reaction, methanolic trimethylamine, methyl acrylate, acrylonitrile, acrolein

Introduction

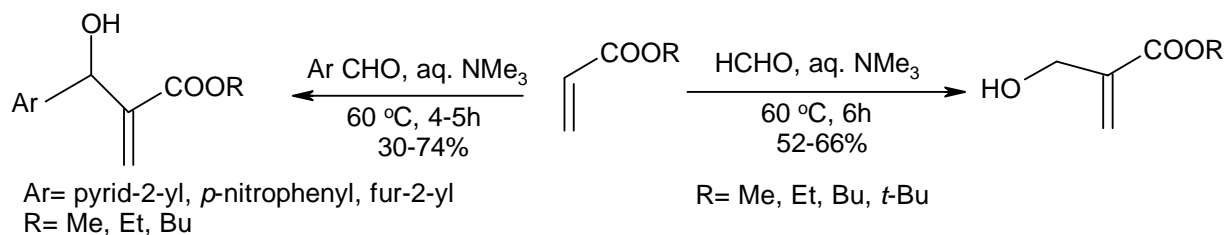
The Baylis–Hillman reaction is an important three components reaction involving an atom economical construction of carbon–carbon bonds, between the α -position of an activated vinylic systems and carbon electrophiles under the influence of tertiary amines (most commonly DABCO), and producing an interesting class of synthetically useful densely functionalized molecules (Eq. 1).¹⁻⁴ These Baylis–Hillman adducts, containing chemo-specific functional groups in close proximity, have been extensively used in a number of transformation methodologies often involving high levels of stereoselectivity.¹⁻²¹



Equation 1. The general Baylis-Hillman reaction.

During the last fifteen years this reaction has seen a tremendous amount of development with respect to the three essential components (Eq. 1). Though the DABCO is the most commonly used tertiary amine catalyst in this fascinating reaction, several other tertiary amines such as 4-DMAP,²² DBU,²³ 3-hydroxyquinuclidine,¹⁻³ 3-quinuclidone,¹⁻³ indolizine,¹⁻³ and pyrrolizidines²⁴ have been successfully employed as catalysts/ medium to perform this reaction. Several non-amine catalysts/systems such as dimethyl sulfide/TiCl₄,^{25,26} TiCl₄,^{27,28} trialkylphosphines and metal complexes such as RhH(PPh₃)₄ and RuH₂(PPh₃)₄ have also been successfully utilized for coupling between activated alkenes and carbon electrophiles.¹⁻³ It is worth mentioning here the most recent work of Hu, who reported a remarkable rate acceleration in the Baylis–Hillman reaction in water–dioxane medium.²⁹

With an objective of developing tertiary amine catalysts containing a minimum number of carbon atoms with lowest possible molecular weight, we have recently employed aqueous trimethylamine to perform the Baylis–Hillman reaction of alkyl acrylates with paraformaldehyde and various reactive aromatic aldehydes (Scheme 1).³⁰ We have also observed that aqueous trimethylamine fails to mediate the Baylis–Hillman reaction of methyl acrylate with benzaldehyde.³⁰



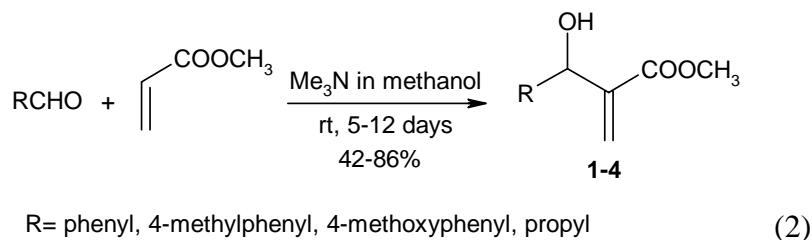
Scheme 1. Aqueous trimethylamine mediated Baylis-Hillman reaction.

Results and Discussion

With a view to understand the scope of application of trimethylamine, and also in order to examine the effect of solvent, we have selected methanolic trimethylamine which is also commercially available and inexpensive as a medium for performing the Baylis–Hillman reaction between benzaldehyde and methyl acrylate. In this direction, the best results were obtained when benzaldehyde (5 mmol) was treated with methyl acrylate (10 mmol) in the presence of methanolic trimethylamine (25% w/w) (5 mmol) at room temperature for 5 days, thus providing the desired adduct *i.e.* methyl 3-hydroxy-2-methylene-3-phenylpropanoate (**1**) in 86% yield. This is a very encouraging result. Then we have extended this reaction to representative aldehydes (Eq. 2 and Table 1). A quick comparison of these results with that of DABCO catalyzed results is also mentioned in the Table 1.

