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Chemo- and diastereoselective $Bi(OTf)_3$-catalyzed benzylation of silyl nucleophiles

Philipp Rubenbauer, Thorsten Bach *

Lehrstuhl für Organische Chemie I, Technische Universität München, Lichtenbergstr. 4, 85747 Garching, Germany

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Abstract

The direct alkylation of silyl enol ethers with *para*-methoxybenzylic alcohols or their corresponding acetates was efficiently catalyzed by $Bi(OTf)_3$ in CH_3NO_2 as the solvent. The reaction provided the α-benzylated carbonyl compounds in high yields after short reaction times using 1–2.5 mol % of the catalyst. Benzylic acetates other than *para*-methoxybenzylic acetates also underwent the reaction. High facial diastereoselectivities were observed with acetates derived from chiral α-branched *para*-methoxybenzylic alcohols. In addition, a catalytic reduction with Et_3SiH as the reducing agent is reported.
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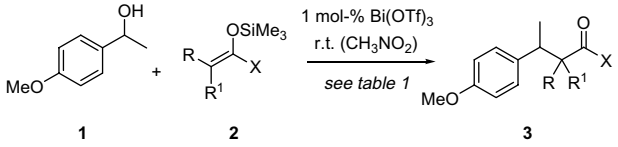
Keywords: Bi catalysis; Benzylic alcohols; Silyl enol ether; Facial diastereoselectivity; Triethylsilane

The counterpart of the conventional enolate alkylation under basic conditions is the acid-promoted alkylation of silyl enol ethers.[1,2] The latter reaction is most frequently applied to substrates which allow for a facile S_N1-type substitution. Important examples include *tert*-alkylation[3] and benzylation[4] reactions, which have been extensively studied in recent years.[2] Our interest in the benzylation and more specifically in the methoxybenzylation of silyl enol ethers stems from previous work, in which we studied the Friedel–Crafts alkylation of various arenes with chiral α-branched *para*-methoxybenzylic alcohols.[5] We envisioned that silyl enol ethers could serve as possible nucleophiles for related reactions under catalytic reaction conditions. It turned out that bismuth tris(trifluoromethanesulfonate) ($Bi(OTf)_3$) is a very efficient catalyst[6] for these reactions and we report in this Letter on our preliminary results in this area.

The suitability of $Bi(OTf)_3$ to activate benzylated alcohols for nucleophilic attack has been demonstrated earlier by Rueping et al.[7,8] Given the high temperatures (55–100 °C) required in these benzylation reactions, it was a pleasant surprise to note that the methoxybenzylation of silyl enol ethers can be achieved at ambient temperature in nitromethane as the solvent (Scheme 1, Table 1).

Sterically more congested *para*-methoxyphenyl-1-ethanol (**1**) was used in a first set of experiments as the alkylating agent (instead of the parent methoxybenzylalcohol) to mimic the situation in α-branched *para*-methoxybenzylic alcohols (vide infra). Silyl enol ethers **2** were prepared according to known procedures.[9] Reactions proceeded smoothly and provided the desired products[10] in high yields (73–96%, entries 1–8). The only exception was observed with the α,α′-disubstituted silyl ketene acetal **2i** (entry 9), which gave only a mediocre result. All reactions



1 **2** **3**

Scheme 1.

* Corresponding author. Tel.: +49 (0)89 289 13330; fax: +49 (0)89 289 13315.
E-mail address: thorsten.bach@ch.tum.de (T. Bach).

