TMSOTf-Catalyzed Stereoselective Isomerization of Acetates of the Baylis–Hillman Adducts

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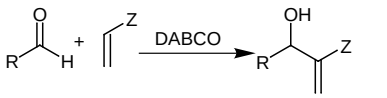
Received 8 September 1999; revised 15 November 1999

Abstract: TMSOTf-catalyzed isomerization of acetates of the Baylis–Hillman adducts, i.e. methyl 3-acetoxy-3-aryl-2-methylenepropanoates and 3-acetoxy-3-aryl-2-methylenepropanenitriles pro-viding methyl (2*E*)-2-(acetoxymethyl)-3-arylprop-2-enoates and (2*E*)-2-(acetoxymethyl)-3-arylprop-2-enenitriles, respectively, is described.

Key words: Baylis–Hillman reaction, trimethylsilyl trifluoromethanesulfonate, isomerization, stereoselectivity, 1,2-interaction

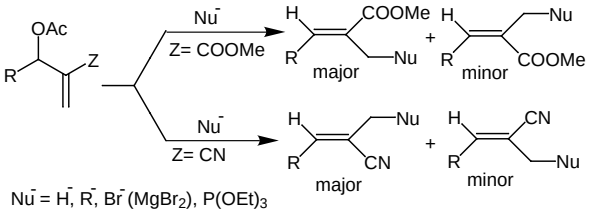
Synthetic applications of trimethylsilyl trifluoromethanesulfonate (TMSOTf) in a variety of stereoselective reactions and transformations have been well documented in the literature and in fact, TMSOTf has become a reagent of choice to the organic chemists in recent years for conducting various interesting organic reactions.[1-6] The Baylis–Hillman reaction is an important carbon–carbon bond forming and atom economy reaction, providing a useful class of molecules possessing chemospecific functional groups (Equation 1) which have been successfully used in a variety of stereoselective processes.[7-20] As a part of our research program aimed at the development of the Baylis–Hillman reaction[14-20] as a source of stereo-selective processes, we herein report trimethylsilyl trifluoromethanesulfonate catalyzed stereoselective isomerization of the acetates of the Baylis–Hillman adducts, i.e. methyl 3-acetoxy-3-aryl-2-methylenepropanoates and 3-acetoxy-3-aryl-2-methylenepropanenitriles into methyl (2*E*)-2-(acetoxymethyl)-3-arylprop-2-enoates and (2*E*)-2-(acetoxymethyl)-3-arylprop-2-enenitriles, respectively.



Z= COOMe, CN, COMe etc. R= aryl or alkyl

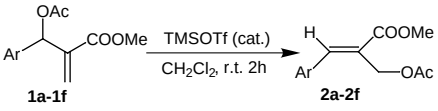
Equation 1

We have observed a remarkable reversal of stereochemical directive effects from ester group to nitrile group in a number of stereoselective transformations (Scheme) involving acetates of the Baylis–Hillman adducts.[16-19] With a view to study the stereochemical directive effects of ester and nitrile groups in the TMSOTf-catalyzed reactions and with a view to examine the application of TMSOTf as a catalyst for stereoselective isomerization of acetates of the Baylis–Hillman adducts, we have undertaken the investigation of the reactions of representative methyl 3-acetoxy-3-aryl-2-methylenepropanoates and 3-acetoxy-3-aryl-2-methylenepropanenitriles with trimethylsilyl trifluoromethanesulfonate.