These results clearly demonstrate that methanolic trimethylamine is a better medium than aqueous trimethylamine for performing the Baylis-Hillman coupling of methyl acrylate with less reactive aldehydes. We next planned to extend the applicability of this reagent to the other activated alkenes such as acrylonitrile. Accordingly, we have first carried out the reaction between acrylonitrile and benzaldehyde in the presence of methanolic trimethylamine. The best results were obtained when a mixture of benzaldehyde (5 mmol), acrylonitrile (10 mmol) and methanolic trimethylamine (25% w/w) (5 mmol) was left at room temperature for 6h, thus producing the corresponding Baylis–Hillman adduct, *i.e.* 3-hydroxy-2-methylene-3-phenylpropanenitrile, in 70% yield. Encouraged by this result, we have subjected various aldehydes to the Baylis–Hillman coupling with acrylonitrile under the influence of methanolic trimethylamine to provide the corresponding adducts in good yields and in reasonable reaction times (Eq. 3 and Table 2). A quick comparison of these results with DABCO catalyzed results is mentioned in the Table 2.

Table 1. Methanolic Me₃N mediated Baylis-Hillman reaction of methyl acrylate with aldehydes^{a,b,c}



| R | Product ^d | Methanolic Me ₃ N | | DABCO (literature results) | | |
|-----------------|---------------------------|------------------------------|-----------|----------------------------|---------------------|---------|
| | | Time (days) | Yield (%) | Time (days) | Yield (%) | Mol (%) |
| Phenyl | 1 ³¹ | 5 | 86 | 6 | 94 ³¹ | 15 |
| 4-Methylphenyl | 2 ³² | 12 | 74 | 30 | 95 ³² | - |
| 4-Methoxyphenyl | 3 ³³ | 12 | 42 | 20 | 90 ³³ | 15 |
| Propyl | 4 ^{34,35} | 12 | 81 | 7 | 85 ^{34,35} | 15 |

^a All reactions were carried out on a 5 mmol scale of the aldehyde with methyl acrylate (10 mmol) in the presence of methanolic trimethylamine (25% w/w) (5 mmol) at room temperature.

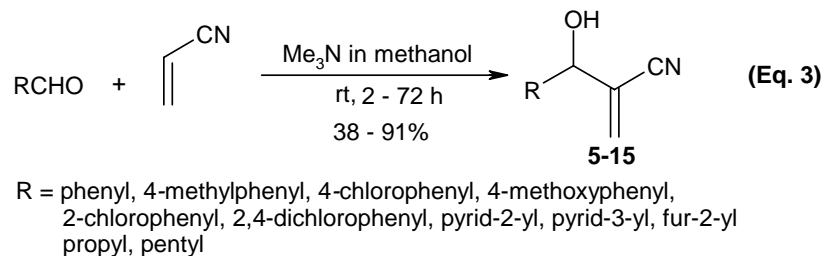
^b All compounds were characterized by IR, ¹H NMR and ¹³C NMR spectral data.

^c Isolated yields of the pure products after silica gel column chromatography (10% EtOAc in hexanes).

^d All these molecules are known in the literature.

We have also successfully utilized the methanolic trimethylamine as a medium for performing the Baylis–Hillman reaction of acenaphthenequinone, a non-enolizable ketone, with acrylonitrile to produce the corresponding adduct 2-(1,2-dihydro-1-hydroxy-2-oxoacenaphthylen-1-yl)prop-2-enitrile **16** in 76% yield at room temperature for 12h in THF (Eq. 4).³⁶

Table 2. Methanolic Me₃N mediated Baylis–Hillman reaction of acrylonitrile with aldehydes^{a,b,c}



| R | Product | Methanolic Me ₃ N | | DABCO (literature results) | | |
|-------------------------|----------------------------|------------------------------|------------------------|----------------------------|--------------------|-----------------|
| | | Time (h) | Yield (%) ^d | Time | Yield (%) | Mol (%) |
| phenyl | 5 ³⁷ | 6 | 83 | 40 h | 70 ³⁸ | 15 |
| 4-Methylphenyl | 6 ^{39,40} | 24 | 71 | 75 h | 64 ³⁹ | 8 |
| 4-Chlorophenyl | 7 ^{32,40} | 3 | 84 | 100 h | 91 ³² | - |
| 4-Methoxyphenyl | 8 ³⁹ | 72 | 62 | 14 d | 29 ³⁹ | 10 ^e |
| 2-Chlorophenyl | 9 ⁴¹ | 3 | 88 | 6 h | 55 ⁴¹ | 11 |
| 2,4-Dichlorophenyl | 10 | 3 | 82 | - | - | - |
| Pyrid-2-yl ^f | 11 ^{3,42} | 2 | 87 | 3 d | 92 ^{3,42} | 5 |
| Pyrid-3-yl ^f | 12 | 2 | 91 | - | - | - |
| Fur-2-yl | 13 | 4 | 63 | - | - | - |
| Propyl | 14 ^{39,43} | 48 | 38 | 5 d | 74 ³⁹ | 6 |
| Pentyl | 15 ³⁸ | 72 | 51 | 3 d | 87 ³⁸ | 30 |

