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Triphosgene mediated chlorination of Baylis–Hillman adducts

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Abstract. An efficient method for the preparation of allyl chlorides from Baylis–Hillman adducts has been developed using triphosgene/pyridine system. This method is best illustrated by its advantages like operational simplicity, excellent yields, short reaction time, simple procedure and stereoselectivity.

Keywords. Baylis–Hillman adducts; triphosgene; chlorination; stereoselectivity; simple procedure.

1. Introduction

Baylis–Hillman reaction[1] is now a standard C–C bond formation reaction widely used in synthetic organic chemistry. The reaction has been extensively studied and various applications are reported in the literature.[2] The derivatives of Baylis–Hillman adducts, in particular, Baylis–Hillman allyl halides have been used as valuable intermediates in the preparation of several heterocyclic compounds and also in stereo-selective processes.[3] Chlorination of Baylis–Hillman adducts using various reagents/protocols are reported in the literature viz., HCl/H_2SO_4,[4] $FeCl_3$ or $InCl_3$,[5] PPh_3/CCl_4,[6] PPh_3/Cl_3CCONH_2,[7] TCT/DMF,[8] $(COCl)_2$/DMF,[9] DMF/$POCl_3$,[10] NEt_3/MsCl,[11] and also using ionic liquid as medium.[12] Unfortunately, many of these suffer from limitations such as harsh reaction conditions, lack of general applicability, longer reaction times, and only one report[6] is available in the literature for the conversion of nitrile containing Baylis–Hillman adducts to their allyl chlorides. Therefore, reinvestigation of the classical conditions seemed warranted for developing suitable conditions for the synthesis of allyl chlorides. Triphosgene [*bis*(trichloromethyl)carbonate] is yet another important chlorinating agent has been found to be an excellent activating agent in several organic reactions.[13] The efficiency of triphosgene (white crystalline compound) as a synthetic auxiliary, as a carbonylating agent, as a chlorinating agent, as a replacement of $POCl_3$ in the preparation of many important classes of organic compounds has been investigated in the last twenty years.[14] In continuation of our interest on the chemical transformations using Baylis–Hillman chemistry,[15] we report here a new and convenient method for the chlorination of Baylis–Hillman adducts to obtain the allyl chlorides in a stereoselective manner. In this paper, we describe the use of triphosgene as an excellent reagent for the easy and mild conversion of Baylis–Hillman adducts into their allyl chlorides. The chlorination using triphosgene is fast, smooth, clean and high yielding.

2. Experimental

2.1 *General*

All the chemicals used were of reagent grade obtained from local suppliers, Aldrich and Fluka. All reactions were performed in oven-dried glassware under nitrogen atmosphere. Analytical thin layer chromatography (TLC) was performed on silica gel plates and TLC visualization was carried out with UV. Melting points were determined on a Mettlers-Temp and are uncorrected. IR Spectra were recorded using a Perkin-Elmer-1600 FT-IR spectrometer; ν in cm^{-1}. ^1H and ^{13}C-NMR spectrum ($CDCl_3$/DMSO-d_6) was recorded with Gemini-200 and Bruker-Avance-300 instruments; chemical shifts δ in ppm relative to $SiMe_4$ as an internal standard, couplings in Hz. HRMS (ESI) data were recorded on a QSTAR XL High resolution mass spectrometer; in m/z (rel. %). GC was recorded on GC-17A Gas Chromatograph SHIMADZU system (column: Zebron-1 C49045 30 m × 53 mm I.D. × 1.5 μ F. T.), Oven program 50°C for 5 min temp. raised 10°C/min to 280°C; hold 5 min; gas flow rate 1 mL/min.

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2.2 *General experimental procedure for the synthesis of allyl chlorides from Baylis–Hillman adducts* (**1a–v**)

To a stirred solution of triphosgene (0.93 g, 3.14 mmol) in dichloromethane (5 mL) at 0°C, pyridine (1.26 mL, 15.72 mmol) was added drop-wise followed by Baylis–Hillman adduct (**1m**) (0.5 g, 3.14 mmol) in DCM (5 mL) and stirred the reaction at room temperature (Monitored by TLC). After completion of the reaction, the reaction mixture was diluted with DCM (10 mL); the organic layer was washed with water (5 mL), sat. $CuSO_4$ solution (5 mL), dried over Na_2SO_4 and the solvent was removed under reduced pressure to get the desired allyl chloride (**2m**) as colourless liquid (0.57 g, 95%) $R_f = 0.8$ (20% EtOAc/hexane). Same experimental procedure was adopted for the preparation of other allyl chlorides.

