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The Baylis-Hillman Reaction: An Expedient Synthesis of (*Z*)-Keto Allyl Bromides and Chlorides#

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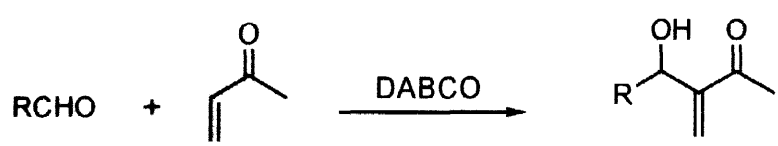
Abstract *: A simple and expedient synthesis of (Z)- keto allyl bromides and chlorides, from the Baylis-Hillman adducts is described.*

The Baylis-Hillman reaction continues to attract organic chemists as it constructs a novel cabon–carbon bond between the α-position of activated alkenes and carbon electrophiles leading to the formation of synthetically attractive and useful class of molecules with chemospecific functional groups.[1-10] The Baylis-Hillman adducts derived from activated alkenes such as acrylate esters, acrylonitrile, and phenyl vinyl sulfone have been successfully employed in a plethora of stereoselective processes.[1-3] However the Baylis-Hillman adducts (eq.1) derived from a very reactive activated alkene, methyl vinyl ketone,[5,11] have not been well exploited for such stereoselective transformations.[6-8] In continuation of our research program[11-16] aimed at developing the Baylis-Hillman reaction as a source for stereoselective processes, we herein report an expedient, simple and convenient synthesis of (3*Z*)-3-(bromomethyl)alk-3-en-2-ones and (3*Z*)-3-(chloromethyl)alk-3-en-2-ones in high yields *via* the reaction of 4-hydroxy-3-methylenealkan-2-ones with aqueous HBr and HCl respectively.



(eq. 1)

The Baylis-Hillman adducts derived from acrylate esters *i.e.* 3-hydroxy-2-methylenealkanoates were transformed into the corresponding (*Z*)-allyl bromides by the treatment with HBr, NBS-Me_2S, or $CuBr_2/SiO_2$ while the Baylis-Hillman adducts derived from acrylonitrile *i.e.* 3-hydroxy-2-methylenealkanenitriles on treatment with HBr or $CuBr_2/SiO_2$ provided the corresponding allyl bromides as a mixture of (*E*)- and (*Z*)-isomers with the (*E*)-isomer predominating.[4,17,18] Though it is possible to predict, it is desirable and also interesting to investigate the stereochemical outcome in the reaction of 4-hydroxy-3-methylenealkan-2-ones with HBr as this study might throw some light on the mechanistic aspect and provide a convenient

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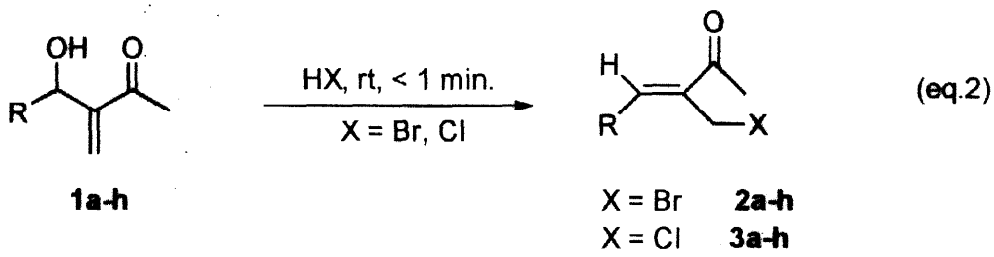
methodology for the synthesis of 3-(bromomethyl)alk-3-en-2-ones with defined stereoselectivity. These allyl bromides are important starting materials for stereoselective synthesis of allylamines and azetidines.[19]

Accordingly, we first treated 4-hydroxy-3-methylene-4-phenylbutan-2-one (**1a**) (1 mmol) with 1 mL of 48% aqueous HBr at room temperature. This reaction is instantaneous and provided the desired (3*Z*)-3-(bromomethyl)-4-phenylbut-3-en-2-one (**2a**) in 81% yield after usual work up and column chromatography. The (*Z*)-stereochemistry was established on the basis of ^{1}H NMR spectral data.[20,21] This was further confirmed by a 2D NOESY experiment. Encouraged by this result we transformed a representative class of 4-hydroxy-3-methylenealkan-2-ones (**1b-h**) into the corresponding (*Z*)-allyl bromides (**2b-h**) by treatment with 48% aqueous HBr (eq.2, Table 1).

