An Environmentally Friendly Mukaiyama Aldol Reaction Catalyzed by a Strong Brønsted Acid in Solvent-Free Conditions

UNIVERSITÀ DEGLI STUDI DI TORINO

Table 1 Mukaiyama aldol trial reactions of (or) with 4a

Entry	Reactant ratio[a]	1 (mol %)	Solvent/t (h)	Products, Yields (%)[b]	dr[c]
1	2:4a = 1.1:1	1	neat / 4	6a, 49 7a, 11	57:43
2	2:4a = 1.5:1	1	neat / 4	6a, 56 7a (n.d.)	55:53
3	2:4a = 2 : 1	1	neat / 4	6a, 68 7a, 5	50:50
4	2:4a = 2 : 1	1–10	CH_2Cl_2 / 48	[d]	
5	2:4a = 2 : 1	1–5	Tol / 5	[d]	
6	3:4a = 1.1:1	1–10	MeCN / 5	[e]	
7	3:4a = 1.1:1	1–10	CH_2Cl_2 / 48	[e]	
8	3:4a = 1.1:1	1–5	neat / 2	9a, 60	
9	3:4a = 1.3:1	2	neat / 2	9a, 87	
10	2:4a = 2 : 1	2[f]	neat / 2	6a, 38 7a, 5	50:50
11	3:4a = 1.3:1	4[f]	neat / 4	9a, 63	

[a] Unless otherwise stated, the reactions were carried out on 2 mmol of at rt (20–25 °C). After completion of the reaction, the reaction mixture was treated with 2 N HCl (2 mL) to hydrolyze to 6a or 8a to 9a. [b] Products identified by and NMR spectra; yields % of isolated products (flash chromatography; PE/AcOEt=7:3). [c] dr (syn/anti) determined by NMR spectroscopy. [d] Expected products were identified, but in low amounts. [e] MeCN decomposes completely to acetophenone, whilst in the acid hydrolysis of does not proceed to completion. [f] 2,4-Dinitrobenzenesulfonic acid was used as the catalyst.

Table 2 Mukaiyama aldol reaction of enol ethers or with aldehydes

Entry	Reactants[a]		1 (mol %)	t (h)	Products, Yields (%);[b] overall yield	dr[c]	Lit. [%][d]
1	2	4a	1	4	6a, 68; 7a, 5; overall 73	50:50	
2	2	4b	2	4	6b, 68; 7b, 16; overall 84	59:41	
3	2	4c	2	6	6c, 51; 7c, 19; overall 70	57:43	58 (56:44)[e], 87 (80:20)[3a]
4	2	4d	3	3[e]	6d, 48; 7d, 15; overall 63	50:50	
5	2	4e	5	6	6e, 48; 7e, 14; overall 62	46:54	
6	3	4a	2	2	9a, 87		97[3d]
7	3	4b	2	1	9b, 88		93[3a,d]
8	3	4c	3	2	9c, 80		96[3a,d]
9	3	4d	4	2	9d, 91		98[3a,d]
10	3	4e	4	2	9e, 96		
11	3	4f	2	3	9f, 98		95[3a,d]
12	3	4g	4	6	9g, 80		
13	3	4h	4	1	9h, 89		91[3d]
14	3	4i	1	1.5	9i, 80; 10, 16		92[3d]
15	3	11[g]	2	24	12,[f] 32		

[a] Unless otherwise stated, the reactions were carried out on 2 mmol of at rt (20–25 °C). The reactant ratio was 2 : 4 = 2 : 1 and 3 : 4 = 1.3 : 1. After completion of the reaction, the reaction mixture was treated with 2 N HCl (2 mL) to hydrolyze to 5 or 8 to 9. [b] Yields % refer to isolated products (flash chromatography; eluent: PE:AcOEt = 7:3 in entries 1–5, 7, 9–10, 14 and PE:AcOEt = 8:2 in entries 6, 8, 11–13). [c] dr (syn/anti) determined by NMR spectroscopy. [d] Yields obtained in Brønsted acid-catalyzed Mukaiyama aldol reactions; dr in parentheses. [e] Reaction temperature was 50 °C. [f] Hexanal (11) was the starting aldehyde.

In the light of these results, the applicability of the acid catalyzed Mukaiyama reaction of with a heteroaromatic and an ,-unsaturated aldehyde was studied (2-thiophenecarboxaldehyde and cinnamaldehyde, 4i). Good results were also obtained in these cases. Interestingly, in the reaction with 4i, 5-oxo-3,5-diphenylpentanal (10) was isolated as the Mukaiyama-Michael addition product in 16% yield (entry 14). In order to favor the 1,2-addition over to the 1,4-, the reaction temperature was lowered to 0 °C and then to –30 °C, but no appreciable variation in the ratio of to was observed.