^a All reactions were carried out on a 5 mmol scale of the aldehyde with acrylonitrile (10 mmol) in the presence of methanolic trimethylamine (25% w/w) (5 mmol) at room temperature.

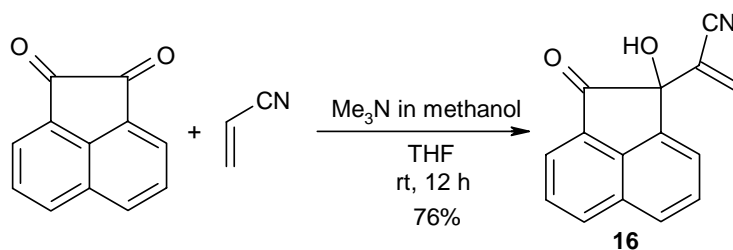
^b The molecules **5-9**, **11**, **14**, **15** are known in the literature.

^c All the compounds (**5-15**) were characterized by IR, ¹H NMR, ¹³C NMR spectral data and the unknown molecules (**10**, **12** & **13**) were further characterized by mass spectral and elemental analyses.

^d Isolated yields of the pure products after silica gel column chromatography (10% EtOAc in hexanes).

^e The reaction was carried out at 42 °C.

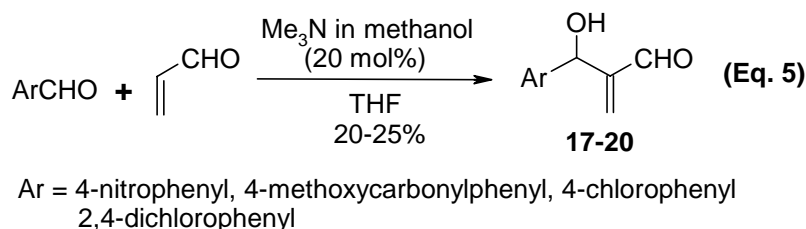
^f Methanolic trimethylamine (25% w/w) (1 mmol) was employed.



Equation 4. The Baylis-Hillman coupling between acenaphthenequinone and acrylonitrile

Though acrolein is an interesting activated alkene, its application in the Baylis–Hillman reaction has not been well studied and only a few reports are available in the literature.^{3,44,45} It occurred to us that methanolic trimethylamine might perform the Baylis–Hillman reaction between acrolein and aldehydes. Thus, the treatment of acrolein (6 mmol) with 4-nitrobenzaldehyde (5 mmol) in the presence of methanolic trimethylamine (25% w/w) (1 mmol) in THF (5 mL) at room temperature for 2h provided the corresponding Baylis–Hillman adduct, *i.e.* 3-hydroxy-2-methylene-3-(4-nitrophenyl)propanal **17**, in 21% yield. We have extended the same reaction to representative aromatic aldehydes (Eq. 5 and Table 3). Though the yields are less in this reaction (Eq. 5), these results demonstrate the application of methanolic trimethylamine as a catalyst for the Baylis–Hillman coupling of acrolein with aldehydes.

Table 3. Methanolic Me₃N mediated Baylis–Hillman reaction of acrolein with aldehydes^{a,b,c}



| Ar | Product | Yield (%) |
|-------------------------|-----------|-----------|
| 4-nitrophenyl | 17 | 21 |
| 4-methoxycarbonylphenyl | 18 | 23 |
| 4-chlorophenyl | 19 | 25 |
| 2,4-dichlorophenyl | 20 | 20 |

^a All reactions were carried out on a 5 mmol scale of the aldehyde with acrolein (6 mmol) in the presence of methanolic trimethylamine (25% w/w) (1 mmol) in 5 mL THF at room temperature for 2h.

^b All compounds **17-20** were characterized by IR, ¹H NMR, ¹³C NMR spectral data and elemental analyses and the molecules **17**, **19** & **20** were further characterized by mass spectral data.

^c Isolated yields of the products after silica gel column chromatography (5% EtOAc in hexanes).

In conclusion, we have successfully demonstrated the applicability of methanolic trimethylamine, the tertiary amine containing minimum number of carbon atoms with lowest possible molecular weight, as a catalyst/ medium for conducting the Baylis-Hillman coupling of representative aldehydes with activated olefins such as methyl acrylate, acrylonitrile and acrolein.