These results led us to examine the reaction of 4-hydroxy-3-methylenealkan-2-ones (**1**) with 36% aqueous HCl to provide a general synthesis of (3*Z*)-3-(chloromethyl)alk-3-en-2-ones. Thus we have examined the reaction of 4-hydroxy-3-methylene-4-phenylbutan-2-one (**1a**) (1 mmol) with 36% aqueous HCl (1 mL) at room temperature. This reaction is also instantaneous and the required (3*Z*)-3-(chloromethyl)-4-phenylbut-3-en-2-one (**3a**) was obtained in 82% yield after usual work up and column chromatography. The (*Z*)-stereochemistry was assigned by a 2D NOESY experiment. We then prepared a variety of (*Z*)-allyl chlorides (**3b-h**) from the corresponding 4-hydroxy-3-methylenealkan-2-ones (**1b-h**) (eq.2, Table 1).

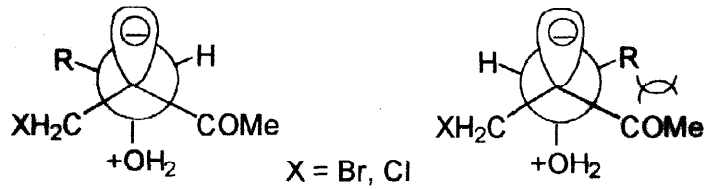


(eq.2)

1a-h

X = Br **2a-h**
X = Cl **3a-h**

The (*Z*)-selectivity in these reactions may be explained on the basis of a mechanism (transition state models **A** and **B**) similar to that proposed by Hoffmann for the stereoselective synthesis of (2*Z*)-2-(bromomethyl)alk-2-enoates.[4]



A
favoured

B
disfavoured

In conclusion our study describes a simple, convenient and expedient synthesis of functionalized trisubstituted alkenes *i.e.* (3*Z*)-3-(bromomethyl)alk-3-en-2-ones and (3*Z*)-3-(chloromethyl)alk-3-en-2-ones and also provides mechanistic evidence supporting the pathway proposed by Hoffmann in the reaction of 3-hydroxy-2-methylenealkanoates with aq.HBr leading to the formation of (2*Z*)-2-bromomethylalk-2-enoates.[4]

Table 1: Synthesis of (*Z*)-keto allyl bromides and chlorides[a, b, c]

substrate	R	allyl bromide	yield[d] (%)	allyl chloride	yield[d] (%)
1a	phenyl	**2a**[e]	81	**3a**[e]	82
1b	*p*-tolyl	**2b**[f]	79	**3b**[g]	81
1c	*p*-chlorophenyl	**2c**[f]	78	**3c**[g]	80
1d	*p*-isopropylphenyl	**2d**[f]	79	**3d**[g]	77
1e	*o*-chlorophenyl	**2e**[f]	80	**3e**[g]	79
1f	*o*-anisyl	**2f**[f]	78	**3f**[g]	78
1g	n-heptyl	**2g**[h]	64	**3g**[h]	66
1h	n-propyl	**2h**[h]	66	**3h**[h]	65

