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An expedient stereoselective synthesis of (*Z*)- and (*E*)-allyl iodides from Baylis–Hillman adducts along with selective iodination of benzylic alcohols using the polymethylhydrosiloxane–iodine system☆

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Abstract—A stereoselective method has been developed for the synthesis of (*Z*)- and (*E*)-allyl iodides from Baylis–Hillman adducts using polymethylhydrosiloxane (PMHS) and iodine in chloroform at room temperature. In addition, the reagent system has been utilized for the iodination of benzylic alcohols selectively.

The Baylis–Hillman reaction is widely utilized as a useful carbon–carbon bond forming reaction in organic synthesis.[1] The Baylis–Hillman adducts, 3-hydroxy-2-methylene-alkanoates (derived from acrylate esters) or 3-hydroxy-2-methylene-alkanenitriles (derived from acrylonitrile) are precursors for stereoselective syntheses of various multifunctional molecules.[1b,2] The development of efficient and stereoselective methods for the preparation of substituted allyl iodides from these adducts is highly desirable, as they are utilized for the construction of different naturally occurring bioactive compounds and their analogues, for example, α-alkylidene-β-lactams,[2a] α-methylene-γ-butyrolactones[2b] and flavonoids.[2c] Different reagents have been reported[3] for the synthesis of allyl halides directly from Baylis–Hillman adducts such as hydrogen halides with strong acids ($HBr–H_2SO_4$, $HI–H_3PO_4$),[2a,4a] organic acid halides (oxalyl chloride, MsCl),[3a,b] NCS/NBS–Me_2S,[3c,e] PBr_3[3f] and Lewis acids ($FeCl_3$, $InCl_3$).[3g,h] On the other hand, methods for the preparation of allyl iodides from Baylis–Hillman adducts are limited[4] and most of the reported methods suffer from disadvantages including the use of strong acids, low stereoselectivity, unsatisfactory yields for some substrates, long reaction times and complex experimental procedures. Recently, a method utilizing TMSCl/NaI was reported[4e] for the preparation of (*Z*)-allyl iodides containing only an aryl group.

In continuation of our work[3g,4d,5a–c] on the conversion of Baylis–Hillman adducts into trisubstituted alkenes, along with our interest in the catalytic application of molecular iodine,[5d–f] we have discovered that treatment of Baylis–Hillman adducts with iodine and polymethylhydrosiloxane (PMHS) in chloroform at room temperature afforded the corresponding allyl iodides in high yields and stereoselectivities, as depicted in Scheme 1.

Baylis–Hillman adducts possessing ester and nitrile moieties underwent the conversion readily and allyl iodides containing aryl as well as alkyl groups were obtained in high yields (Table 1). Aryl groups substituted with electron-donating or electron-withdrawing functionalities

Keywords: Baylis–Hillman adduct; (*Z*)- and (*E*)-Allyl iodides; Polymethylhydrosiloxane (PMHS); Iodine; Benzylic iodide.

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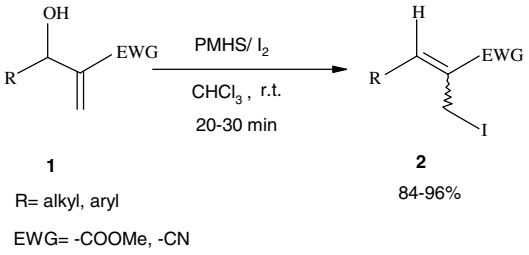