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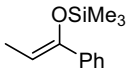
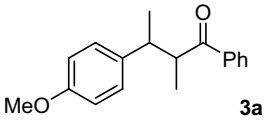
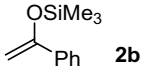
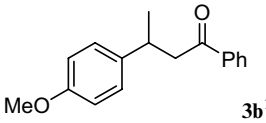
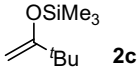
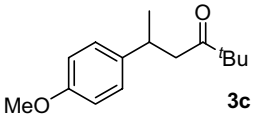
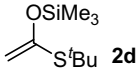
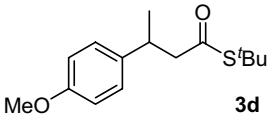
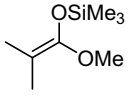
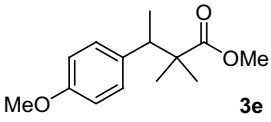
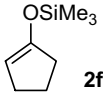
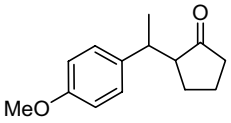
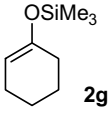
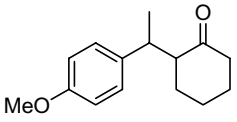
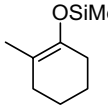
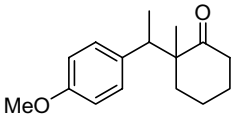
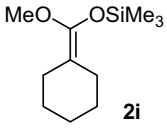
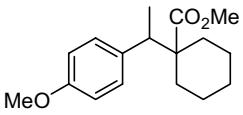
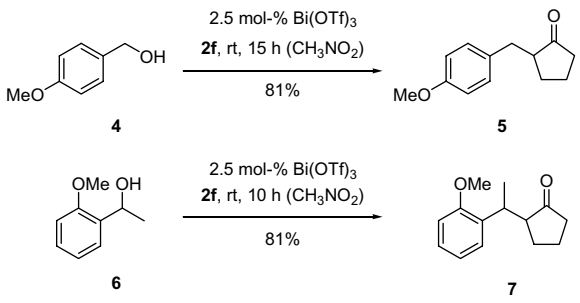
Table 1
Reaction of alcohol **1** with different silyl enol ethers **2** (cf. Scheme 1)

Entry	Enol ether	Product	Time (h)	Yield[a] (%)
1	 **2a**	 **3a**	4	89[b]
2	 **2b**	 **3b**[11]	3	76
3	 **2c**	 **3c**	5	79
4	 **2d**	 **3d**	4	77
5	 **2e**	 **3e**	4	73
6	 **2f**	 **3f**	2	91[c]
7	 **2g**	 **3g**	1	96[c]
8	 **2h**	 **3h**	1	96[c]
9	 **2i**	 **3i**	0.5	48

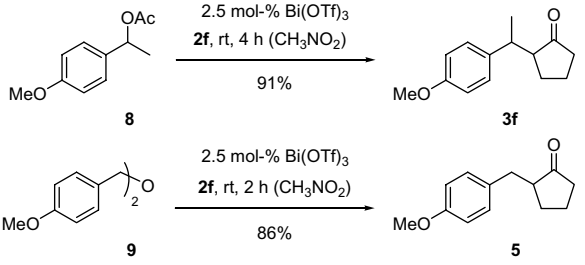
[a] Yield of isolated product after column chromatography.
[b] Diasteromeric ratio (^{1}H NMR) dr = 69:31.
[c] Diasteromeric ratio (^{1}H NMR) dr = 50:50.

were run at room temperature with the initially clear solution becoming slightly turbid after ca. 15 min.

It was shown in a second set of experiments (Scheme 2) with silyl enol ether **2f** as the nucleophile that other methoxybenzylic alcohols can be equally well employed as electrophile precursors. The parent alcohol **4** yielded the substitution product ketone **5**[12] and *ortho*-methoxyphenyl-1-ethanol (**6**) gave with the same silyl nucleophile product **7** (Scheme 2). Yields were high but a larger amount of $Bi(OTf)_3$ had to be employed for full conversion and reaction times were required to be longer.



Scheme 2.

