Trimethylsilyl Trifluoromethanesulfonate-Catalyzed Aldol Reaction of Various Aldehydes with Silyl Enol Ethers

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The aldol reaction of trimethylsilyl enol ethers (1—3) with various aldehydes in the presence of a catalytic amount of trimethylsilyl trifluoromethanesulfonate was investigated. With benzaldehyde (4) the β -hydroxycarbonyl compounds were obtained in good yields. The effect of a substituent on the benzene ring was also examined. Aliphatic aldehydes (11, 13, and 14) were found not to be suitable substrates for this catalytic aldol reaction. On treatment with *tert*-butyldimethylsilyl enol ethers (30 and 31) under the same conditions, benzaldehydes (4, 5, 7, 8) yielded the corresponding aldol products with good *threo*-selectivity.

Keywords trimethylsilyl trifluoromethanesulfonate; *tert*-butyldimethylsilyl trifluoromethanesulfonate; aldol reaction; catalytic amount; silyl enol ether; benzaldehyde derivative; *erythro* isomer; *threo* isomer

The aldol reaction is a very well-known reaction which is well recognized as the most obvious route for construction of the β -hydroxy carbonyl functionality. Over the past few decades many efforts have been made to develop stereoselective aldol reactions.^{1–3)} Recently we reported the *erythro*-selective aldol reaction of cobalt-complexed propynals with silyl enol ethers in the presence of a Lewis acid.⁴⁾ The *erythro*/*threo* ratio in this reaction was found to be virtually insensitive to the identity of the Lewis acid employed. Trimethylsilyl trifluoromethanesulfonate (TMSOTf) is of particular interest among various Lewis acids examined because even a catalytic amount of TMSOTf worked well in this *erythro*-selective aldol reaction.

In 1980 Noyori *et al.*⁵⁾ introduced TMSOTf for the generation of a stabilized cationic intermediate from acetal species. This stabilized cation was then captured by nucleophilic silyl enol ethers to give the *erythro* isomer selectively. This useful aldol reaction, however, was found not to be applicable to the parent aldehydes themselves. Actually no reaction took place when trimethylsilyloxy-cyclohexene (3) was treated with benzaldehyde (4) instead of the corresponding dimethyl acetal. These results are in contrast to our results⁴⁾ that the aldol products were smoothly obtained from the reaction of cobalt-complexed propynals with silyl enol ethers in the presence of TMSOTf.

In connection with recent progress in the development of the aldol reaction under catalytic conditions,^{6–9)} we have been interested in the aldol reaction catalyzed by TMSOTf. We report here the scope and limitations of the

TMSOTf-catalyzed aldol reaction in detail.

Initially we investigated the aldol reaction of benzaldehyde derivatives with silyl enol ethers. Treatment of the silyl enol ether (1) with benzaldehyde (4) in dry methylene chloride at -78°C in the presence of 5 mol% of TMSOTf afforded the corresponding β -hydroxy derivative (17) in 89% yield. The results obtained under similar conditions are summarized in Table I. The *Z*-silyl enol ether (2), on treatment with 4, provided the condensation product (18) as a mixture of the *erythro* and *threo* isomers in a ratio of 74 to 26. The stereochemical assignment of both isomers and the *erythro*/*threo* ratio were obtained by careful analysis of the 400 MHz proton nuclear magnetic resonance ($^1\text{H-NMR}$) spectra. The benzylic proton of the *erythro* isomer appeared at δ 5.24 ppm as a doublet with $J=3.2$ Hz, while the *threo* isomer showed the corresponding peak at δ 4.99 ppm as a doublet with $J=8.0$ Hz. These chemical shifts as well as coupling constants are in good agreement with the general observation^{1,2)} that the β -hydrogen of an *erythro* isomer resonates at lower field than that of the *threo* isomer, and the vicinal coupling constant between α - and β -hydrogen of the *erythro* isomer is smaller than that of the *threo* isomer.