2.2a *(Z)-Methyl 2-(chloromethyl)-3-phenylacrylate* (**2a**): Colourless liquid; Yield 95%; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.83$ (*s*, 1H), 7.52–7.43 (*m*, 2H), 7.45–7.25 (*m*, 3H), 4.43 (*s*, 2H), 3.87 (*s*, 3H); IR (Neat): 2988, 2853, 1750, 1630, 1250, 1170 cm^{-1}; MS (EI): m/z 210 [M$^+$], 176 (100), 131, 115; GC: $Z{:}E = 97{:}3$.

2.2b *(Z)-Methyl 2-(chloromethyl)-3-(4-chlorophenyl) acrylate* (**2b**): Colourless liquid; Yield 92%; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.71$ (*s*, 1H), 7.49 (*d*, $J = 8.8$ Hz, 2H), 7.42 (*d*, $J = 7.8$ Hz, 2H), 4.39 (*s*, 2H), 3.87 (*s*, 3H); IR (Neat): 2953, 2849, 1718, 1633, 1599, 1509, 1439, 1278, 1230, 1163 cm^{-1}; MS (EI): m/z 244 [M$^+$], 209, 149 (100), 130, 115; GC: $Z{:}E = 95{:}5$.

2.2c *(Z)-Methyl 2-(chloromethyl)-3-(4-ethylphenyl) acrylate* (**2c**): Colourless liquid; Yield 95%; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.80$ (*s*, 1H), 7.40 (*d*, 2H, $J = 7.9$ Hz), 7.26 (*d*, 2H, $J = 7.9$ Hz), 4.45 (*s*, 2H), 3.86 (*s*, 3H), 2.72 (*q*, 2H, $J = 7.5$ Hz), 1.29 (*t*, 3H, $J = 7.5$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 166.8$, 146.4, 143.9, 131.4, 129.8, 128.8, 128.4, 52.3, 39.3, 28.7, 15.2; IR (Neat): 2965, 1718, 1628, 1509, 1436, 1272 cm^{-1}; MS (ESI): m/z 261 [M+Na]$^+$; HRMS (ESI) calcd. for $C_{13}H_{15}ClO_2Na$: 261.0658; found: 261.0653; GC: $Z{:}E = 96{:}4$.

2.2d *(Z)-Methyl 2-(chloromethyl)-3-(4-isopropylphenyl) acrylate*(**2d**): Colourless liquid; Yield 93%; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.79$ (*s*, 1H), 7.47 (*d*, $J = 7.9$ Hz, 2H), 7.28 (*s*, $J = 8.9$ Hz, 2H), 4.44 (*s*, 2H), 3.85 (*s*, 3H), 2.94 (*m*, $J = 6.9$ Hz, 1H), 1.27 (*d*, $J = 6.9$ Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 166.8$, 150.9, 143.8, 129.9, 128.9, 126.9, 126.6, 126.2, 52.3, 39.3, 34.0, 23.7. IR (Neat): 2961, 1717, 1628, 1509, 1436, 1281 cm^{-1}; MS (ESI): m/z 275 [M+Na]$^+$; HRMS (ESI) calcd. for $C_{14}H_{17}ClO_2Na$: 275.0814; found: 275.0826; GC: $Z{:}E = 96{:}4$.

2.2e *(Z)-Methyl 2-(chloromethyl)-3-(4-methoxyphenyl) acrylate* (**2e**): Colourless liquid; Yield 90%; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.77$ (*s*, 1H), 7.54 (*d*, $J = 8.3$ Hz, 2H), 6.95 (*d*, $J = 9.0$ Hz, 2H), 4.47 (*s*, 2H), 3.86 (*s*, 3H), 3.84 (*s*, 3H); IR (Neat): 2960, 2840, 1908, 1718, 1633, 1599, 1439, 1278 cm^{-1}; MS (EI): m/z 240 [M$^+$], 205, 145 (100) 131, 115; GC: $Z{:}E = 95{:}5$.