a) all reactions were carried out on 1 mmol scale (alcohols **1a-h**) with 1 mL of 48% aq.HBr (**2a-h**) or 36% aq.HCl (**3a-h**). b) satisfactory spectral [IR, ^{1}H NMR (200 MHz), ^{13}C NMR (50 MHz)] and elemental analyses were obtained for all molecules (**2a-h** and **3a-h**). c) ^{1}H NMR and ^{13}C NMR indicate the absence of any (*E*)-isomer. d) isolated yields of the products after column chromatography (2% ethyl acetate in hexanes). e) (*Z*)-stereochemistry was assigned by 2D NOESY experiment. f) (*Z*)-stereochemistry was assigned on the basis of the ^{1}H NMR chemical shift value of the vinylic proton in comparison with that of **2a**. g) (*Z*)-stereochemistry was assigned on the basis of the ^{1}H NMR chemical shift value of the vinylic proton and ^{13}C NMR chemical shift value of allylic methylene carbon in comparison with that of **3a**. h) (*Z*)-stereochemistry was assigned on the basis of ^{1}H NMR spectral analysis.[22]

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Experimental

All melting points were recorded on a Superfit (India) capillary melting point apparatus and are uncorrected. IR spectra were recorded on JASCO-FT-IR model 5300 or Perkin Elmer model 1310 spectrometer using samples as neat liquids or as solution in $CHCl_3$. ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) spectra were recorded in deuterochloroform ($CDCl_3$) on Bruker-AC-200 spectrometer using tetramethylsilane (TMS, $\delta = 0$) as internal standard. Elemental analyses were recorded on Perkin-Elmer 240C-CHN analyzer. Mass spectra were recorded on a micromass VG 7070H instrument. All the required Baylis-Hillman products (starting materials) were prepared by the reaction of the corresponding aldehydes with methyl vinyl ketone in presence of a catalytic amount of DABCO according to the literature procedure.[11, 23]

General procedure for the preparation of (Z)- allyl bromides and (Z)- allyl chlorides

To the Baylis-Hillman adduct (1 mmol), aq.HBr (48%) or aq.HCl (36%) (1 mL) was added at room temperature and swirled thoroughly for a minute (monitored by TLC) . The reaction mixture was immediately worked up by adding 1-2 mL of water and extracted with ether (2 × 5 mL). The combined organic layer was washed with aqueous potassium carbonate solution and dried over anhydrous sodium sulfate and concentrated to afford the crude product which on purification by column chromatography (silica gel, 2% ethyl acetate in

hexanes) afforded the pure allyl bromide or chloride.

(3*Z*)-3-(Bromomethyl)-4-phenylbut-3-en-2-one (2a): Colorless crystals. Yield: 81%; m.p.: 50-51°C (lit.[19] 49-50°C); IR ($CHCl_3$): 1672, 1620 cm^{-1}; ^1H NMR: δ 2.50 (s, 3H), 4.35 (s, 2H), 7.43-7.67 (m, 6H) ; ^{13}C NMR: δ 25.16, 25.89, 128.93, 129.61, 129.71, 134.28, 137.41, 142.68, 197.07; MS (m/z): 238 & 240 (M^+). Analysis calcd. for $C_{11}H_{11}OBr$: C, 55.26; H, 4.64; found: C, 55.20; H, 4.64.

(3*Z*)-3-(Bromomethyl)-4-(4-methylphenyl)but-3-en-2-one (2b): Colorless oil. Yield: 79 %; IR (neat): 1661, 1615 cm^{-1}; ^1H NMR: δ 2.39 (s, 3H), 2.47 (s, 3H), 4.36 (s, 2H), 7.27 (d, 2H, J = 7.7 Hz), 7.50 (d, 2H, J = 7.7 Hz), 7.60 (s, 1H); ^{13}C NMR : δ 21.41, 25.45, 25.84, 129.71, 129.88, 131.41, 136.54, 140.29, 143.02, 197.14; Analysis calcd. for $C_{12}H_{13}OBr$: C, 56.94; H, 5.18; found: C, 56.79; H, 5.20.