The cyclic silyl enol ether (*E*-silyl enol ether) (3) also gave the aldol product (19) in 69% yield (*erythro*/*threo* = 63/37). *p*-Chlorobenzaldehyde (5) exhibited similar reactivity toward 3, but the stereoselectivity was reversed (*erythro*/*threo* = 36/64) in the presence of 1 mol% of TMSOTf (entry 4). Similar yield and selectivity were observed with 20 mol%

Chart 1

of TMSOTf (entry 5). An electron-withdrawing group on the aromatic ring diminished the reactivity. Indeed, *p*-nitrobenzaldehyde (**6**) produced **21** in low yield (35%) on treatment with **3** in the presence of 5 mol% of TMSOTf (entry 7). The yield (46%) was slightly improved by increasing the amount of TMSOTf to 20 mol% (entry 6). Interestingly, no characteristic diastereoselectivity was observed in this reaction.

In the cases of the compounds (**7** and **8**) having an electron-donating group on the aromatic ring, the starting materials smoothly disappeared within 1 h, but the desired product could not be isolated, probably due to over-reaction of the aldol product under the acidic conditions. Similar behavior was observed when furfural (**9**) was exposed to a catalytic amount of TMSOTf (entry 10). Benzophenone (**10**)

TABLE I. Aldol Reaction of Trimethylsilyl (TMS) Enol Ethers (1–3) with Benzaldehyde Derivatives and Related Compounds in the Presence of a Catalytic Amount of TMSOTf

Entry	Silyl enol ether	Carbonyl compound	TMSOTf (mol%)	Product	Yield (%)	erythro:threo
1	1	4	5	17	89	
2	2	4	1	18	89	74:26
3	3	4	1	19	69	63:37
4	3	5	1	20	64	36:64
5	3	5	20	20	71	38:62
6	3	6	20	21	46	54:46
7	3	6	5	21	35	54:46
8	3	7	1	—		
9	3	8	2	—		
10	3	9	2	22	25	20:80
11	3	10	5	n.r.		

n.r.: no reaction.

TABLE II. Aldol Reaction of TMS Enol Ethers (**1** and **3**) with Aliphatic Aldehydes and Related Compounds in the Presence of a Catalytic Amount of TMSOTf

Entry	Silyl enol ether	Carbonyl compound	TMSOTf (mol%)	Product	Yield (%)	erythro:threo
1	1	11	2	23	29	
2	1	12	5	24	(29 : 52)	
3	1	13	2	25	33	(29 : 64)
4	3	14	4	26	21	(29 : 44)
5	3	15	2	27	24	n.d.
6	3	16	2	28	48	51:49
					37	n.d.

n.d.: not determined.

was inactive under the standard condition (entry 11).

Table I indicates that the aldol reaction of silyl enol ethers with benzaldehyde derivatives and related aldehydes catalyzed by TMSOTf gave the corresponding aldol products, although the reactivity depended strongly on the electronic properties of the benzene ring. In addition, this aldol reaction was found to be stereorandom, in contrast to the reaction of acetals⁵⁾ where the *erythro*-selectivity was observed regardless of the stereochemistry of the starting silyl enol ethers.

The aldol reaction of silyl enol ethers with aliphatic aldehydes was next performed (see Table II). Isobutyraldehyde (**11**) was treated with the silyl enol ether (**1**) in the presence of 2 mol% of TMSOTf to give the aldol product (**23**) in 29% yield along with acetophenone (**29**; 52%). Cyclohexanone (**12**) and β -phenylpropionaldehyde (**14**) also afforded similar results (entries 2 and 4). No remarkable improvement of the yield was achieved by either prolonging the reaction time or using a relatively large amount of TMSOTf. These three carbonyl compounds (**11**, **12**, and **14**) have acidic protons next to the carbonyl moiety as a common structural feature which might cause some difficulty in contrast to benzaldehyde derivatives. Trimethylacetaldehyde (**13**) provided the aldol product (**25**) in

TABLE III. Aldol Reaction of TBDMS Enol Ethers (**30** and **31**) with Various Carbonyl Compounds in the Presence of a Catalytic Amount of TMSOTf