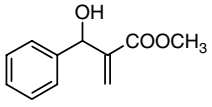
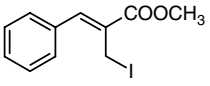
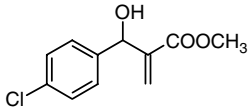
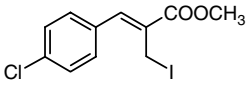
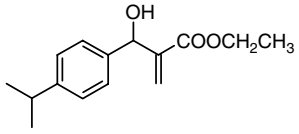
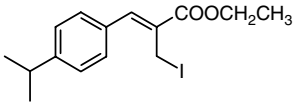
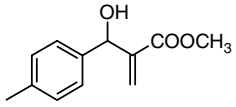
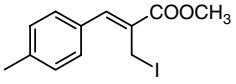
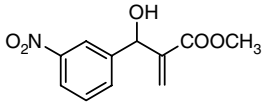
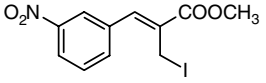
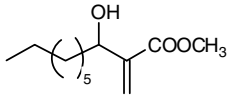
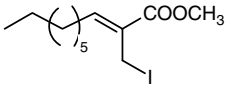
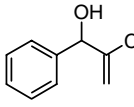
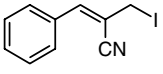
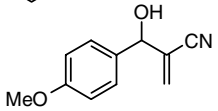
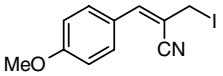
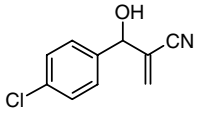
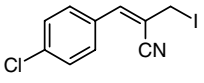
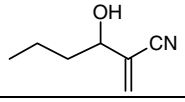
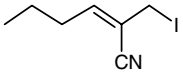
Scheme 1.

did not alter the rate of the reaction. Allyl iodides containing an ester moiety were formed with (*Z*)-configuration while those possessing a nitrile moiety gave exclusively (*E*)-configured products. The ^{1}H NMR spectra of the products[6] were used to establish their structures and stereochemistry by comparison with reported data for known compounds.[4d]

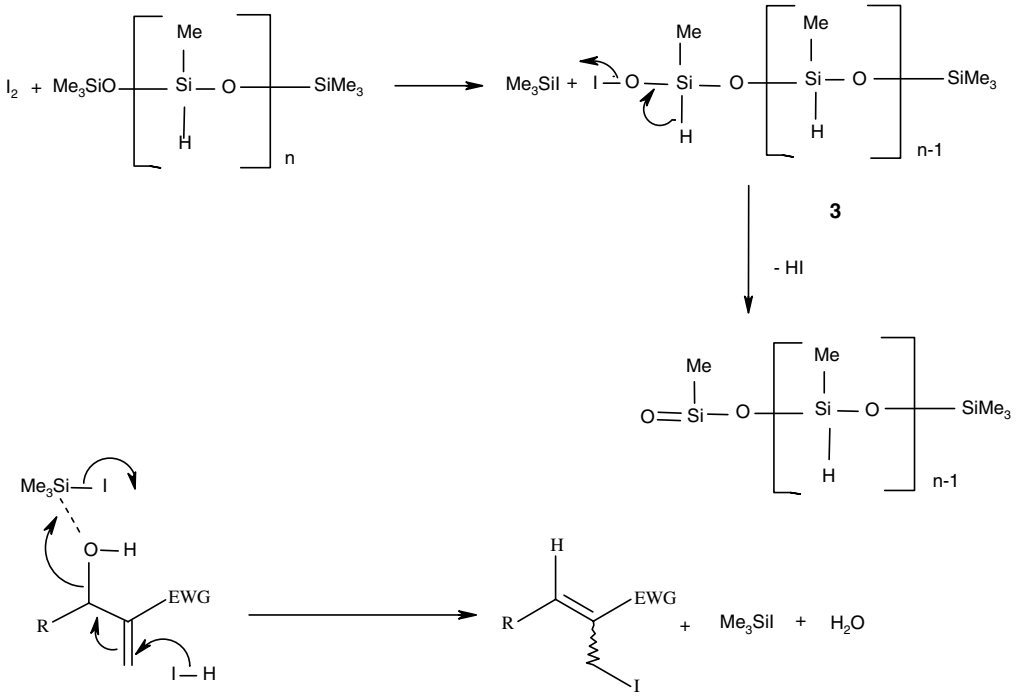
The utility of polymethylhydrosiloxane (PMHS), a co-product of the silicone industry, as an attractive, inert reducing agent for environmentally benign processes is well documented.[7] However, to our knowledge its use in combination with iodine for the synthesis of allyl iodides has not previously been explored.