Scheme

Accordingly, we first examined the isomerization of methyl 3-acetoxy-2-methylene-3-phenylpropanoate (**1a**) under the catalytic influence of TMSOTf. The best results were obtained when the isomerization of **1a** (1 mmol) was carried out in the presence of TMSOTf (11 mol%) in dichloromethane at room temperature for 2 hours, thus providing the required methyl (2*E*)-2-(acetoxymethyl)-3-phenylprop-2-enoate (**2a**) in 100% (*E*)-selectivity as evidenced by the ^{1}H NMR spectral analysis.[21] Encouraged by this result, we then transformed a representative class of methyl 3-acetoxy-3-aryl-2-methylenepropanoates under the catalytic influence of TMSOTf into methyl (2*E*)-2-(acetoxymethyl)-3-arylprop-2-enoates (Equation 2, Table). It is worth mentioning that the isomerization of methyl 3-acetoxy-3-aryl-2-methylenepropanoates to methyl 2-(acetoxymethyl)-3-arylprop-2-enoates was reported earlier in high *(E)*-selectivity, under the catalytic influence of DABCO.[22-24]

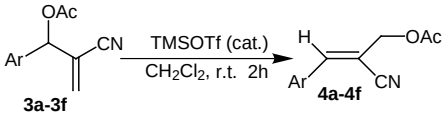


Ar = phenyl, 4-methylphenyl, 4-ethylphenyl, 4-isopropylphenyl, 4-chlorophenyl, 2-methylphenyl

Equation 2

With a view to understanding the stereochemical directive effect of the nitrile group in the TMSOTf catalyzed reactions, we next examined the isomerization of 3-acetoxy-2-methylene-3-phenylpropanenitrile with a catalytic amount of TMSOTf at room temperature for 2 hours. This reaction provided a simple and convenient synthesis of the

desired 2-(acetoxymethyl)-3-phenylprop-2-enenitrile with exclusive (*E*)-stereoselectivity (Equation 3) in high yields. The (*E*)-stereochemistry was assigned on the basis of a 2D NOESY NMR experiment. This reaction clearly demonstrates that there is a reversal in the stereochemical directive effect of the nitrile group with respect to the ester group. We then synthesized a representative class of (2*E*)-2-(acetoxymethyl)-3-arylprop-2-enenitriles via TMSOTf induced isomerization of various 3-acetoxy-3-aryl-2-methylenepropanenitriles (Equation 3, Table). Our attempts to isomerize methyl 3-acetoxy-2-methyleneoctanoate and 3-acetoxy-2-methyleneoctanenitrile under the catalytic influence of TMSOTf were unsuccessful.



Ar = phenyl, 4-methylphenyl, 4-ethylphenyl, 4-isopropylphenyl, 4-chlorophenyl, 2-methylphenyl

Equation 3

The reversal of stereochemical directive effects from the ester group to the nitrile group is consistent with our earlier results and can be possibly explained through the Claisen type rearrangement (transition state models **I**, **II**, **III**, and **IV**). In the case of molecules **1,** the unusual 1,2-interaction may be more predominant than the classical 1,3-interaction (transition state models **I, II**) leading to (*E*)-selectivity. In the case of molecules **3,** however, the classical 1,3- interaction may be more predominant than the unusual 1,2-interaction (transition state models **III, IV**) resulting in (*E*)- selectivity.[26]

Another possible explanation for the reversal of stereochemical directive effects of the nitrile group with respect to the ester group is that the products are those of thermodynamic control in all these cases. That is, the more sterically demanding ester group requires a particular conformation for optimal conjugation compared to the slim cyano group with local cylindrical symmetry. Thus, the molecules **1a-f** provide trisubstituted alkenes **2a**−**f** having the aryl group *trans* to the ester group, whereas compounds **3a**−f produce trisubstituted alkenes **4a**−**f** having the aryl group *cis* to the nitrile group.