Experimental Section

General Procedures. All melting points were recorded on a Superfit (India) capillary melting point apparatus and are uncorrected. IR spectra were recorded on a Jasco-FT-IR model 5300 spectrometer using liquid samples as neat liquids and solid samples as KBr plates. ^1H NMR (200 MHz) and ^{13}C NMR (50 MHz) spectra were recorded in deuteriochloroform (CDCl_3) on a Bruker-AC-200 spectrometer using tetramethylsilane (TMS, $\delta = 0$) as internal standard. Coupling constants (J) are given in Hz. Elemental analyses were recorded on a Perkin-Elmer 240C-CHN analyzer. Mass spectra were recorded on a Autospec mass spectrometer (EI) and Shimadzu GCMS-QP5050A gas chromatograph mass spectrometer.

General procedure for the molecules 1-16

A mixture of aldehyde (5 mmol), methyl acrylate (10 mmol, 0.9 mL) or acrylonitrile (10 mmol, 0.66 mL) and methanolic trimethylamine (25% w/w) (5 mmol, 1.56 mL) was left at room temperature. After the required time (Table 1 and 2), the reaction mixture was diluted with ether (20 mL), washed with 2N HCl and water. The organic layer was dried over anhydrous Na_2SO_4 . Solvent was evaporated and the residue thus obtained, was purified by silica gel column chromatography (Table 1 and 2) to provide the corresponding Baylis-Hillman adduct. The molecules **1-9**, **11**, **14** and **15** are known in the literature. The complete spectral data (IR, ^1H & ^{13}C NMR and elemental analyses) for the molecules **4**^{34,35} and **11**⁴² were reported in the literature. Since the complete spectral data (IR, ^1H & ^{13}C NMR) were not reported for most of these molecules, we are furnishing here the spectral data (IR, ^1H & ^{13}C NMR) for all the molecules except for the molecules **4** and **11** (our spectral data is in agreement with the reported data) and mass spectral data (m/z , M^+) and elemental analyses for unknown molecules **10**, **12**, **13**.

Methyl 3-hydroxy-2-methylene-3-phenylpropanoate (1). Colorless oil. Yield: 86%; ^1H -NMR δ 3.09 (1H, b), 3.70 (3H, s), 5.54 (1H, s), 5.80 (1H, s), 6.31 (1H, s), 7.28–7.41 (5H, m); ^{13}C -NMR δ 51.58, 72.63, 125.39, 126.57, 127.55, 128.17, 141.46, 142.32, 166.54; IR ν 3433, 1720, 1630 cm^{-1} .

Methyl 3-hydroxy-2-methylene-3-(4-methylphenyl)propanoate (2). Colorless oil. Yield: 74%; ^1H -NMR δ 2.36 (3H, s), 2.90 (1H, b), 3.74 (3H, s), 5.56 (1H, s), 5.87 (1H, d, $J = 2.2$), 6.35 (1H, s), 7.18 (2H, d, $J = 8.2$), 7.30 (2H, d, $J = 8.2$); ^{13}C -NMR δ 21.07, 51.82, 72.93, 125.60, 126.57, 129.09, 137.46, 138.49, 142.28, 166.75; IR ν 3445, 1722, 1630 cm^{-1} .

Methyl 3-hydroxy-3-(4-methoxyphenyl)-2-methylenepropanoate (3). Colorless oil. Yield: 42%; $^1\text{H-NMR}$ δ 2.06 (1H, bs), 3.75 (3H, s), 3.83 (3H, s), 5.56 (1H, s), 5.87 (1H, s), 6.35 (1H, s), 6.90 (2H, d, $J = 8.6$), 7.32 (2H, d, $J = 8.6$); $^{13}\text{C-NMR}$ δ 51.87, 55.28, 72.77, 113.92, 125.48, 127.96, 133.63, 142.41, 159.33, 166.83; IR ν 3439, 1720, 1628 cm^{-1} .

3-Hydroxy-2-methylene-3-phenylpropanenitrile (5). Colorless oil. Yield: 83%; $^1\text{H-NMR}$ δ 2.95 (1H, bs), 5.26 (1H, s), 6.00 (1H, s), 6.08 (1H, s), 7.32–7.52 (5H, m); $^{13}\text{C-NMR}$ δ 73.77, 116.96, 126.17, 126.41, 128.68, 130.05, 139.18; IR ν 3449, 2229, 1624 cm^{-1} .