2.2f *(Z)-Methyl 2-(chloromethyl)-3-(4-fluorophenyl) acrylate* (**2f**): Colourless liquid; Yield 93%; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.78$ (*s*, 1H), 7.56 (*t*, $J = 8.8$ Hz, $J = 7.8$ Hz, 2H), 7.15 (*t*, $J = 8.8$ Hz, 2H), 4.40 (*s*, 2H), 3.80 (*s*, 3H); IR (Neat): 2952, 1718, 1631, 1490, 1438, 1312, 1281, 1208, 1090 cm^{-1}; MS (EI): m/z 228 [M$^+$], 193, 133 (100), 115, 107; GC: $Z{:}E = 98{:}2$.

2.2g *(Z)-Methyl 2-(chloromethyl)-3-(2-chlorophenyl) acrylate* (**2g**): Colourless liquid; Yield 90%; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.92$ (*s*, 1H), 7.69–7.65 (*m*, 1H), 7.46–7.32 (*m*, 3H), 4.32 (*s*, 2H), 3.90 (*s*, 3H); IR (Neat): 2982, 1717, 1636, 1469, 1439, 1371, 1288, 1208, 1179 cm^{-1}; MS (EI): m/z 244 [M$^+$], 209, 149 (100), 130, 115; GC: $Z{:}E = 98{:}2$.

2.2h *(Z)-Ethyl 2-(chloromethyl)-3-(4-chlorophenyl) acrylate* (**2h**): Colourless solid; Yield 92%; M.p.: 78–80°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.76$ (*s*, 1H), 7.50 (*d*, $J = 8.30$ Hz,2H), 7.47 (*d*, $J = 8.6$ Hz, 2H), 4.39 (*s*, 2H), 4.36 (*q*, $J = 7.1$ Hz, 2H), 1.41 (*t*, $J = 7.1$ Hz, 3H); IR (KBr): 2924, 2853, 1701, 1624, 1489, 1378, 1263, 1213, 1179 cm^{-1}; MS (EI): 258 [M$^+$], 223, 195, 159 (100), 149, 131, 115; GC: $Z{:}E = 97{:}3$.

2.2i *(Z)-Ethyl 2-(chloromethyl)-3-(4-methoxyphenyl) acrylate* (**2i**): Colourless liquid; Yield 90%; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.78$ (*s*, 1H), 7.57 (*d*, $J = 8.3$ Hz, 2H), 6.94 (*d*, $J = 9.0$ Hz, 2H), 4.49 (*s*, 2H), 4.36 (*q*, $J = 7.1$ Hz, 2H), 3.86 (*s*, 3H), 1.39 (*t*, $J = 7.1$ Hz, 3H). IR (Neat): 2966, 2848, 1908, 1708, 1633, 1599, 1439, 1278 cm^{-1}; MS (EI): 254 [M$^+$], 219 (100) 145, 131, 115. GC: $Z{:}E = 98{:}2$.

2.2j *(Z)-Ethyl 2-(chloromethyl)-3-(2,4-dichlorophenyl) acrylate* (**2j**): Colourless solid; Yield 90%; M.p.: 74–76°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.82 (*s*, 1H), 7.63 (*d*, *J* = 7.8 Hz, 2H), 7.40 (*s*, 1H), 7.36 (*d*, *J* = 7.8 Hz, 2H), 4.35 (*q*, *J* = 6.8 Hz, 2H), 4.29 (*s*, 2H), 1.41 (*t*, *J* = 6.8 Hz, 3H); IR (KBr): 2980, 2928, 1717, 1583, 1469, 1375, 1280, 1251, 1178 cm^{-1}; MS (EI): 292 [M$^+$], 257, 247, 229, 193 (100), 149, 113; GC: *Z*:*E* = 98:2.

2.2k *(Z)-Ethyl 2-(chloromethyl)-3-(4-nitrophenyl) acrylate* (**2k**): Yellow solid; Yield 93%; M.p.: 77–79°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.33 (*d*, *J* = 9.0 Hz, 2H), 7.83 (*s*, 1H), 7.72 (*d*, *J* = 9.0 Hz, 2H), 4.39 (*q*, *J* = 6.7 Hz, 2H), 4.36 (*s*, 2H), 1.43 (*t*, *J* = 6.7 Hz, 3H); IR (KBr): 2920, 2855, 1595, 1510, 1438, 1344, 1258, 1105 cm^{-1}; MS (EI): 269 [M$^+$], 234, 150, 129, 115, 79 (100); GC: *Z*:*E* = 95:5.