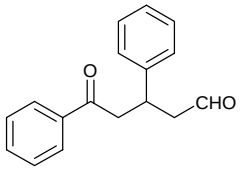
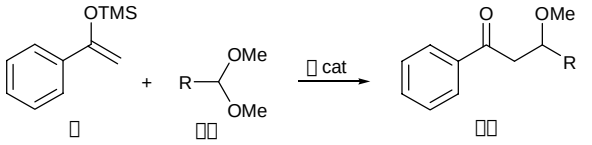


Fig. 2 5-Oxo-3,5-diphenylpentanal (10)

The literature yields of the aldol products 8 and 9, obtained in Brønsted acid catalyzed Mukaiyama reactions, are also reported in Table 2 for ease of comparison. Only few examples have been recovered and the yields are comparable. Owing to these encouraging results, some aliphatic aldehydes were then tested, although only the bulky tris(trimethylsilyl)silyl enol ethers of acetaldehyde and propanal have so far been reported to react in a Mukaiyama reaction with aliphatic aldehydes under similar reaction conditions (HNTf$_2$ or TTMSSNTf$_2$ as the catalysts).[3b]

Unfortunately, phenylacetaldehyde, cyclohexanecarbaldehyde, and pivalaldehyde never reacted, even under various reaction conditions (neat or in MeCN, in the presence of 2–5 mol % of 1, at rt or by heating to 50 °C, prolonged times). Only hexanal (11) gave the expected aldol product 12 in reaction with 3 in 32% yield (Table 2, entry 15). Keeping in mind that dimethyl acetals have been used as aldehyde surrogates,[10a] the dimethyl acetals of some aliphatic aldehydes were then reacted with 3 in neat conditions and in the presence of 1a as the catalyst (Scheme 2). The reaction was achieved, although moderate to good results were obtained, as reported in Table 3.



3 and 13a–c) R = C_5H_{11}; b) R = c-C_6H_{11}; c) R = Bn

Scheme 2. Mukaiyama-aldol type reaction catalyzed by 1.

Table 3. Mukaiyama aldol-type reaction of 3 with dimethyl acetals 13.

Entry	Reactants[a]		1 (mol %)	t (h)	Yields[b] of 14 (%)
1	3	13a	2	30	14a, 81
2	3	13b	2	4	14b, 61
3	3	13c	3	24	14c, 33

[a] The reactions were carried out on 2 mmol of 13a at rt (20–25 °C). The reactant ratio was 13 : 3 = 1.3 : 1. [b] Yields % refer to isolated products (flash chromatography; eluent: PE:AcOEt = 9:1).

Furthermore, although (*R*)-2,2'-binaphthyldisulfonimide (15)[12] does not show any evidence of an enantiomeric induction, the model Mukaiyama reaction between 2 and 4a was carried out in its presence in the same optimized catalytic amounts of 1. Binaphthyl-derived chiral disulfonimides have recently received growing interest as Brønsted acid organocatalysts.[4,13] In general, the presence of bulky aryl substituents at the 3,3'-positions is needed for effective enantioselective catalysis. So it was not a surprise to isolate, from the reaction mixture, a diastereomeric mixture of *syn* and *anti* 6a in a ratio which was unaltered with respect to entry 1 in Table 2.

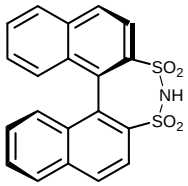
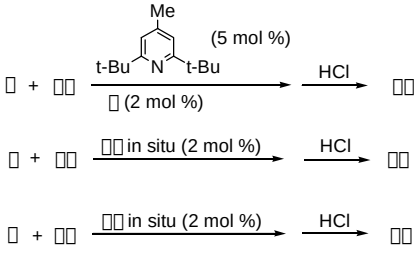


Fig. 3 (*R*)-2,2'-Binaphthyldisulfonimide (15)

Finally, some mechanistic studies have been undertaken in order to clarify the real nature of the catalyst involved. The results are reported in Table 4 and illustrated in Scheme 3.



Scheme 3. Mechanistic studies between 2 or 3 and 4b or 4f.

In order to differentiate between Lewis and Brønsted acid catalysis, the reaction between 1-trimethylsilyloxystyrene (3) and 2-methylbenzaldehyde (4f) was first performed in the presence of 2,6-di-*t*-butyl-4-methylpyridine (DBMP) (Table 4, entry 1). This hindered base is known to act as a proton scavenger that inhibits any protic acid catalysis.[3a-b,4] Under reaction conditions of entry 11, Table 2, and in the presence of 5 mol

% of DBMP, the reaction did not proceed to completion within the same time (1 h). Moreover, when it was quenched after 24 h, traces of **3** and low amounts of **4f** were still recovered. Acid hydrolysis gave the aldol product **9f** in a 83% yield.