3-Hydroxy-2-methylene-3-(4-methylphenyl)propanenitrile (6). Colorless oil. Yield: 71%; $^1\text{H-NMR}$ δ 2.36 (3H, s), 2.78 (1H, bs), 5.23 (1H, s), 6.00 (1H, s), 6.08 (1H, d, $J = 1.7$), 7.16–7.35 (4H, m); $^{13}\text{C-NMR}$ δ 20.92, 73.61, 116.99, 126.34, 129.31, 129.63, 136.28, 138.39; IR ν 3447, 2229, 1616 cm^{-1} .

3-(4-Chlorophenyl)-3-hydroxy-2-methylenepropanenitrile (7). Colorless solid. Yield: 84%; mp: 53–54 $^{\circ}\text{C}$ (lit.³² 52 $^{\circ}\text{C}$); $^1\text{H-NMR}$ δ 2.58 (1H, d, $J = 3.8$), 5.30 (1H, d, $J = 3.8$), 6.04 (1H, s), 6.11 (1H, d, $J = 1.2$), 7.28–7.46 (4H, m); $^{13}\text{C-NMR}$ δ 73.23, 116.76, 125.96, 127.85, 128.92, 130.42, 134.51, 137.77; IR ν 3449, 2231, 1622 cm^{-1} .

3-Hydroxy-3-(4-methoxyphenyl)-2-methylenepropanenitrile (8). Colorless oil. Yield: 62%; $^1\text{H-NMR}$ δ 2.69 (1H, b), 3.80 (3H, s), 5.24 (1H, s), 6.01 (1H, s), 6.09 (1H, d, $J = 1.2$), 6.91 (2H, d, $J = 8.6$), 7.29 (2H, d, $J = 8.6$); $^{13}\text{C-NMR}$ δ 55.18, 73.36, 114.10, 117.06, 126.37, 127.78, 129.53, 131.42, 159.67; IR ν 3444, 2228, 1611 cm^{-1} .

3-(2-Chlorophenyl)-3-hydroxy-2-methylenepropanenitrile (9). Colorless solid. Yield: 88%; mp: 50–52 $^{\circ}\text{C}$; $^1\text{H-NMR}$ δ 2.86 (1H, d, $J = 4.2$), 5.76 (1H, d, $J = 4.2$), 6.06 (2H, s), 7.29–7.44 (3H, m), 7.55–7.70 (1H, m); $^{13}\text{C-NMR}$ δ 70.23, 116.69, 124.64, 127.43, 127.92, 129.61, 129.83, 131.38, 132.47, 136.56; IR ν 3433, 2231, 1624 cm^{-1} .

3-(2,4-Dichlorophenyl)-3-hydroxy-2-methylenepropanenitrile (10). Colorless solid. Yield: 82%; mp: 70–72 $^{\circ}\text{C}$; $^1\text{H-NMR}$ δ 2.68 (1H, d, $J = 4.6$), 5.72 (1H, d, $J = 4.6$), 6.07 (2H, s), 7.35 (1H, dd, $J = 8.6$ & 1.9), 7.41 (1H, d, $J = 1.9$), 7.58 (1H, d, $J = 8.6$); $^{13}\text{C-NMR}$ δ 69.84, 116.53, 124.32, 127.81, 128.88, 129.39, 131.73, 133.07, 135.07, 135.26; IR ν 3429, 2233, 1622 cm^{-1} ; MS (m/z) (GCMS): 227 (M^+), 229 ($\text{M}^+ + 2$), 231 ($\text{M}^+ + 4$); Anal. Calcd for $\text{C}_{10}\text{H}_7\text{NOCl}_2$: C, 52.66; H, 3.09; N, 6.14. Found: C, 52.52; H, 3.10; N, 6.10.

3-Hydroxy-2-methylene-3-(pyrid-3-yl)propanenitrile (12). Colorless solid. Yield: 91%; mp: 82–84 $^{\circ}\text{C}$; $^1\text{H-NMR}$ δ 2.65 (1H, b), 5.39 (1H, s), 6.11 (1H, s), 6.20 (1H, s), 7.32–7.46 (1H, m), 7.77–7.88 (1H, m), 8.50–8.62 (2H, m); $^{13}\text{C-NMR}$ δ 71.39, 116.70, 124.03, 126.14, 130.39, 135.09, 136.31, 147.18, 148.60; IR ν 3070, 2220, 1618 cm^{-1} ; MS (m/z) (GCMS): 160 (M^+); Anal. Calcd for $\text{C}_9\text{H}_8\text{N}_2\text{O}$: C, 67.49; H, 5.03; N, 17.49. Found: C, 67.42; H, 5.06; N, 17.55.