2.2l *(Z)-Ethyl 2-(chloromethyl)pent-2-enoate* (**2l**): Colourless liquid; Yield 89%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.96 (*t*, *J* = 7.7 Hz, 1H), 4.28 (*s*, 2H), 4.27 (*q*, *J* = 7.1 Hz, 2H), 2.40 (*q*, *J* = 7.5 Hz, 2H), 1.35 (*t*, *J* = 7.1 Hz, 3H), 1.17 (*t*, *J* = 7.5 Hz, 3H); IR (Neat): 2977, 2938, 1779, 1717, 1645, 1460, 1374, 1279, 1181 cm^{-1}; MS (EI): 176 [M$^+$], 157, 141, 133, 113, 99, 57 (100); GC: *Z*:*E* = 90:10.

2.2m *(E)-2-(Chloromethyl)-3-phenylacrylonitrile* (**2m**): Colourless liquid; Yield 95%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.78–7.75 (*m*, 2H), 7.44 (*t*, 3H), 7.18 (*s*, 1H), 4.29 (*s*, 2H); IR (Neat): 2955, 2830, 2210, 1602, 1590, 1510, 1439, 1258, 1105 cm^{-1}; MS (EI): 177 [M$^+$], 142, 127, 115 (100), 102; GC: *Z*:*E* = 3:97.

2.2n *(E)-2-(Chloromethyl)-3-(4-ethylphenyl) acrylonitrile* (**2n**): Colourless liquid; Yield 95%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.71 (*d*, *J* = 8.1 Hz, 2H), 7.26 (*d*, *J* = 8.1 Hz, 2H), 7.10 (*s*, 1H), 4.28 (*s*, 2H), 2.70 (*q*, *J* = 7.5 Hz, 2H), 1.20 (*t*, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.3, 146.7, 129.4, 128.7, 128.5, 117.2, 106.3, 46.2, 28.8, 15.1; IR (Neat): 2968, 2217, 1607, 1621, 1266 cm^{-1}; MS (ESI): *m*/*z* 228 [M+Na]$^+$. HRMS (ESI) calcd. for $C_{12}H_{12}ClNNa$: 228.0555; found: 228.0553; GC: *Z*:*E* = 5:95.

2.2o *(E)-2-(Chloromethyl)-3-(3-fluorophenyl) acrylonitrile* (**2o**): Colourless solid; Yield 88%; M.p.: 72–74°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.58 (*d*, *J* = 7.9 Hz, 2H), 7.48–7.41 (*m*, 3H), 7.16 (*s*, 1H), 4.29 (*s*, 2H); IR (KBr): 2963, 2855, 2210, 1891, 1602, 1510, 1417, 1246, 1169 cm^{-1}; MS (EI): *m*/*z* 195 [M$^+$], 160, 140, 133, 120; GC: *Z*:*E* = 10:90.

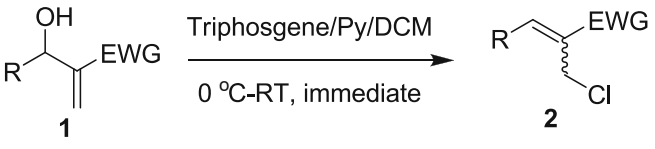
2.2p *(E)-3-(3-Bromophenyl)-2-(chloromethyl) acrylonitrile* (**2p**): Colourless solid; Yield 85%; M.p.: 76–78°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.82 (*d*, *J* = 9.0 Hz, 2H), 7.58–7.55 (*m*, 1H), 7.36–7.30 (*t*, *J* = 8.3 Hz, 1H), 7.13 (*s*, 1H), 4.29 (*s*, 2H); IR (KBr): 2963, 2925, 2214, 1314, 1467, 1268, 1215 cm^{-1}; MS (EI): *m*/*z* 254 [M$^+$], 220, 141 (100) 114; GC: *Z*:*E* = 4:96.

2.2q *(E)-2-(Chloromethyl)-3-(3-chlorophenyl) acrylonitrile* (**2q**): Colourless solid; Yield 88%; M.p.: 75–77°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.75–7.73 (*m*, 1H), 7.66 (*s*, 1H), 7.41–7.39 (*m*, 2H), 7.14 (*s*, 1H), 4.28 (*s*, 2H); IR (KBr): 2925, 2855, 2212, 1616, 1587, 1486, 1407, 1266, 1090 cm^{-1}; MS (EI): *m*/*z* 212 [M$^+$], 176, 160, 140 (100), 133, 125, 113; GC: *Z*:*E* = 10:90.