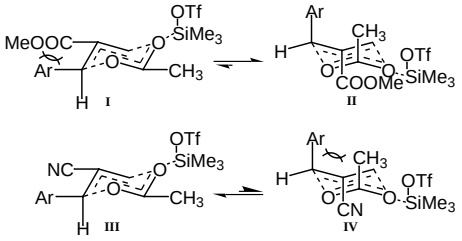


Table TMSOTf-Catalyzed Isomerization Acetates of the Baylis–Hillman Adducts[a,b,c]

Substrate	Ar	Z	Product	Yield[d] (%)
1a	phenyl	COOMe	**2a**[21]	73
1b	4-methylphenyl	COOMe	**2b**[e]	65
1c	4-ethylphenyl	COOMe	**2c**[e]	88
1d	4-isopropylphenyl	COOMe	**2d**[e]	83
1e	4-chlorophenyl	COOMe	**2e**[e]	80
1f	2-methylphenyl	COOMe	**2f**[e,f]	77[g]
3a	phenyl	CN	**4a**[h]	85
3b	4-methylphenyl	CN	**4b**[i]	68
3c	4-ethylphenyl	CN	**4c**[i]	78
3d	4-isopropylphenyl	CN	**4d**[i]	74
3e	4-chlorophenyl	CN	**4e**[i]	65
3f	2-methylphenyl	CN	**4f**[i]	84

[a] All reactions were carried out on 1 mmol scale of acetates of the Baylis–Hillman adducts with TMSOTf (11 mol %) at r.t. for 2 h.
[b] All compounds were obtained as colorless liquids and characterized by IR, ^{1}H NMR, ^{13}C NMR spectral data and microanalysis.
[c] ^{1}H and ^{13}C NMR indicate the absence of any (*Z*)-isomer.
[d] Isolated yield of the products after column chromatography (3% EtOAc in hexanes).
[e] (*E*)-Stereochemistry was assigned on the basis of the chemical shift value of the olefinic proton in ^{1}H NMR and allylic methylene carbon in ^{13}C NMR spectra in analogy with **2a**.[25]
[f] This compound contains ≈10% impurity and was further purified by preparative HPLC (Shim-Pack PREP-ODS column, (20 mm x 25 cm), MeOH, flow rate 3mL/min, Rt: 20 min
[g] Isolated yield after purification by preparative HPLC.
[h] (*E*)-Stereochemistry was assigned by a **2D NOESY** experiment.
[i] (*E*)-Stereochemistry was assigned on the basis of the ^{13}C NMR chemical shift value of the allylic methylene carbon in comparison with that of **4a**.[25]

In conclusion, we have stereoselectively transformed acetates of the Baylis−Hillman adducts, i.e., methyl 3-acetoxy-3-aryl-2-methylenepropanoates and 3-acetoxy-3-aryl-2-methylenepropanenitriles under the catalytic influence of trimethylsilyl trifluoromethanesulfonate into methyl (2*E*)-2-(acetoxymethyl)-3-arylprop-2-enoates and (2*E*)-2-(acetoxymethyl)-3-arylprop-2-enenitriles, respectively. Thus, we have demonstrated the synthetic applications of trimethylsilyl trifluoromethanesulfonate, and the importance of the Baylis−Hillman adducts in stereoselective organic synthesis.

IR spectra were recorded on JASCO-FT-IR model 5300 spectrometer using samples as neat liquids. ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) spectra were recorded in $CDCl_3$ on a Bruker-AC-200 spectrometer using TMS as internal standard. Elemental analyses were recorded on Perkin−Elmer 240C-CHN analyzer. The required acetates of the Baylis−Hillman adducts (**1** and **3**) were prepared by the reaction of the corresponding Baylis−Hillman adducts (obtained from corresponding aldehydes via the reaction with methyl acrylate and acrylonitrile, respectively, in presence of a catalytic amount of DABCO according to the literature procedure)[7,8] with acetyl chloride in presence of pyridine.

Isomerization of Acetates of the Baylis-Hillman Adducts; General Procedure

To a stirred solution of acetates of the Baylis−Hillman adduct (**1a**−**f** and **3a**−**f**, 1 mmol) in CH_2Cl_2 (2 mL), was added TMSOTf (0.02 mL, 11 mol %, 0.0245 g)) at r.t. After 2 h, the reaction mixture was

diluted with H_2O (3 mL) and extracted with Et_2O (3 x 10 mL). The combined organic layer was dried (Na_2SO_4), the solvent was evaporated and the crude product thus obtained was purified by column chromatography (silica gel, 3% EtOAc in hexanes) to provide the desired products (**2a**–**f** and **4a**–**f**).