Entry	Silyl enol ether	Carbonyl compound	TMSOTf (mol%)	Product	Yield (%)	erythro:threo
1	30	4	4	32	56	59:41
2	31	4	2	33	76	20:80
3	31	5	2	34	63	28:72
4	31	5	TBDMSOTf (2)	34	63	29:71
5	31	6	10	35	26	51:49
					(6 : 64)	
6	31	7	2	36	72	17:83
7	31	8	2	37	85	16:84
8	31	8	TBDMSOTf (2)	37	84	20:80
9	31	9	2	38	91	14:86
10	31	15	2	39	33	48:52
11	31	16	2	40	60	n.d.
12	31	14	10	n.r.		
13	31	11	2	n.r.		
14	31	12	2	n.r.		
15	30	11	10	n.r.		
16	30	12	10	n.r.		

n.r.: no reaction. n.d.: not determined.

Chart 2

only 21% yield, although **13** does not have any acidic protons. In this case, the low yield can be attributed to the bulky *tert*-butyl group next to the aldehyde functionality. Phenylpropynal (**15**) and *trans*-cinnamaldehyde (**16**), neither of which possesses an acidic proton, furnished the condensation products (**27** and **28**) in 48 and 37% yields, respectively. These yields of **27** and **28** are higher than that of the corresponding saturated compound (**26**), but somewhat low compared to the case of benzaldehyde derivatives.

These results in combination with the earlier observation summarized in Table I strongly suggest that this catalytic aldol reaction can be satisfactorily applied to benzaldehyde derivatives (also to propynals). However, carbonyl compounds having acidic protons or severe steric hindrance are not suitable substrates for this catalytic aldol reaction.

As mentioned above, benzaldehyde derivatives (**7** and **8**) possessing an electron-donating substituent on the benzene ring did not afford the desired aldol products. We speculated that these results would be mainly due to the labile free hydroxy group at the benzylic position in the desired products. Therefore, we envisioned that this problem might be overcome by changing the TMS group to the *tert*-butyldimethylsilyl (TBDMS) group in silyl enol ethers, because the TBDMS group on the secondary hydroxy functionality¹⁰⁾ is well known to be stable enough to handle.

On the basis of this assumption, the aldol reaction of TBDMS enol ether (**31**) with benzaldehyde derivatives (**7** and **8**) was carried out. The desired aldol reaction products (**36** and **37**), β -*tert*-butyldimethylsilyloxy ketones, were obtained in excellent yields without desilylation, as expected. The other results obtained under the standard conditions are summarized in Table III. The reaction of the *Z*-silyl enol ether (**30**) with **4** gave the aldol product (**32**) in 56% yield nonselectively (*erythro*/*threo* = 59/41). On the other hand, the cyclic silyl enol ether (*E*-silyl enol ether) (**31**), on treatment with benzaldehyde derivatives except *p*-ni-

trobenzaldehyde (**6**), afforded the corresponding β -*tert*-butyldimethylsilyloxy derivatives in good yields (entries 2, 3, 6 and 7). The *threo* isomers were obtained as a main product in these reactions. This was also true in the case of furfural (**9**) (entry 9). These results, as well as the nonselectivity for the *Z*-enolate (**30**) (entry 1), seem to be in accordance with the results reported by Chan *et al.*,¹¹⁾ who studied the aldol reaction of ketene silyl acetals of ethyl propionate with aldehydes in the presence of titanium tetrachloride. In the case of **6**, 10 mol% of TMSOTf was insufficient to complete the condensation and the starting material (**6**) was recovered in 64% yield (entry 5).