2.2r *(E)-2-(Chloromethyl)-3-(4-chlorophenyl) acrylonitrile* (**2r**): Colourless solid; Yield 92%; M.p. 73–75°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.73 (*d*, *J* = 8.3 Hz, 2H), 7.43 (*d*, *J* = 8.3 Hz, 2H), 7.14 (*s*, 1H), 4.28 (*s*, 2H); IR (KBr): 2925, 2855, 2212, 1616, 1587, 1486, 1407, 1266, 1090 cm^{-1}; MS (EI): *m*/*z* 212 [M$^+$], 176 (100) 140, 113, 99; GC: *Z*:*E* = 1:99.

2.2s *(E)-3-(4-Bromophenyl)-2-(chloromethyl) acrylonitrile* (**2s**): Colourless solid; Yield 93%; M.p.: 72–74°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.66 (*d*, *J* = 8.3 Hz, 2H), 7.59 (*d*, *J* = 8.3 Hz, 2H), 7.13 (*s*, 1H), 4.27 (*s*, 2H); IR (KBr): 2924, 2855, 2211, 1616, 1582, 1481, 1403, 1261, 1071 cm^{-1}; MS (EI): *m*/*z* 254 (100) [M$^+$], 220, 140, 114, 100; GC: *Z*:*E* = 5:95.

2.2t *(E)-2-(Chloromethyl)-3-(4-fluorophenyl) acrylonitrile* (**2t**): Colourless solid; Yield 96%; M.p.: 70–72°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.98



EWG = COOEt, COOMe, CN

R = alkyl, aryl

Scheme 1. Chlorination of Baylis–Hillman adducts.

Table 1. Comparison study of bases in chlorination of Baylis–Hillman adducts using triphosgene for the reference reaction (**1m–2m**).

S. No	Base	Time	Isolated yield (%)*
1	Pyridine	10 min	95
2	DMAP	15 min	90
3	DBU	4 h	85
4	DABCO	12 h	20
5	Piperidine	12 h	30
6	Diisopropyl Ethyl Amine	12 h	–
7	Et_3N	12 h	–

*Reaction was carried out at 0°C in DCM as solvent

(t, $J = 8.8$ Hz, 2H), 7.31 (s, 1H), 7.30 (d, $J = 8.8$ Hz, 2H), 4.45 (s, 2H); IR (KBr): 2965, 2214, 1891, 1602, 1510, 1417, 1246, 1163 cm^{-1}; MS (EI): m/z 195 [M^+], 160 (100) 140, 133, 120,106; GC: $Z:E = 2:98$.

2.2u *(E)-2-(Chloromethyl)-3-(4-methoxyphenyl) acrylonitrile* (**2u**): Colourless solid; Yield 93%; M.p.: 71–73°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.77$ (d, $J = 8.8$ Hz, 2H), 7.09 (s, 1H), 6.93 (d, $J = 8.8$ Hz, 2H), 4.27 (s, 2H), 3.80 (s, 3H); IR (KBr): 2962, 2841, 2214, 1601, 1511, 1260, 1179 cm^{-1}; MS (EI): m/z 207 [M^+], 172 (100), 157, 140, 128, 115, 102; GC: $Z:E = 5:95$.

2.2v *(E)-2-(Chloromethyl)-3-(4-nitrophenyl) acrylonitrile* (**2v**): Light yellow solid; Yield 90%; M.p.: 78–80°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.32$ (d, $J = 8.8$ Hz, 2H), 7.94 (d, $J = 8.8$ Hz, 2H), 7.29 (s, 1H), 4.32 (s, 1H); IR (KBr): 2925, 2852, 2219, 1595, 1510, 1438, 1344, 1258, 1105 cm^{-1}; MS (EI): m/z 222 [M^+], 187, 170, 140 (100), 114; GC: $Z:E = 6:94$.