A possible reaction mechanism is shown in Scheme 2. Iodine may react initially with PMHS to produce trimethylsilyliodide and the unstable intermediate **3**,[7c] which then leads to in situ formation of hydroiodic acid

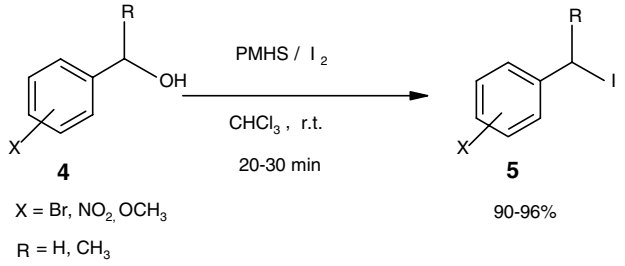
Table 1. Preparation of (*Z*)- and (*E*)-allyl iodides from Baylis–Hillman adducts using PMHS/I_2[a]

Entry	Adduct **1**	Product **2**	Time (min)	Isolated yield (%)
a			30	96
b			25	94
c			20	90
d			25	92
e			30	94
f			30	87
g			25	86
h			25	88
i			30	92
j			30	84

[a] The structures of the alkenes were determined from their spectral (IR, ^{1}H NMR and MS) and analytical data. The allyl iodides in entries a–f were formed with (*Z*)-configuration while those of entries g–j were formed with (*E*)-configuration.



Scheme 2.



Scheme 3.

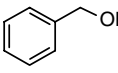
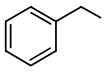
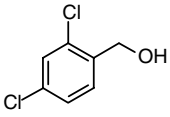
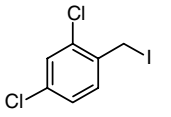
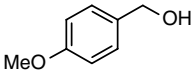
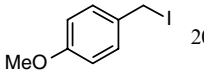
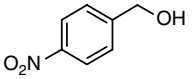
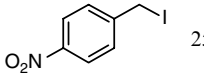
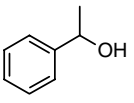
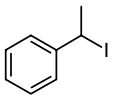
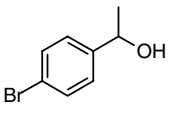
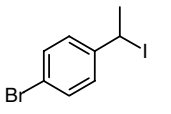
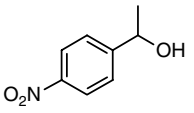
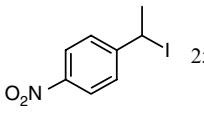
which might react with the Baylis–Hillman adduct to give the corresponding allyl iodide.

Encouraged by the successful results obtained with the Baylis–Hillman adducts we further studied the effect of the PMHS–I_2 system on other types of alcohols. The reaction was found to be highly efficient with primary and secondary benzylic alcohols leading to the corresponding benzylic iodides in high yields (Scheme 3). Electron-donating as well as electron-withdrawing substituents on the aromatic rings of the benzylic alcohols did not show any significant effect on the yields of the products.

The reaction was unsuccessful with aliphatic alcohols and phenols (Table 2). Even with allylic alcohols no monoiodinated unsaturated compounds were obtained. Thus the present method seems to be chemoselective towards iodination of benzylic alcohols.

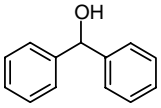
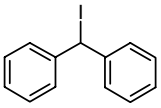
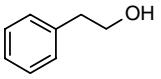
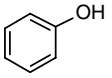
In conclusion, the PMHS–I_2 system has been utilized for the synthesis of both (*Z*)- and (*E*)-allyl iodides from

Table 2. Conversion of primary and secondary benzylic alcohols to iodides using PMHS/I_2[a]

Entry	Alcohol **4**	Iodide **5**	Time (min)	Isolated yield (%)
a			20	96
b			30	94
c			20	94
d			25	93
e			30	92
f			25	90
g			25	94

(*continued on next page*)

Table 2 (*continued*)

Entry	Alcohol **4**	Iodide **5**	Time (min)	Isolated yield (%)
h			30	88
i		No reaction	120	—
j		No reaction	120	—
k	CH_3–$(CH_2)_7$OH	No reaction	120	—

[a] The structures of the iodides were determined from their spectral (IR, ^{1}H NMR and MS) and analytical data.