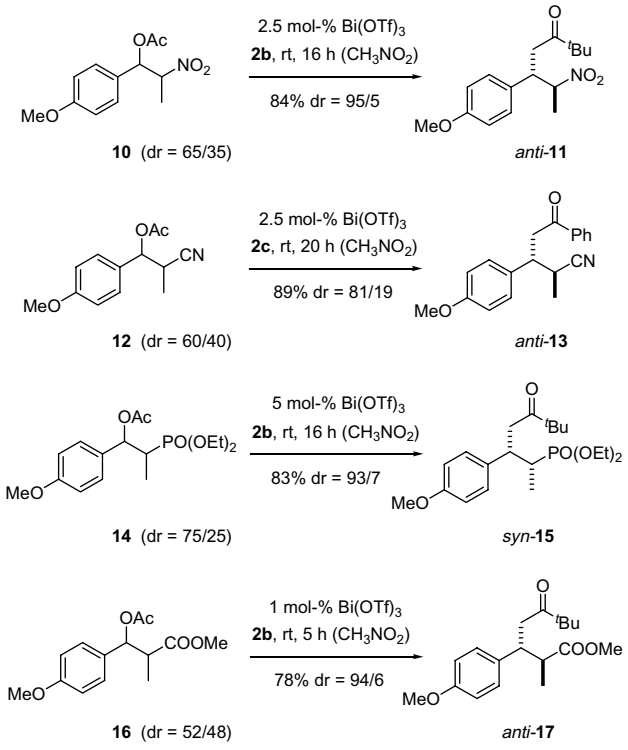


Scheme 3.

Further, electrophile variation revealed that acetate **8** of alcohol **1** was also an appropriate starting material for the alkylation reaction delivering ketone **3f** in 91% yield (Scheme 3). In the experiments with alcohol **4** (Scheme 2), it appeared as if the corresponding dibenzylether **9** was formed as side product/intermediate, which was consumed in the further course of the reaction. Indeed, we could show that this ether is an equally efficient starting material in the methoxybenzylation providing ketone **5** in 86% yield.

While dibenzylether formation is reversible, crossover experiments clearly established that the formation of products **3** is irreversible. Stirring of ketone **3c** or **3d** in the presence of catalytic quantities of $Bi(OTf)_3$ and of excess silyl enol ether **2f**, for example, did not give a hint for the formation of ketone **3f**.

Various precursors were screened to optimize the reactions of *para*-methoxybenzylic alcohols with a stereogenic center in α-position.[5b] Acetates proved to be the best choice providing the desired ketones in high yield with good facial diastereoselectivity (Scheme 4).[13] The selectivities achieved in these transformations are, of course, dependent on the substitution pattern at the stereogenic center.[5]



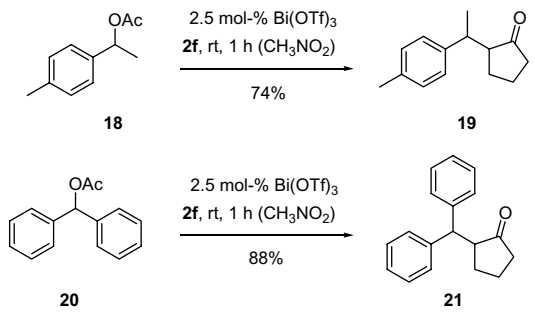
Scheme 4.

The nitro-substituted substrate **10** delivered ketone *anti*-**11** with almost perfect stereoselectivity while the selectivity in the reaction of cyanoacetate **12** (to ketone *anti*-**13**) was lower. Phosphonate **14** delivered a major diastereoisomer to which the *syn*-configuration *syn*-**15** was assigned. This and the other assignments are based on the close analogy to the previously studied diastereoselective arylation reactions.[5b] In the case of product *syn*-**15**, the configuration assignment was further supported by ^1H and ^{13}C NMR data.[13] Aldol-derived acetate **16** gave product *anti*-**17** with excellent diastereoselectivity (dr = 94:6). In all the cases, 1–5 mol % of the catalyst was required to achieve full conversion. The substrate dr is given in brackets for every acetate, which was used (Scheme 4). As expected for S_N1 type reactions, the diastereomeric composition of the starting materials did not influence the product diastereoselectivity. The reactions proceeded in a stereoconvergent fashion.