3-(Fur-2-yl)-3-hydroxy-2-methylenepropanenitrile (13). Pale yellow oil. Yield: 63%; $^1\text{H-NMR}$ δ 2.43 (1H, b), 5.35 (1H, s), 6.12 (1H, s), 6.17 (1H, s), 6.36–6.55 (2H, m), 7.43 (1H, s); $^{13}\text{C-NMR}$ δ 67.43, 108.45, 110.56, 116.71, 123.30, 131.48, 143.15, 151.57; IR ν 3441, 2231, 1626 cm^{-1} ; MS (m/z) (GCMS): 149 (M^+); Anal. Calcd for $\text{C}_8\text{H}_7\text{NO}_2$: C, 64.42; H, 4.73; N, 9.39. Found: C, 64.66; H, 4.78; N, 9.32.

3-Hydroxy-2-methylenehexanenitrile (14). Colorless oil. Yield: 38%; $^1\text{H-NMR}$ δ 0.97 (3H, t, $J = 7.3$), 1.27–1.96 (4H, m), 2.28 (1H, b), 4.27 (1H, t, $J = 7.3$), 5.98 (1H, s), 5.99 (1H, s); $^{13}\text{C-NMR}$ δ 13.60, 18.28, 37.66, 71.91, 117.11, 127.06, 129.82; IR ν 3439, 2227, 1624 cm^{-1} .

3-Hydroxy-2-methyleneoctanenitrile (15). Colorless oil. Yield: 51%; $^1\text{H-NMR}$ δ 0.91 (3H, t, $J = 6.0$), 1.21–1.95 (8H, m), 2.51 (1H, b), 4.25 (1H, t, $J = 6.4$), 5.98 (1H, s), 5.99 (1H, s); $^{13}\text{C-NMR}$ δ 13.80, 22.38, 24.65, 31.37, 35.58, 72.17, 117.09, 127.14, 129.72; IR ν 3443, 2226, 1622 cm^{-1} .

2-(1,2-Dihydro-1-hydroxy-2-oxoacenaphthylen-1-yl)prop-2-enenitrile (16). Colorless solid. Yield: 76%; mp: 124–126 $^{\circ}\text{C}$; $^1\text{H-NMR}$ δ 3.33 (1H, b), 6.18 (1H, s), 6.28 (1H, d, $J = 1.2$), 7.72–7.89 (3H, m), 7.97–8.11 (2H, m), 8.22 (1H, d, $J = 8.2$); $^{13}\text{C-NMR}$ δ 80.07, 115.88, 121.76, 123.60, 126.82, 128.87, 129.09, 129.81, 130.89, 131.46, 133.03, 136.27, 142.07, 200.54; IR ν 3362, 2224, 1712, 1601 cm^{-1} ; MS (EIMS): 235 (M^+); Anal. Calcd for $\text{C}_{15}\text{H}_9\text{NO}_2$: C, 76.59; H, 3.86; N, 5.95. Found: C, 76.76; H, 3.84; N, 6.00.

General procedure for the molecules 17-20

These molecules were prepared by the reaction between aldehyde (5 mmol) and acrolein (6 mmol, 0.4 mL) in THF (5 mL) for two hours in the presence of methanolic trimethylamine (25% w/w) (1 mmol, 0.31 mL) at room temperature. Low boiling liquids were evaporated and the residue thus obtained, was purified by silica gel column chromatography (Table 3) to provide the corresponding Baylis–Hillman adducts.

3-Hydroxy-2-methylene-3-(4-nitrophenyl)propanal (17). Colorless solid. Yield: 21%; mp: 68–70 $^{\circ}\text{C}$; $^1\text{H-NMR}$ δ 2.90 (1H, b), 5.73 (1H, s), 6.23 (1H, s), 6.46 (1H, s), 7.58 (2H, d, $J = 8.7$), 8.21 (2H, d, $J = 8.7$), 9.59 (1H, s); $^{13}\text{C-NMR}$ δ 69.89, 123.57, 127.41, 135.36, 147.37, 148.39, 150.46, 193.59; IR ν 3512, 1684, 1622 cm^{-1} ; MS, m/z (relative intensity %) (EIMS): 206 ($\text{M}^+ - \text{H}$, 12), 207 (M^+ , 2); Anal. Calcd for $\text{C}_{10}\text{H}_9\text{NO}_4$: C, 57.97; H, 4.38; N, 6.76. Found: C, 57.87; H, 4.41; N, 6.80.