When a catalytic amount of TBDMSOTf was employed instead of TMSOTf, **5** and **8** gave **34** and **37** in 63 and 84% yields, respectively (entries 4 and 8). The yield and stereoselectivity in this reaction were quite similar to those obtained with TMSOTf (entries 3 and 7). Therefore, it is not necessary to use more expensive TBDMSOTf instead of TMSOTf for this aldol reaction from a practical point of view, although TBDMSOTf seems to be theoretically⁵⁾ better than TMSOTf in this reaction. The stereochemical assignment of *O*-protected β -hydroxy compounds was unambiguously established by conversion into the corresponding known compounds. The TBDMS-protected compound (**32**), for instance, was exposed to 47% hydrofluoric acid in acetonitrile¹²⁾ at room temperature to give **18** (82%) as a mixture of the *erythro* and *threo* isomers in a ratio of 61 to 39. Similarly **33** furnished the desilylated product (**19**; 91%, *erythro*/*threo* = 19/81). Phenylpropynal (**15**) was not as good as benzaldehyde derivative in the aldol reaction of TBDMS enol ethers (entry 10). *trans*-Cinnamaldehyde (**16**), however, provided the aldol product in moderate yield (60%) (entry 11), although the diastereoselectivity could not be evaluated because the benzylic protons of both isomers have very similar chemical shifts and their signals overlap each other in the ¹H-NMR spectrum. Aliphatic carbonyl compounds did not react at

TABLE IV. Physical and Spectral Data for β -Hydroxycarbonyl Compounds

Compd.	¹ H-NMR (ppm) (Hz)	IR (cm ⁻¹)	MS <i>m/z</i> (%)	Formula	High MS Calcd (Found)
17	5.32 (1H, t, <i>J</i> = 6)	3475, 1660	226 (M ⁺ , 14.5), 106 (44), 105 (100), 77 (50)	C ₁₅ H ₁₄ O ₂	226.0992 (226.0970)
18	5.24 (74/100H, d, <i>J</i> = 3.2), 4.99 (26/100H, d, <i>J</i> = 8.0)	3500, 1660	240 (M ⁺ , 5), 134 (100), 105 (99), 77 (98)	C ₁₆ H ₁₆ O ₂	240.1150 (240.1153)
19	5.38 (63/100H, d, <i>J</i> = 2.2), 4.88 (37/100H, d, <i>J</i> = 8.8)	3525, 1690	204 (M ⁺ , 2.2), 105 (41), 98 (100), 70 (37)	C ₁₃ H ₁₆ O ₂	204.1149 (204.1169)
20	5.36 (36/100H, d, <i>J</i> = 2.5), 4.76 (64/100H, d, <i>J</i> = 8.8)	3525, 1690	238 (M ⁺ , 6.4), 139 (46), 98 (100), 70 (38)	C ₁₃ H ₁₅ ClO ₂	238.0759 (238.0759)
21	5.49 (54/100H, d, <i>J</i> = 2.2), 4.90 (46/100H, d, <i>J</i> = 8.5)	3525, 1690	249 (M ⁺ , 2), 151 (40), 98 (100), 77 (47)	C ₁₃ H ₁₅ NO ₄	249.1000 (249.1013)
22	5.27 (20/100H, d, <i>J</i> = 3.0), 4.84 (80/100H, d, <i>J</i> = 8.5)	3500, 1690	194 (M ⁺ , 16), 98 (79), 97 (100), 70 (35)	C ₁₁ H ₁₄ O ₃	194.0942 (194.0961)
23	3.88—4.16 (1H, m)	3425, 1670	192 (M ⁺ , 0.8), 149 (62), 105 (100), 77 (34)	C ₁₂ H ₁₆ O ₂	192.1150 (192.1177)
24	3.12 (2H, s) (α -protons)	3475, 1660	218 (M ⁺ , 2.6), 162 (25), 120 (40), 105 (100)	C ₁₄ H ₁₈ O ₂	218.1305 (218.1279)
25	3.90 (1H, dd, <i>J</i> = 9.5, 2.5)	3500, 1660	206 (M ⁺ , 0.2), 149 (38), 105 (100), 77 (16)	C ₁₃ H ₁₈ O ₂	206.1305 (206.1303)
26	3.49—4.20 (1H, m)	3500, 1690	232 (M ⁺ , 5.5), 117 (100), 104 (70), 91 (97)	C ₁₅ H ₂₀ O ₂	232.1467 (232.1470)
27	4.97 (51/100H, d, <i>J</i> = 3.0), 4.82 (49/100H, d, <i>J</i> = 7.5)	3500, 2200, 1690	228 (M ⁺ , 11), 199 (84), 131 (100), 98 (31)	C ₁₅ H ₁₆ O ₂	228.1148 (228.1122)
28	4.20—4.72 (1H, m)	3500, 1690	230 (M ⁺ , 42), 133 (87), 131 (100), 98 (100)	C ₁₅ H ₁₈ O ₂	230.1305 (230.1299)