(3*Z*)-3-(Bromomethyl)-4-(4-chlorophenyl)but-3-en-2-one (2c): Pale yellow oil. Yield: 78 %; IR (neat) : 1670, 1624 cm^{-1}; ^1H NMR : δ 2.51 (s, 3H), 4.32 (s, 2H), 7.47 (d, 2H, J = 8.0 Hz), 7.56 (d, 3H, J = 8.0 Hz) ; ^{13}C NMR: δ 24.75, 25.84, 129.15, 130.88, 132.62, 135.75, 137.64, 141.19, 196.75. Analysis calcd. for $C_{11}H_{10}OBrCl$: C, 48.30; H, 3.68; found: C, 48.50; H, 3.66.

(3*Z*)-3-(Bromomethyl)-4-(4-isopropylphenyl)but-3-en-2-one (2d): Colorless oil. Yield: 79 %; IR (neat): 1665, 1620 cm^{-1}; ^1H NMR: δ 1.28 (d, 6H, J = 7.0 Hz), 2.49 (s, 3H), 2.98 (sept., 1H, J = 7.0 Hz), 4.39 (s, 2H), 7.35 (d, 2H, J = 8.4 Hz), 7.57 (d, 2H, J = 8.4 Hz), 7.62 (s, 1H); ^{13}C NMR: δ 23.73, 25.55, 25.90, 34.07, 127.14, 130.09, 131.79, 136.55, 143.05, 151.18, 197.20. Analysis calcd. for $C_{14}H_{17}OBr$: C, 59.80; H, 6.09; found : C, 59.52; H, 6.12.

(3*Z*)-3-(Bromomethyl)-4-(2-chlorophenyl)but-3-en-2-one (2e): Colorless oil. Yield: 80 %; IR (neat): 1670, 1625 cm^{-1}; ^1H NMR: δ 2.53 (s, 3H), 4.23 (s, 2H), 7.39-7.55 (m, 3H), 7.75-7.88 (m, 2H); ^{13}C NMR: δ 24.47, 25.86, 126.95, 129.44, 129.62, 130.56, 132.58, 134.07, 138.46, 138.95, 196.60. Analysis calcd. for : $C_{11}H_{10}OBrCl$: C, 48.30; H, 3.68; found: C, 48.41; H, 3.69.

(3*Z*)-3-(Bromomethyl)-4-(2-methoxyphenyl)but-3-en-2-one (2f): Pale yellow crystals. Yield: 78 %; m.p.: 85-86°C; IR ($CHCl_3$): 1668, 1615 cm^{-1}; ^1H NMR: δ 2.51 (s, 3H), 3.88 (s, 3H), 4.33 (s, 2H), 6.95 (d, 1H, J = 8.3 Hz), 7.08 (m, 1H), 7.42 (m, 1H), 7.75 (d, 1H, J = 7.9 Hz), 7.89 (s, 1H); ^{13}C NMR: δ 25.79, 26.04, 55.61, 110.73, 120.80, 123.39, 129.59, 131.44, 137.03, 138.74, 157.81, 197.44. Analysis calcd. for $C_{12}H_{13}O_2Br$: C, 53.55; H, 4.87; found: C, 53.28; H, 4.84.

(3*Z*)-3-(Bromomethyl)undec-3-en-2-one (2g): Colorless oil. Yield: 64 %; IR (neat): 1676, 1637 cm^{-1}; ^1H NMR: δ 0.83 (t, 3H, J = 6.5 Hz), 1.17-1.65 (m, 10H), 2.21-2.42 (m, 5H), 4.19 (s, 2H), 6.83 (t, 1H, J = 7.6 Hz); ^{13}C NMR: δ 13.94, 22.49, 25.31, 28.18, 28.94, 29.23, 29.31, 31.61, 138.35, 148.51, 196.21. Analysis calcd. for $C_{12}H_{21}OBr$: C, 55.18; H, 8.10; found : C, 55.40; H, 8.06.

(3*Z*)-3-(Bromomethyl)hept-3-en-2-one (2h): Pale yellow oil. Yield: 66%; IR (neat): 1670, 1640 cm^{-1}; ^1H NMR: δ 0.99 (t, 3H, J = 7.6 Hz), 1.57 (m, 2H), 2.25-2.45 (m, 5H), 4.18 (s, 2H), 6.80 (t, 1H, J = 7.6 Hz); ^{13}C NMR: δ 13.98, 21.64, 22.61, 25.51, 31.28, 138.74, 148.37, 196.63; Analysis calcd. for $C_8H_{13}OBr$: C, 46.85;

H, 6.39; found: C, 46.67; H, 6.42.