3-Hydroxy-3-(4-methoxycarbonylphenyl)-2-methylenepropanal (18). Colorless solid. Yield: 23%; mp: 80–82 $^{\circ}\text{C}$; $^1\text{H-NMR}$ δ 2.95 (1H, b), 3.91 (3H, s), 5.66 (1H, s), 6.17 (1H, s), 6.41 (1H, s), 7.44 (2H, d, $J = 8.0$), 8.00 (2H, d, $J = 8.0$), 9.56 (1H, s); $^{13}\text{C-NMR}$ δ 51.95, 69.87, 126.46, 129.52, 134.59, 146.34, 151.01, 166.77, 193.39; IR ν 3452, 1710, 1693, 1608 cm^{-1} ; Anal. Calcd for $\text{C}_{12}\text{H}_{12}\text{O}_4$: C, 65.45; H, 5.49. Found: C, 65.66; H, 5.47.

3-(4-Chlorophenyl)-3-hydroxy-2-methylenepropanal (19). Colorless oil. Yield: 25%; $^1\text{H-NMR}$ δ 2.74 (1H, d, $J = 4.2$), 5.59 (1H, d, $J = 4.2$), 6.16 (1H, s), 6.41 (1H, s), 7.31 (4H, s), 9.57 (1H, s); $^{13}\text{C-NMR}$ δ 69.83, 127.99, 128.45, 133.47, 134.38, 139.66, 151.09, 193.57; IR ν 3437, 1689, 1628 cm^{-1} ; MS, m/z (relative intensity %) (EIMS): 195 ($\text{M}^+ - \text{H}$, 26), 196 (M^+ , 6), 197 ($\text{M}^+ - \text{H} + 2$, 9), 198 ($\text{M}^+ + 2$, 2); Anal. Calcd for $\text{C}_{10}\text{H}_9\text{O}_2\text{Cl}$: C, 61.08; H, 4.61. Found: C, 60.79; H, 4.56.

3-(2,4-Dichlorophenyl)-3-hydroxy-2-methylenepropanal (20). Colorless oil. Yield: 20%; $^1\text{H-NMR}$ δ 3.12 (1H, d, $J = 4.8$), 5.94 (1H, d, $J = 4.8$), 6.13 (1H, s), 6.17 (1H, s), 7.32 (1H, dd, $J = 8.1$ & 1.8), 7.40 (1H, d, $J = 1.8$), 7.52 (1H, d, $J = 8.1$), 9.64 (1H, s); $^{13}\text{C-NMR}$ δ 66.93, 127.40, 129.21, 129.27, 133.19, 134.26, 135.41, 136.81, 149.52, 193.81; IR ν 3437, 1689, 1610 cm^{-1} ;

MS, m/z (relative intensity %) (EIMS): 229 ($M^+ - H$, 32), 230 (M^+ , 7), 231 ($M^+ - H + 2$, 20), 232 ($M^+ + 2$, 4), 233 ($M^+ - H + 4$, 3); Anal. Calcd for $C_{10}H_8O_2Cl_2$: C, 51.98; H, 3.49. Found: C, 52.25; H, 3.53.

Acknowledgements

We thank DST (New Delhi) for funding this project. We thank UGC (New Delhi) for the Special Assistance Program in Organic Chemistry in the School of Chemistry, University of Hyderabad. AJR thanks CSIR (New Delhi) and MK thanks UGC (New Delhi) for their research fellowships.