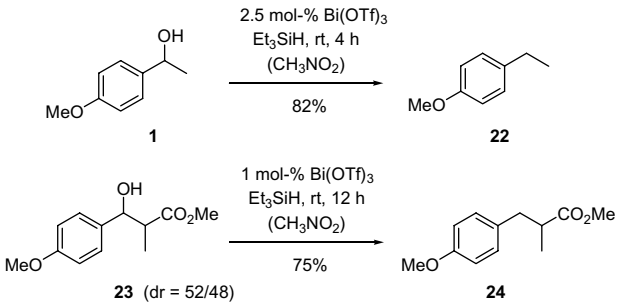
Other benzyl acetates but *para*-methoxybenzyl were identified as suitable benzylation reagents in combination with $Bi(OTf)_3$. While the corresponding alcohols, from which acetates **18** and **20** are derived, did not undergo a benzylation reaction, the corresponding acetates did. The product ketones **19** and **21** were obtained in very good yields (Scheme 5). Benzylic alcohols without an electron releasing substituent at the phenyl ring, for example, the parent benzylic alcohol (BnOH), or their acetates did not react.

Given the mechanistic similarity of the S_N1-type substitution by silyl enol ethers and the acid-catalyzed reduction by hydrosilanes,[14] we briefly looked into a possible $Bi(OTf)_3$-catalyzed reduction of *para*-methoxybenzylic alcohols.[15] We were pleased to find that the reactions of this type proceeded smoothly employing Et_3SiH[16] as the hydride source (Scheme 6). Benzylic alcohol **1** was converted into the corresponding hydrocarbon **22**[17] using 2.5 mol % $Bi(OTf)_3$. The aldol addition product **23** was readily reduced to *para*-methoxyphenylpropionate **24**[18] employing as little as 1 mol % of the catalyst.

In summary, we have shown that $Bi(OTf)_3$ can be an efficient catalyst to promote C–C bond forming reactions between methoxybenzylic alcohols and silyl enol ethers. The reactions proceed under mild conditions in very good yields. Related cation precursors, such as acetates and



Scheme 5.



Scheme 6.

ethers, can be employed and a diastereoselective reaction is feasible with appropriately substituted substrates. In addition, C–H bond formation is possible under similar conditions using Et_3SiH as the reducing agent.