3. Results and discussion

The starting material, Baylis–Hillman adducts are synthesized by modifying the reported procedure by treating various aldehydes with acrylates/acrylonitrile in presence of 30 mol% DABCO as a catalyst under solvent-free conditions. In a reference reaction, we have studied the reaction conditions elaborately like selection of base, temperature, and solvent system for the efficacy of the chlorination of Baylis–Hillman adducts. After numerous trails, triphosgene/pyridine/DCM at 0°C is found to be the best reaction condition for the effective conversion (scheme 1). Comparative studies of different bases in chlorination of Baylis–Hillman adduct (**1m**) using triphosgene is tabulated in table 1. The results of table 1 reveal that aromatic bases like pyridine and DMAP are most effective in this chlorination reaction. The other aliphatic bases viz., DBU, DABCO and piperidine gives moderate to low yields with more reaction time due to their higher reactivity in the reaction. It was noticed that the reaction was found not progressing using DIPEA and triethylamine. In almost all cases, starting material only recovered from the reaction mixture. Pyridine has chosen as suitable base for the conversion due to its inexpensiveness and with respect to reaction yield/time. The variation of temperature and time does not show any appreciable change in the reaction. To demonstrate the general utility of the reaction, the method was successfully applied to various Baylis–Hillman adducts having both ester (**1a–l**) and nitrile (**1m–v**) moieties (table 2). The reaction underwent smoothly in all the cases and excellent

Table 2. Synthesis of allyl chlorides from Baylis–Hillman adducts.

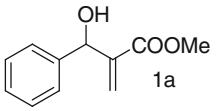
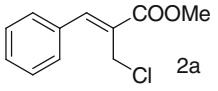
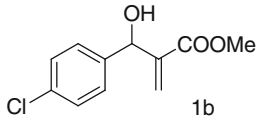
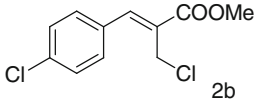
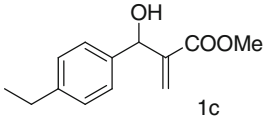
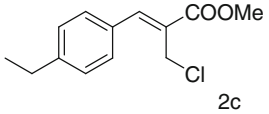
S. No	Substrate	Product	Isolated yield	$Z:E$ Ratio[a]
1	 1a	 2a	95	97:3
2	 1b	 2b	92	95:5
3	 1c	 2c	95	96:4