References and Notes

1. Drewes, S. E.; Roos, G. H. P. *Tetrahedron* **1988**, *44*, 4653.
2. Basavaiah, D.; Dharma Rao, P.; Suguna Hyma, R. *Tetrahedron* **1996**, *52*, 8001.
3. Ciganeck, E. *Organic Reactions*; New York 1997; 51, pp 201-350.
4. Langer, P. *Angew. Chem., Int. Ed.* **2000**, *39*, 3049.
5. Hoffmann, H. M.R.; Rabe, J. *Angew. Chem., Int. Ed.* **1983**, *22*, 795.
6. Bailey, M.; Staton, I.; Ashton, P. R.; Marko, I. E.; Ollis, W. D. *Tetrahedron: Asymmetry* **1991**, *2*, 495.
7. Iwabuchi, Y.; Nakatani, M.; Yokoyama, N.; Hatakeyama, S. *J. Am. Chem. Soc.* **1999**, *121*, 10219.
8. Pringle, W.; Sharpless, K. B. *Tetrahedron Lett.* **1999**, *40*, 5151.
9. Racker, R.; Doring, K.; Reiser, O. *J. Org. Chem.* **2000**, *65*, 6932.
10. Trost, B. M.; Tsui, H. -C.; Toste, F. D. *J. Am. Chem. Soc.* **2000**, *122*, 3534.
11. Kim, J. N.; Kim, H. S.; Gong, J. H.; Chung, Y. M. *Tetrahedron Lett.* **2001**, *42*, 8341.
12. Frank, S. A.; Mergott, D. J.; Roush, W. R. *J. Am. Chem. Soc.* **2002**, *124*, 2404.
13. Shi, M.; Jiang, J. K.; Li, C. Q. *Tetrahedron Lett.* **2002**, *43*, 127.
14. Basavaiah, D.; Gowriswari, V. V. L. *Tetrahedron Lett.* **1986**, *27*, 2031.
15. Basavaiah, D.; Bakthadoss, M.; Padiaraju, S. *Chem. Commun.* **1998**, 1639.
16. Basavaiah, D.; Krishnamacharyulu, M.; Suguna Hyma, R.; Sarma, P. K. S.; Kumaragurubaran, N. *J. Org. Chem.* **1999**, *64*, 1197.
17. Basavaiah, D.; Satyanarayana, T. *Org. Lett.* **2001**, *3*, 3619.
18. Basavaiah, D.; Kumaragurubaran, N.; Sharada, D. S. *Tetrahedron Lett.* **2001**, *42*, 85.
19. Basavaiah, D.; Sreenivasulu, B.; Srivardhanarao, J. *Tetrahedron Lett.* **2001**, *42*, 1147.
20. Basavaiah, D.; Mallikarjuna Reddy, R.; *Tetrahedron Lett.* **2001**, *42*, 3025.
21. Basavaiah, D.; Satyanarayana, T. *Tetrahedron Lett.* **2002**, *43*, 4301.
22. Rezgui, F.; El Gaied, M. M. *Tetrahedron Lett.* **1998**, *39*, 5965.
23. Aggarwal, V. K.; Mereu, A. *Chem. Commun.* **1999**, 2311.

24. Baret, A. G. M.; Cook, A. S.; Kamimura, A. *Chem. Commun.* **1998**, 2533.
25. Kataoka, T.; Kinoshita, H.; Kinoshita, S.; Iwamura, T.; Watanabe, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 2358.
26. Basavaiah, D.; Muthukumar, K.; Sreenivasulu, B. *Synlett* **1999**, 1249.
27. Li, G.; Wei, H. -X.; Gao, J. J.; Caputo, T. D. *Tetrahedron Lett.* **2000**, *41*, 1.
28. Basavaiah, D.; Sreenivasulu, B.; Mallikarjuna Reddy, R.; Muthukumar, K. *Synth. Commun.* **2001**, *31*, 2987.
29. Yu, C.; Liu, B.; Hu, L. *J. Org. Chem.* **2001**, *66*, 5413.
30. Basavaiah, D.; Krishnamacharyulu, M.; Jaganmohan Rao, A. *Synth. Commun.* **2001**, *30*, 2061.
31. Fort, Y.; Berthe, M. C.; Caubre, P. *Tetrahedron* **1992**, *48*, 6371.
32. Foucaud, A.; Rouille, E. *Synthesis* **1990**, 787.
33. Foucaud, A.; El Guemmout, F. *Bull. Soc. Chim. Fr.* **1989**, 403.
34. Mateus, C. R.; Feltrin, M. P.; Costa, A. M.; Coelho, F.; Almeida, W. P. *Tetrahedron* **2001**, *57*, 6901.
35. Hoffman, H. M. R.; Rabe, J. *J. Org. Chem.* **1985**, *50*, 3849.
36. The Baylis-Hillman reaction of acenaphthenequinone with acrylonitrile in the presence of DABCO failed to give the corresponding product.
37. Imagawa, T.; Uemura, K.; Nagai, Z.; Kawanisi, M. *Synth. Commun.* **1984**, *14*, 1267.
38. Basavaiah, D.; Gowriswari, V. V. L. *Synth. Commun.* **1987**, *17*, 587.
39. Hill, J. S.; Isaacs, N. S. *J. Chem. Res. (S)* **1988**, 330; *J. Chem. Res. (M)* **1988**, 2641.
40. Basavaiah, D.; Sarma, P. K. S. *J. Chem. Soc. Chem., Commun.* **1992**, 955.
41. Amri, H.; Villieras, J. *Tetrahedron Lett.* **1986**, *27*, 4307.
42. Bode, M. L.; Kaye, P. T. *J. Chem. Soc., Perkin Trans I* **1993**, 1809.
43. Basavaiah, D.; Pandiaraju, S. *Tetrahedron Lett.* **1995**, 757.
44. Golubev, A. S.; Galakhov, M. V.; Kolomietes, A. F.; Fokin, A. V. *Bull. Rus. Acad. Sci.* **1992**, *41*, 2193.
45. Kawamura, M.; Kobayashi, S. *Tetrahedron Lett.* **1999**, *40*, 1539.