TABLE V. Physical and Spectral Data for β -*tert*-Butyldimethylsilyloxycarbonyl Compounds

Compd.	¹ H-NMR (ppm) (Hz)	IR (cm ⁻¹)	MS <i>m/z</i> (%)	Formula	High MS Calcd (Found)
32	4.96 (59/100H, d, <i>J</i> = 7.3), 4.84 (41/100H, d, <i>J</i> = 9.5)	1670	339 (M ⁺ - 15, 1.7), 297 (92), 191 (100), 75 (51)	C ₂₂ H ₃₀ O ₂ Si	a
33	5.33 (20/100H, d, <i>J</i> = 4.0), 5.09 (80/100H, d, <i>J</i> = 8.0)	1700	300 (M ⁺ - 15, 4.2), 261 (100), 155 (100), 75 (61)	C ₁₉ H ₃₀ O ₂ Si	b
34	5.26 (28/100H, d, <i>J</i> = 4.5), 5.13 (72/100H, d, <i>J</i> = 6.8)	1700	337 (M ⁺ - 15, 1.7), 295 (100), 155 (98), 75 (49)	C ₁₉ H ₂₉ ClO ₂ Si	c
35	5.38 (51/100H, d, <i>J</i> = 4.8), 5.31 (49/100H, d, <i>J</i> = 6.0)	1700	348 (M ⁺ - 15, 1.6), 306 (100), 155 (84), 75 (39)	C ₁₉ H ₂₉ NO ₄ Si	d
36	5.24 (17/100H, d, <i>J</i> = 4.4), 5.05 (83/100H, d, <i>J</i> = 7.8)	1700	348 (M ⁺ , 3.9), 291 (100), 251 (33), 155 (32)	C ₂₀ H ₃₂ O ₃ Si	348.2119 (348.2138)
37	5.21 (16/100H, d, <i>J</i> = 4.4), 5.01 (84/100H, d, <i>J</i> = 7.7)	1720	362 (M ⁺ , 0.5), 305 (100), 265 (38), 155 (41)	C ₂₀ H ₃₀ O ₄ Si	362.1912 (362.1927)
38	5.32 (14/100H, d, <i>J</i> = 5.0), 5.17 (86/100H, d, <i>J</i> = 7.8)	1700	293 (M ⁺ - 15, 1.7), 251 (100), 155 (64), 75 (25)	C ₁₇ H ₂₈ O ₃ Si	e
39	5.13 (48/100H, d, <i>J</i> = 1.5), 5.08 (52/100H, d, <i>J</i> = 3.2)	2200, 1700	342 (M ⁺ , 2.3), 285 (100), 183 (61), 155 (42)	C ₂₁ H ₃₀ O ₂ Si	f
40	4.68—4.96 (1H, m)	1700	344 (M ⁺ , 0.2), 287 (100), 247 (72), 155 (49)	C ₂₁ H ₃₂ O ₂ Si	344.2170 (344.2196)

a, *Anal.* Calcd: C, 74.54; H, 8.53. Found: C, 74.51; H, 8.75. b, *Anal.* Calcd: C, 71.64; H, 9.49. Found: C, 71.36; H, 9.71. c, *Anal.* Calcd: C, 64.65; H, 8.28. Found: C, 64.63; H, 8.45. d, *Anal.* Calcd: C, 62.78; H, 8.04; N, 3.85. Found: C, 62.55; H, 8.14; N, 3.65. e, *Anal.* Calcd: C, 66.19; H, 9.15. Found: C, 65.84; H, 9.45. f, *Anal.* Calcd: C, 73.63; H, 8.83. Found: C, 73.85; H, 8.82.

all with TBDMS enol ethers (**30** and **31**). This result is quite predictable from the observations in Table II.