Methyl (2*E*)-2-(Acetoxymethyl)-3-phenylprop-2-enoate (2a)
Colorless liquid; yield: 73%; R_f = 0.58 (hexanes/EtOAc, 9:1).

IR (neat): ν_{max} = 1741, 1720, 1635 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 2.10 (s, 3H), 3.84 (s, 3H), 4.95 (s, 2H), 7.39 (s, 5H), 7.98 (s, 1H).

^{13}C NMR ($CDCl_3$): δ = 20.78, 52.14, 59.26, 126.77, 128.64, 129.37, 129.47, 134.19, 145.25, 167.19, 170.49.

Anal. Calcd for $C_{13}H_{14}O_4$: C, 66.65, H, 6.02. Found: C, 66.89, H, 6.05.

Methyl (2*E*)-2-(Acetoxymethyl)-3-(4-methylphenyl)prop-2-enoate (2b)
Colorless liquid; yield: 65%; R_f = 0.56 (hexanes/EtOAc, 9:1).

IR (neat): ν_{max} = 1740, 1718, 1633 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 2.11 (s, 3H), 2.39 (s, 3H), 3.85 (s, 3H), 4.98 (s, 2H), 7.22 (d, 2H, *J* = 8.0 Hz), 7.30 (d, 2H, *J* = 8.0 Hz), 7.96 (s, 1H).

^{13}C NMR ($CDCl_3$): δ = 20.75, 21.22, 52.03, 59.34, 125.74, 129.37, 129.50, 131.33, 139.87, 145.37, 167.31, 170.49.

Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73, H, 6.50. Found: C, 67.86, H, 6.49.

Methyl (2*E*)-2-(Acetoxymethyl)-3-(4-ethylphenyl)prop-2-enoate (2c)
Colorless liquid; yield: 88%; R_f = 0.52 (hexanes/EtOAc, 9:1).

IR (neat): ν_{max} = 1741, 1718, 1633 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.25 (t, 3H, *J* = 7.6 Hz), 2.11 (s, 3H), 2.68 (q, 2H, *J* = 7.6 Hz), 3.85 (s, 3H), 4.97 (s, 2H), 7.24 (d, 2H, *J* = 8.0 Hz), 7.32 (d, 2H, *J* = 8.0 Hz), 7.97 (s, 1H).

^{13}C NMR ($CDCl_3$): δ = 15.12, 20.76, 28.60, 52.03, 59.36, 125.66, 128.16, 129.60, 131.52, 145.43, 146.13, 167.31, 170.53.

Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.69, H, 6.92. Found: C, 68.54, H, 6.96.

Methyl (2*E*)-2-(Acetoxymethyl)-3-(4-isopropylphenyl)prop-2-enoate (2d)
Colorless liquid; yield: 83%; R_f = 0.50 (hexanes/EtOAc, 9:1).

IR (neat): ν_{max} = 1741, 1718, 1631 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.26 (d, 6H, *J* = 6.8 Hz), 2.10 (s, 3H), 2.94 (m, 1H), 3.84 (s, 3H), 4.97 (s, 2H), 7.20–7.45 (m, 4H), 7.96 (s, 1H).

^{13}C NMR ($CDCl_3$): δ = 20.82, 23.66, 33.95, 52.07, 59.44, 125.74, 126.80, 129.68, 131.71, 145.44, 150.77, 167.36, 170.58.

Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.55, H, 7.30. Found: C, 69.30, H, 7.28.