(3*Z*)-3-(Chloromethyl)-4-phenylbut-3-en-2-one (3a): Colorless oil. Yield: 82 %; IR (neat): 1672, 1624 cm^{-1}; ^1H NMR: δ 2.51 (s, 3H), 4.46 (s, 2H), 7.40-7.65 (m, 5H), 7.70 (s, 1H); ^{13}C NMR: δ 25.77, 37.55, 128.86, 129.55, 129.76, 134.13, 137.08, 143.43, 197.13; MS (m/z): 194 (M^+) & 196 (M^++2); Analysis calcd. for $C_{11}H_{11}OCl$: C, 67.87; H, 5.70; found: C, 67.57; H, 5.68.

(3*Z*)-3-(Chloromethyl)-4-(4-methylphenyl)but-3-en-2-one (3b): Colorless oil. Yield: 81 %; IR ($CHCl_3$): 1664, 1625 cm^{-1}; ^1H NMR: δ 2.40 (s, 3H), 2.48 (s, 3H), 4.45 (s, 2H), 7.27 (d, 2H, J = 8.0 Hz), 7.49 (d, 2H, J = 8.0 Hz), 7.66 (s, 1H); ^{13}C NMR: δ 21.48, 25.89, 37.82, 129.77, 129.90, 131.41, 136.42, 140.47, 143.86, 197.39; Analysis calcd. for $C_{12}H_{13}OCl$: C, 69.07; H, 6.28; found: C, 69.32; H, 6.30.

(3*Z*)-3-(Chloromethyl)-4-(4-chlorophenyl)but-3-en-2-one (3c): Colorless oil. Yield: 80 %; IR (neat): 1664, 1620 cm^{-1}; ^1H NMR: δ 2.49 (s, 3H), 4.40 (s, 2H), 7.44 (d, 2H, J = 8.6 Hz), 7.53 (d, 2H, J = 8.6 Hz), 7.62 (s, 1H); ^{13}C NMR: δ 25.91, 37.36, 129.29, 130.97, 132.63, 136.07, 137.56, 142.09, 197.03; Analysis calcd. for $C_{11}H_{10}OCl_2$: C, 57.67; H, 4.40; found: C, 57.49; H, 4.42.

(3*Z*)-3-(Chloromethyl)-4-(4-isopropylphenyl)but-3-en-2-one (3d): Colorless oil. Yield: 77 %; IR (neat): 1665, 1620 cm^{-1}; ^1H NMR: δ 1.26 (d, 6H, J = 6.8 Hz), 2.48 (s, 3H), 2.95 (sept., 1H, J = 6.8 Hz), 4.46 (s, 2H), 7.33 (d, 2H, J = 7.7 Hz), 7.53 (d, 2H, J = 7.7 Hz), 7.66 (s, 1H); ^{13}C NMR: δ 23.77, 25.87, 34.11, 37.83, 127.13, 130.05, 131.72, 136.36, 143.84, 151.30, 197.35; Analysis calcd. for $C_{14}H_{17}OCl$: C, 71.03; H, 7.24; found: C, 70.89; H, 7.26.

(3*Z*)-3-(Chloromethyl)-4-(2-chlorophenyl)but-3-en-2-one (3e): Colorless oil. Yield : 79 %; IR (neat): 1665, 1620 cm^{-1}; ^1H NMR : δ 2.52 (s, 3H), 4.32 (s, 2H), 7.30-7.51 (m, 3H), 7.66-7.75 (m, 1H), 7.81 (s, 1H); ^{13}C NMR: δ 25.98, 37.34, 127.14, 129.77, 130.07, 130.83, 132.67, 134.23, 138.40, 139.98, 196.95; Analysis calcd. for $C_{11}H_{10}OCl_2$: C, 57.67; H, 4.40; found : C, 57.94; H, 4.38.