In summary, the aldol reaction of silyl enol ethers with benzaldehyde derivatives, in other words, aldehydes without acidic protons, in the presence of a catalytic amount of TMSOTf gave the corresponding aldol products. In the case of TMS enol ethers, the aldol condensation produced the β -hydroxycarbonyl compounds, the stereoselectivity of which was unpredictable. On the other hand, TBDMS enol ethers (especially cyclic enol ether) afforded the β -*tert*-butyldimethylsilyloxycarbonyl derivatives with good *threo*-selectivity. The latter procedure seems to have some advantages from the synthetic point of view. Since the β -hydroxy group of the aldol product can be spontaneously protected by the TBDMS group in this reaction and the retro-aldol reaction must be avoided, this procedure would be applicable for an intramolecular ring closure which results in the formation of a highly strained cyclic product. A synthesis of natural products based on this method is in progress.

Experimental

Silica gel (Silica gel 60, 230—400 mesh, Nacalai Tesque) was used for flash chromatography. Organic extracts were dried over anhydrous Na₂SO₄. All reactions were performed under a nitrogen atmosphere. Infrared (IR) spectra were measured with a JASCO A-102 spectrometer in CHCl₃, mass spectra (MS) with a Hitachi M-80 mass spectrometer, and ¹H-NMR spectra with a JEOL JNM-GX 400 spectrometer in CDCl₃ using tetramethylsilane as an internal standard.

General Procedure for the Aldol Reaction of TMS Enol Ethers (1—3) and TBDMS Enol Ethers (30, 31) in the Presence of a Catalytic Amount of TMSOTf A solution of 0.1 M TMSOTf in CH₂Cl₂ (0.1—1.0 ml; 1—10 mol%) was added to a solution of a silyl enol ether (**1**, **2**, **3**, **30**, or **31**) (1.1 mmol) and the aldehyde (or ketone) (1.0 mmol) in CH₂Cl₂ (5 ml) at -78 °C. The reaction was monitored by thin layer chromatography (TLC). After several hours (2—7 h), the reaction was quenched by addition of water (1 ml) at -78 °C. The CH₂Cl₂ layer was separated and the aqueous layer was extracted with CH₂Cl₂ three times. The combined organic layers were washed with saturated NaHCO₃ solution, water, and brine, dried, and concentrated to dryness. Flash chromatography of the residue with ethyl acetate/hexane (or CH₂Cl₂) gave the aldol product as a *erythro*/*threo* mixture. The physical and spectral data of the aldol products are summarized in Tables IV and V.

General Procedure for Conversion of β -*tert*-Butyldimethylsilyloxycarbonyl Compounds to β -Hydroxycarbonyl Compounds A 47% hydrofluoric acid solution (0.2—0.4 ml) was added to a stirred solution of a β -*tert*-butyldimethylsilyloxycarbonyl compound (**32**, **33**, or **39**) (0.1 mmol) in acetonitrile (0.4 ml) at room temperature. After stirring for 30 min, the reaction mixture was poured into water and extracted with CH₂Cl₂. The organic layer was washed with saturated NaHCO₃ solution, water, and brine, dried, and concentrated to dryness. Flash chromatography of the residue afforded the corresponding β -hydroxy derivative (**18**, **19**, or **27**), which was identified by comparison with an authentic sample.

Compound **32** (*erythro*/*threo* = 59/41) provided **18** in 82% yield as a mixture of *erythro* and *threo* isomer in a ratio of 61 to 39. Compound **33** (*erythro*/*threo* = 20/80) gave **19** (91%; *erythro*/*threo* = 19/81) and compound **39** (*erythro*/*threo* = 48/52) afforded **27** (91%; *erythro*/*threo* = 45/55).

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