Methyl (2*E*)-2-(Acetoxymethyl)-3-(4-chlorophenyl)prop-2-enoate (2e)
Colorless liquid; yield: 80%; R_f = 0.61 (hexanes/EtOAc, 9:1).

IR (neat): ν_{max} = 1740, 1720, 1637 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 2.10 (s, 3H), 3.85 (s, 3H), 4.92 (s, 2H), 7.25–7.46 (m, 4H), 7.91 (s, 1H).

^{13}C NMR ($CDCl_3$): δ = 20.82, 52.31, 59.05, 127.32, 129.00, 130.73, 132.62, 135.71, 143.89, 167.02, 170.51.

Anal. Calcd for $C_{13}H_{13}O_4Cl$: C, 58.11, H, 4.88. Found: C, 58.38, H, 4.86.

Methyl (2*E*)-2-(Acetoxymethyl)-3-(2-methylphenyl)prop-2-enoate (2f)
Colorless liquid; yield: 77%; R_f = 0.57 (hexanes/EtOAc, 9:1).

IR (neat): ν_{max} = 1740, 1722, 1637 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 2.07 (s, 3H), 2.31 (s, 3H), 3.86 (s, 3H), 4.83 (s, 2H), 7.16–7.37 (m, 4H), 8.06 (s, 1H).

^{13}C NMR ($CDCl_3$): δ = 19.81, 20.75, 52.12, 59.36, 125.84, 127.43, 128.54, 129.24, 130.11, 133.46, 136.91, 144.53, 166.95, 170.44.

Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73, H, 6.50. Found: C, 67.83, H, 6.55.

(2*E*)-2-(Acetoxymethyl)-3-phenylprop-2-enenitrile (4a)
Colorless liquid; yield: 85%; R_f = 0.55 (hexanes/EtOAc, 9:1).

IR (neat): ν_{max} = 2216, 1747, 1626 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 2.16 (s, 3H), 4.82 (s, 2H), 7.23 (s, 1H), 7.45 (m, 3H), 7.79 (m, 2H).

^{13}C NMR ($CDCl_3$): δ = 20.51, 65.02, 105.88, 117.04, 128.81, 129.02, 130.94, 132.52, 147.05, 169.99.

Anal. Calcd for $C_{12}H_{11}NO_2$: C, 71.63, H, 5.51, N, 6.96. Found: C, 71.31, H, 5.53, N, 6.93.

(2*E*)-2-(Acetoxymethyl)-3-(4-methylphenyl)prop-2-enenitrile (4b)
Colorless liquid; yield: 68%; R_f = 0.53 (hexanes/EtOAc, 9:1).

IR (neat): ν_{max} = 2214, 1745, 1625 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 2.14 (s, 3H), 2.39 (s, 3H), 4.80 (s, 2H), 7.18 (s, 1H), 7.24 (d, 2H, *J* = 8.2 Hz), 7.69 (d, 2H, *J* = 8.2 Hz).

^{13}C NMR ($CDCl_3$): δ = 20.68, 21.48, 65.36, 104.56, 117.43, 129.22, 129.64, 129.92, 141.76, 147.35, 170.20.

Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.54, H, 6.09, N, 6.51. Found: C, 72.74, H, 6.07, N, 6.55.

(2*E*)-2-(Acetoxymethyl)-3-(4-ethylphenyl)prop-2-enenitrile (4c)

Colorless liquid; yield: 78%; R_f = 0.49 (hexanes/EtOAc, 9:1).

IR (neat): ν_{max} = 2214, 1747, 1625 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.25 (t, 3H, *J* = 8.0 Hz), 2.15 (s, 3H), 2.69 (q, 2H, *J* = 8.0 Hz), 4.81 (s, 2H), 7.20 (s, 1H), 7.28 (d, 2H, *J* = 8.0 Hz), 7.73 (d, 2H, *J* = 8.0 Hz).

^{13}C NMR ($CDCl_3$): δ = 14.97, 20.52, 28.66, 65.21, 104.44, 117.34, 128.30, 129.19, 130.02, 147.22, 147.82, 170.03.

Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34, H, 6.59, N, 6.11. Found: C, 73.52, H, 6.54, N, 6. 09.

(2*E*)-2-(Acetoxymethyl)-3-(4-isopropylphenyl)prop-2-enenitrile (4d)
Colorless liquid; yield: 74%; R_f = 0.47 (hexanes/EtOAc, 9:1).

IR (neat): ν_{max} = 2214, 1747, 1626 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.27 (d, 6H, J = 8.0 Hz), 2.15 (s, 3H), 2.95 (m, 1H), 4.81 (s, 2H), 7.20 (s, 1H), 7.30 (d, 2H, J = 8.2 Hz), 7.74 (d, 2H, J = 8.2 Hz).

^{13}C NMR ($CDCl_3$): δ = 20.66, 23.61, 34.11, 65.35, 104.67, 117.44, 127.04, 129.37, 130.29, 147.33, 152.58, 170.17.

Anal. Calcd for $C_{15}H_{17}NO_2$: C, 74.05, H, 7.04, N, 5.76. Found: C, 73.74, H, 7.07, N, 5.73.

(2*E*)-2-(Acetoxymethyl)-3-(4-chlorophenyl)prop-2-enenitrile (4e)

Colorless liquid; yield: 65%; R_f = 0.55 (hexanes/EtOAc, 9:1).

IR (neat): ν_{max} = 2212, 1743, 1624 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 2.15 (s, 3H), 4.80 (s, 2H), 7.17 (s, 1H), 7.42 (d, 2H, *J* = 8.8 Hz), 7.72 (d, 2H, *J* = 8.8 Hz).

^{13}C NMR ($CDCl_3$): δ = 20.71, 65.04, 106.75, 116.93, 129.34, 130.45, 131.10, 137.23, 145.72, 170.20.

Anal. Calcd for $C_{12}H_{10}NO_2Cl$: C, 61.16, H, 4.28, N, 5.94. Found: C, 61.02, H, 4.27, N, 5.99.

(2*E*)-2-(Acetoxymethyl)-3-(2-methylphenyl)prop-2-enenitrile (4f)

Colorless liquid; yield: 84%; R_f = 0.53 (hexanes/EtOAc, 9:1).

IR (neat): ν_{max} = 2218, 1747, 1624 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 2.16 (s, 3H), 2.35 (s, 3H), 4.83 (s, 2H), 7.09–7.50 (m, 4H), 7.83 (m, 1H).

^{13}C NMR ($CDCl_3$): δ = 19.58, 20.65, 64.89, 107.95, 116.87, 126.32, 127.79, 130.46, 130.59, 131.83, 137.26, 146.13, 170.15.

Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.54, H, 6.09, N, 6.51. Found: C, 72.87, H, 6.12, N, 6.49.

Acknowledgement

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

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(24) Foucaud reported similar isomerization using metal salts (1 equiv) under the catalytic influence of benzyltriethylammonium chloride (4 mol %).[23]
(25) In the ^{13}C NMR spectra of trisubstituted olefins the allylic carbon *cis* to aryl group appears upfield while the same carbon *trans* to aryl group appears downfield.[17,27] The ^{13}C NMR spectral data indicate the absence of any (*Z*)-isomer in the case of molecules **2a** and **4a**.
(26) We have recently invoked the possibility of unusual 1,2-interactions in the Johnson–Claisen rearrangement to explain the stereoselectivity. See: Basavaiah, D.; Pandiaraju, S.; Krishnamacharyulu, M. *Synlett* **1996**, 747.
(27) Funabiki, T.; Hosomi, H.; Yoshida, S.; Tarama, K. *J. Am. Chem. Soc*. **1982**, *104*, 1560.

Article Identifier:
1437-210X,E;2000,0,04,0545,0548,ftx,en;Z06599SS.pdf