Acknowledgments

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10. *General procedure*: *para*-methoxyphenyl-1-ethanol (**1**, 76 mg, 0.5 mmol) and a silyl enol ether **2** (1.0 mmol) were dissolved in nitromethane (2 mL). At ambient temperature $Bi(OTf)_3{\cdot}xH_2O$ ($1 < x < 4$)[6a] (8 mg, 12.5 μmol) was added in one portion and the solution was stirred for the indicated time. The reaction was quenched by the addition of EtOAc/water (10:10 mL) and the aqueous layer was extracted with ethyl acetate (2 × 20 mL). The combined organic layers were washed with water (20 mL) and brine (20 mL), dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (cyclohexane/ethyl acetate 40:1). Analytical data for some selected compounds:
Compound **3c**: R_f: 0.11 (cyclohexane/EtOAc 40:1); IR (film): $\tilde{\nu} = 2964\ cm^{-1}$ (s), 2834 (m), 1706 (vs), 1612 (m), 1513 (vs), 1464 (m), 1249 (vs), 1178 (m), 1039 (s), 829 (m). ^1H NMR (360 MHz, $CDCl_3$): $\delta = 1.05$ (s, 9H), 1.21 (d, $^3J = 7.0$ Hz, 3H), 2.66 (dd, $^2J = 17.1$ Hz, $^3J = 7.7$ Hz, 1H), 2.73 (dd, $^2J = 17.1$ Hz, $^3J = 6.3$ Hz, 1H), 3.33 (pseudo sextet, $^3J \cong 7.0$ Hz, 1H), 3.78 (s, 3H), 6.82 (d, $^3J = 8.7$ Hz, 2H), 7.13 (d, $^3J = 8.7$ Hz, 2H). ^{13}C NMR (90.6 MHz, $CDCl_3$): $\delta = 21.9$ (q), 26.3 (q), 34.3 (d), 44.2 (s), 45.7 (t), 55.4 (q), 113.9 (d), 127.9 (d), 139.1 (s), 158.0 (s), 214.5 (s). HRMS ($C_{15}H_{22}O_2$): calcd.: 234.1620, found: 234.1616.
Compound **3e**: R_f: 0.09 (cyclohexane/EtOAc 40:1); IR (film): $\tilde{\nu} = 2972\ cm^{-1}$ (s), 2835 (m), 1731 (vs), 1611 (w), 1513 (vs), 1461 (m), 1249 (vs), 1133 (s), 1036 (m), 833 (m). ^1H NMR (360 MHz, $CDCl_3$): $\delta = 1.05$ (s, 3H), 1.10 (s, 3H), 1.22 (d, $^3J = 7.2$ Hz, 3H), 3.11 (q, $^3J = 7.2$ Hz, 1H), 3.64 (s, 3H), 3.79 (s, 3H), 6.81 (d, $^3J = 8.7$ Hz, 2H), 7.08 (d, $^3J = 8.7$ Hz, 2H). ^{13}C NMR (90.6 MHz, $CDCl_3$): $\delta = 16.2$ (q), 20.9 (q), 23.9 (q), 45.9 (s), 46.7 (d), 51.7 (q), 55.3 (q), 113.3 (d), 130.1 (d), 134.7 (s), 158.4 (s), 178.4 (s). HRMS ($C_{14}H_{20}O_3$): calcd.: 236.1412, found: 236.1412.
Compounds **3h** (50:50 mixture of diastereoisomers): R_f: 0.09 (cyclohexane/EtOAc 40:1); IR (film): $\tilde{\nu} = 2935\ cm^{-1}$ (s), 2835 (m), 1703 (vs), 1610 (w), 1513 (vs), 1455 (m), 1247 (vs), 1180 (s), 1031 (m), 832 (s). ^1H NMR (360 MHz, $CDCl_3$): $\delta = 0.87$ (s, 1.5H), 0.92 (s, 1.5H), 1.10 (d, $^3J = 7.2$ Hz, 1.5H), 1.23 (d, $^3J = 7.1$ Hz, 1.5H), 1.20–1.28 (m, 0.5H), 1.45–1.51 (m, 0.5H), 1.60–1.71 (m, 2H), 1.74–1.87 (m, 2H), 1.97–2.10 (m, 1H), 2.33–2.43 (m, 1H), 2.49–2.60 (m, 1H), 3.36–3.45 (m, 1H), 3.77 (s, 1.5H), 3.80 (s, 1.5H), 6.79 (d, $^3J = 8.6$ Hz, 1H), 6.84 (d, $^3J = 8.6$ Hz, 1H), 7.05 (d, $^3J = 8.6$ Hz, 1H), 7.13 (d, $^3J = 8.6$ Hz, 1H). ^{13}C NMR (90.6 MHz, $CDCl_3$): $\delta = 15.8$ (q), 16.1 (q), 17.9 (q), 20.7 (t), 21.2 (t), 22.2 (q), 26.6 (t), 28.2 (t), 34.2 (t), 38.1 (t), 39.3 (t), 39.5 (t), 40.4 (d), 42.5 (d), 52.4 (s), 52.8 (s), 55.3 (q), 55.4 (q), 113.3 (d), 113.3 (d), 129.9 (d), 130.3 (d), 134.0 (s), 135.0 (s), 158.2 (s), 158.4 (s), 215.5 (s), 216.2 (s). Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 78.13; H, 9.36.
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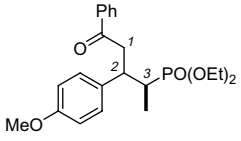
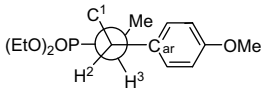
13. *Analytical data of compound anti*-**13**: R_f: 0.37 (cyclohexane/EtOAc 3:1); IR (film): $\tilde{\nu} = 2936\ cm^{-1}$ (s), 2836 (w), 1687 (vs), 1612 (m), 1514 (vs), 1448 (m), 1252 (vs), 1180 (m), 1033 (m), 831 (w). ^1H NMR (360 MHz, $CDCl_3$): $\delta = 1.23$ (d, $^3J = 7.1$ Hz, 3H), 2.94 (pseudo quintet, $^3J \cong 7.1$ Hz, 1H), 3.50–3.62 (m, 3H), 3.76 (s, 3H), 6.83 (d, $^3J = 8.7$ Hz, 2H), 7.18 (d, $^3J = 8.7$ Hz, 2H), 7.42–7.46 (m, 2H), 7.53–7.57 (m, 1H), 7.89–7.92 (m, 2H). ^{13}C NMR (90.6 MHz, $CDCl_3$): $\delta = 16.7$ (q), 32.0 (d), 42.3 (t), 43.3 (d), 55.4 (q), 114.3 (d), 122.2 (s), 128.2 (d), 128.8 (d), 128.9 (d), 132.3 (s), 133.4 (d), 136.9 (s), 159.0 (s), 197.3 (s). Anal. Calcd for $C_{19}H_{19}NO_2$: C, 77.79; H, 6.53; N, 4.77. Found: C, 77.86; H, 6.44; N, 4.68.
Analytical data of compound syn-**15**: R_f: 0.39 (EtOAc); IR (film): $\tilde{\nu} = 3462\ cm^{-1}$ (br), 2980 (s), 2836 (w), 2360 (w), 1682 (s), 1581 (m), 1514 (vs), 1391 (s), 1251 (s), 1029 (m), 957 (m), 836 (w). ^1H NMR (360 MHz, $CDCl_3$): $\delta = 1.15$–1.32 (m, 9H), 2.18 (dqd, $^3J_{HP} = 21.5$ Hz, $^3J = 7.4$ Hz, $^3J = 3.4$ Hz, 1H), 3.45–3.56 (m, 2H), 3.75 (s, 3H), 3.82–3.94 (m, 1H), 3.99–4.12 (m, 4H), 6.79 (d,