Baylis–Hillman adducts and benzylic iodides from benzylic alcohols in excellent yields at room temperature. Operational simplicity, short reaction times, high yields and impressive stereo- and chemoselectivities are advantages of this method.

Acknowledgement

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References and notes

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6. General procedure for the preparation of allyl iodides and benzylic iodides: To a solution of Baylis–Hillman adduct (0.5 mmol) or benzylic alcohol (0.5 mmol) and PMHS (0.75 mmol) in chloroform (5 mL), iodine (0.5 mmol) was added. The reaction was allowed to stir at room temperature for 20–30 min. The reaction was monitored by TLC. On completion of the reaction, the solvent was evaporated under vacuum and the reaction mixture was dissolved in hexane and passed through a silica gel column using hexane–ethyl acetate as eluent. Evaporation of the solvent afforded the iodinated product in pure form. Spectral and analytical data of novel allyl iodides and benzyl iodides are given below.
Compound **2c**: IR (KBr): 1709, 1606, 1509, 1462, 1263 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.62 (1H, s), 7.42 (2H, d, $J = 8.0$ Hz), 7.22 (2H, d, $J = 8.0$ Hz), 4.28 (2H, s), 4.22 (2H, q, $J = 7.0$ Hz), 2.85 (1H, m), 1.33 (3H, t, $J = 7.0$ Hz), 1.25 (6H, d, $J = 7.0$ Hz); EIMS: m/z 231 ($M^{+\cdot}$–I); Anal. Calcd for $C_{15}H_{19}IO_2$: C, 50.28; H, 5.28. Found: C, 50.18; H, 5.31.
Compound **2h**: IR (KBr): 2210, 1686, 1599, 1509, 1261, 1176 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.72 (2H, d, $J = 8.0$ Hz), 7.14 (1H, s), 6.88 (2H, d, $J = 8.0$ Hz), 4.14 (2H, s), 3.82 (3H, s); EIMS: m/z 172 ($M^{+\cdot}$–I); Anal. Calcd for $C_{11}H_{10}ION$: C, 44.15; H, 3.34. Found: C, 44.22; H, 3.26.
Compound **2j**: IR (KBr): 2225, 1634, 1460, 1163, 1114 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 6.42 (1H, t, $J = 7.0$ Hz), 3.91 (2H, s), 2.35 (2H, q, $J = 7.0$ Hz), 1.62–1.47 (2H, m), 0.90 (3H, t, $J = 7.0$ Hz); EIMS: m/z 108 ($M^{+\cdot}$–I); Anal. Calcd for $C_7H_{10}IN$: C, 35.74; H, 4.26. Found: C, 35.62; H, 4.24.
Compound **5b**: IR (KBr): 3012, 2910, 1594, 1507, 1410, 1172, 1150, 810, 718 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.32 (1H, d, $J = 2.0$ Hz), 7.20 (1H, dd, $J = 8.0$, 2.0 Hz), 7.08 (1H, d, $J = 8.0$ Hz), 4.44 (2H, s); EIMS: m/z 160, 162, 164 ($M^{+\cdot}$–I); Anal. Calcd for $C_7H_5Cl_2I$: C, 29.27; H, 1.74. Found: C, 29.34; H, 1.78.
Compound **5g**: IR (KBr): 3062, 2986, 1595, 1521, 1416, 1212, 1112, 838, 675 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.12 (2H, d, $J = 8.0$ Hz), 7.50 (2H, d, $J = 8.0$ Hz), 5.28 (1H, q, $J = 7.0$ Hz), 2.16 (3H, d, $J = 7.0$ Hz); EIMS: m/z 150 ($M^{+\cdot}$–I); Anal. Calcd for $C_8H_8IO_2N$: C, 34.66; H, 2.89. Found: C, 34.58; H, 2.84.
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