(3*Z*)-3-(Chloromethyl)-4-(2-methoxyphenyl)but-3-en-2-one (3f): Colorless crystals. Yield: 78 %; m.p.: 65-67^{0}C; IR ($CHCl_3$): 1666, 1618 cm^{-1}; ^1H NMR: δ 2.50 (s, 3H), 3.88 (s, 3H), 4.42 (s, 2H), 6.95 (d, 1H, J = 8.4 Hz), 7.08 (m, 1H), 7.40 (m, 1H), 7.69 (m, 1H), 7.93 (s, 1H); ^{13}C NMR: δ 25.95, 38.10, 55.56, 110.66, 120.76, 123.23, 129.89, 131.54, 136.72, 139.57, 157.73, 197.51; Analysis calcd. for $C_{12}H_{13}O_2Cl$: C, 64.15; H, 5.83; found: C, 64.31; H, 5.81.

(3*Z*)-3-(Chloromethyl)undec-3-en-2-one (3g): Colorless oil. Yield: 66 %; IR (neat): 1676, 1639 cm^{-1}; ^1H NMR: δ 0.90 (t, 3H, J = 6.7 Hz), 1.20-1.66 (m, 10H), 2.25-2.45 (m, 5H), 4.31 (s, 2H), 6.85 (t, 1H, J = 7.6 Hz); ^{13}C NMR: δ 14.09, 22.67, 25.48, 28.60, 29.09, 29.31, 29.45, 31.77, 35.61, 138.42, 148.98, 196.83; Analysis calcd. for $C_{12}H_{21}OCl$: C, 66.50; H, 9.77; found: C, 66.16; H, 9.79.

(3*Z*)-3-(Chloromethyl)hept-3-en-2-one (3h): Colorless oil. Yield: 65 %; IR (neat): 1674, 1639 cm^{-1}; ^1H NMR: δ 0.99 (t, 3H, J = 7.6 Hz), 1.45-1.66 (m, 2H), 2.25-2.46 (m, 5H), 4.30 (s, 2H), 6.84 (t, 1H, J = 7.6 Hz); ^{13}C NMR: δ 13.81, 21.74, 25.34, 31.09, 35.48, 138.42, 148.65, 196.68; Analysis calcd. for $C_8H_{13}OCl$: C,

59.81; H, 8.16; found: C, 59.67; H, 8.19.

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20. Earlier this molecule was synthesized by Cromwell *et al.*[19] *via* the reaction of *trans* α-methylbenzalacetone, with NBS in the presence of a catalytic amount of benzoyl peroxide. Suzuki *et al.*[24] synthesized the same molecule *via* the reaction between B-bromo-9-borabicyclo[3.3.1]nonane, benzaldehyde and methyl vinyl ketone and reported its ^{1}H NMR spectral data. The ^{1}H NMR spectral data of **2a** is in accordance with the reported data.[19, 24]
21. In ^{1}H NMR spectrum of ethyl (4*E*)-5-phenyl-4-acetylpent-4-enoate the vinylic proton appears at δ 7.55 while same proton in the (*Z*)-isomer appears at δ 6.81.[25] In the ^{1}H NMR spectrum of **2a** the vinylic proton appears at δ 7.64 (partly merged with aromatic protons). Therefore we assigned (*Z*)-stereochemistry to **2a**.
22. In the ^{1}H NMR spectrum of trisubstituted alkenes with ketone group, the vinylic proton *cis* to the carbonyl group appears downfield in comparison with that of the vinylic proton *trans* to carbonyl.[26, 27] In the ^{1}H NMR spectrum of **2g, h** and **3g, h** the vinylic proton appears at ≈ δ 6.80 as a triplet. Therefore in analogy with aromatic substituted molecules we assigned (*Z*)-stereochemistry to these molecules *i.e.* **2g, h & 3g, h**.
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