Table 2. *(continued).*

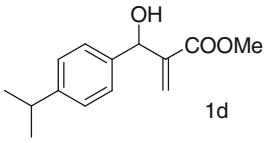
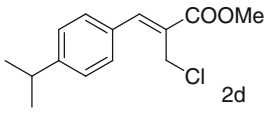
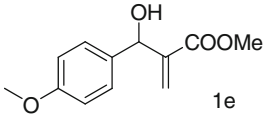
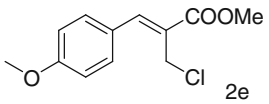
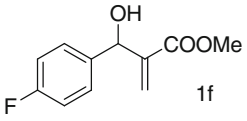
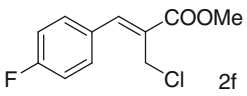
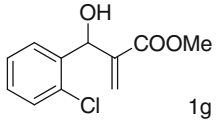
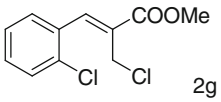
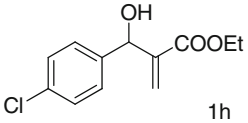
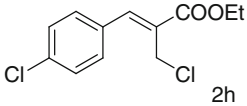
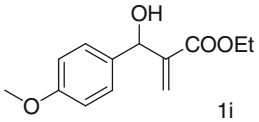
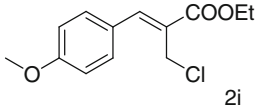
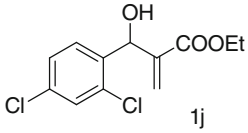
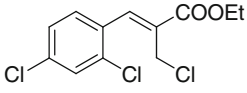
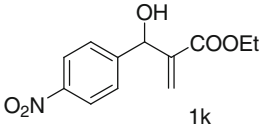
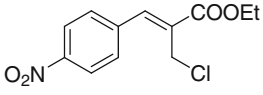
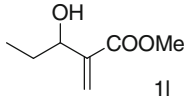
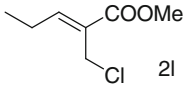
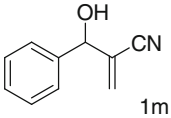
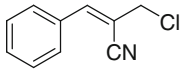
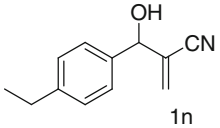
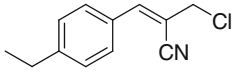
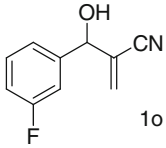
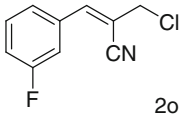
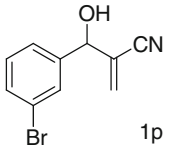
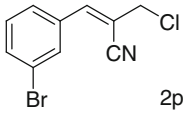
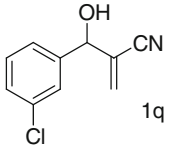
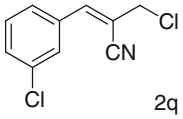
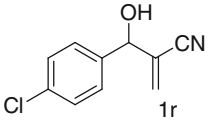
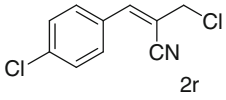
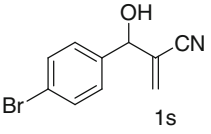
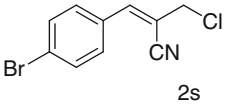
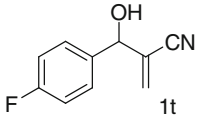
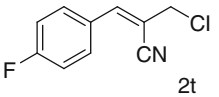
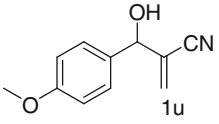
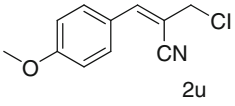
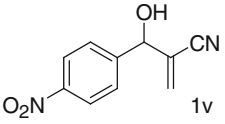
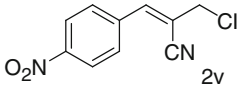
S. No	Substrate	Product	Isolated yield	*Z*:*E* Ratio[a]
4	 1d	 2d	93	96:4
5	 1e	 2e	90	95:5
6	 1f	 2f	93	98:2
7	 1g	 2g	90	98:2
8	 1h	 2h	92	97:3
9	 1i	 2i	90	98:2
10	 1j	 2j	90	98:2
11	 1k	 2k	93	95:5
12	 1l	 2l	89	90:10
13	 1m	 2m	95	3:97
14	 1n	 2n	95	5:95
15	 1o	 2o	88	10:90

Table 2. *(continued).*

S. No	Substrate	Product	Isolated yield	*Z*:*E* Ratio[a]
16	 1p	 2p	85	4:96
17	 1q	 2q	88	10:90
18	 1r	 2r	92	1:99
19	 1s	 2s	93	5:95
20	 1t	 2t	96	2:98
21	 1u	 2u	93	5:95
22	 1v	 2v	90	6:94

[a]*Z*/*E* ratio was determined by ^{1}H NMR and GC analysis

yields were obtained in short reaction times (immediately). Another importance of the reaction was no column chromatography is required for the isolation of product. Several functionalities such as halogen, nitro, ether, and ester remained intact. The adducts containing electron donating as well as withdrawing groups have been utilized effectively in this protocol and 22 examples are depicted in table 2. See supplementary information.

The stereoselectivity of present conversion was studied in detailed. There are a few reports in the literature regarding stereochemistry of Baylis–Hillman allyl chlorides.[7–11,16] Following earlier reports, according to ^{1}H NMR data and iterative GC analysis of prepared chlorides, revealed that the stereochemistry of ester containing Baylis–Hillman allyl chlorides major isomer is *Z* and nitrile containing Baylis–Hillman allyl chlorides major isomer is *E*. The ratio of the *E*–*Z* products as measured by GC is listed in the table 2.

4. Conclusions

In summary, we have described a mild and efficient method for the chlorination of Baylis–Hillman adducts using triphosgene. The advantages of triphosgene/pyridine system are; more convenient to handle, operational simplicity, excellent yields, no chromatography, and simple workup procedure. This is a versatile, inexpensive, environmentally benign method and makes this a valid contribution in upgrading to the existing methodologies. Application of this strategy to

the preparation of new heterocyclic entities from allyl chlorides is currently being pursued.

Supporting information

The supplementary information for experimental procedure, characteristic data and spectra of new compounds **2c**, **2d** and **2n** can be seen in the website (www.ias.ac.in/chemsci).

Acknowledgements

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