$^3J = 8.7$ Hz, 2H), 7.17 (d, $^3J = 8.7$ Hz, 2H), 7.41–7.45 (m, 2H), 7.50–7.55 (m, 1H), 7.94–7.97 (m, 2H). ^{13}C NMR (90.6 MHz, $CDCl_3$): $\delta = 10.1$ (dq, $^2J_{CP} = 3.8$ Hz), 16.5 (dq, $^3J_{CP} = 5.9$), 16.6 (dq, $^3J_{CP} = 5.6$ Hz), 37.2 (dd, $^1J_{CP} = 137$ Hz), 39.2 (dt, $^2J_{CP} = 1.9$), 39.4 (dd, $^3J_{CP} = 1.8$), 55.3 (q), 61.6 (dt, $^2J_{CP} = 7.1$ Hz), 61.8 (dt, $^2J_{CP} = 7.0$ Hz), 113.8 (d), 128.3 (d), 128.6 (d), 129.2 (d), 133.0 (d), 134.3 (d, $^3J_{CP} = 13.9$ Hz), 137.3 (s), 158.4 (s), 198.9 (s). Anal. Calcd for $C_{22}H_{29}O_5P$: C, 65.33; H, 7.23. Found: C, 64.91; H, 7.06. Configuration assignment by ^{1}H and ^{13}C NMR data. ^3J(P–C_{ar}) = 13.8 Hz (⇒*anti*-periplanar); ^3J(P–C^1) = 1.9 Hz (⇒*syn*-clinal); ^3J(H^2–H^3) = 3.4 Hz (⇒*syn*-clinal).



15



syn-**15**

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