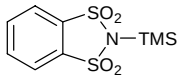


Fig. 4 *N*-Trimethylsilyl-1,2-benzenedisulfonimide (**16**)

Then, in order to assess the transfer of the trimethylsilyl group from **2** or **3** to **1** and therefore the *in situ* formation of the Lewis acid catalyst **16**, **1** (1.0 equiv) was added to the enol ether (**2** or **3**). ^{1}H NMR spectra (anhydrous $CDCl_3$) showed the immediate hydrolysis of the silyl enol ether **2** or **3** (with the respective disappearance of singlets at 0.12 ppm and 0.23 ppm) and the appearance of a new singlet centered at 0.59 ppm, which has been attributed to the Me_3Si group of *N*-trimethylsilyl-1,2-benzenedisulfonimide (**16**).[14] Afterwards, a 1:1 mixture of **1** and **2** (or **3**) (2 mol % with respect to remaining reagents) was prepared and then **2a** and **4b** (or **3** and **4f**) were added. ^{1}H NMR spectra of both reaction mixtures showed the immediate formation of **16** and both reactions proceeded in a similar fashion. In both cases, the reagent **2** (or **3**) was consumed more quickly, but with lower product yields with respect to results obtained previously (see entries 2 and 3 of Table 4 and entries 2 and 11 of Table 2).

Finally, several attempts were made to prepare and isolate derivative **16** by treating **1** with allyltrimethylsilane in MeCN at rt, but unsuccessfully.[15] Although ^{1}H NMR spectra showed a singlet at 0.59 ppm, other signals, probably due to the decomposition of **16**, were always predominant.

Table 4 Mechanistic studies

Entry	Reactants[a]		1 (mol %)	t (h)	Products; Yields (%)[b]
1	3	4f	2[c]	24	9f; 83
2	2	4b	2[d]	2	6b, 60 (54:46)[e]; 7b, 23
3	3	4f	2[d]	0.3	9f; 83

[a] The reactions were carried out on 2 mmol of **4**, at rt (20–25 °C), following reaction conditions as in Table 2. [b] Yields % refer to isolated products (flash chromatography; eluent: PE:AcOEt = 8:2 in entries 1–3 and PE:AcOEt = 7:3 in entry 2). [c] The reaction was run in the presence of 4-methyl-2,6-di(t-butyl)pyridine 5 mol %. [d] Reactions performed by previously preparing *in situ* Lewis acid **16** as the catalyst. [e] In parentheses dr (*syn*/*anti*) determined by ^{1}H NMR spectroscopy.

Compared to literature reports, our results are in better agreement with those of Yamamoto and coworkers[3a,3d] (which obtained them by using the same silyl enol ether as the enol equivalent) than with those of List and coworkers[4]. In our conditions, the *in situ* formed Lewis acid catalyst appears to be less efficient than the parent imide. This behaviour could be interpreted as a result of many possible reasons. The low nucleophilicity of its conjugate base could prevent the inter and intramolecular transfer of the silyl group. This topic has been previously discussed in Mukaiyama reactions induced by silyl Lewis acid catalysts with conjugate bases of various nucleophile strengths.[16] In neat conditions, acid **1** could activate electrophilic aldehydes through hydrogen bonding. Nevertheless, experimental findings suggest that the Brønsted acid itself is a more efficient catalyst than the silylated one.

Conclusions

In summary, a new application of the organocatalyst benzenedisulfonimide (**1**) has been reported. This strong bench-stable Brønsted acid has been shown to efficiently catalyze the Mukaiyama aldol reaction between various aromatic aldehydes and silyl enol ethers as enol equivalents, in solvent-free conditions. In the case of less reactive aliphatic aldehydes, the corresponding dimethyl acetals have been used as source of highly electrophilic oxocarbenium ions, in the presence of catalytic amounts of **1**. Mechanistic studies are in better agreement with the involvement of a Brønsted acid than a Lewis acid catalysis

Experimental

General experimental

All the reactions were conducted in vials using analytical grade reagents, and were monitored by GC and GC-MS spectrometry. GC-MS spectra were recorded with an AT5973N mass selective detector connected to an AT6890N GC cross-linked methyl silicone capillary column. IR spectra were recorded using a Perkin Elmer Spectrum BX FT-IR spectrometer in neat conditions or as solutions in $CHCl_3$. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ with a Bruker Avance 200 spectrometer at 200 MHz and 50 MHz, respectively; chemical shifts are given in ppm relative to $CDCl_3$. TLC were performed on Fluka silica gel TLC-PET foils GF 254, 2–25 µm, layer thickness 0.2 mm, medium pore diameter 60 Å. Plates were visualized using UV light (254 nm) or treatment with an

appropriate revelatory agent (*p*-anisaldehyde), followed by heating. Column flash chromatography was carried out on SiO_2 (particle size 0.032–0.063 mm/230–400 mesh). Petroleum ether refers to the fraction boiling in the range 40–60 °C and is abbreviated as PE. Commercially available reagents and solvents were purchased from Aldrich and were used without purification or distillation prior to use; Dowex 50X8 ion-exchange resin was purchased from Fluka. *o*-Benzenedisulfonimide (**1**) was prepared as described in literature.[17] Moisture-sensitive **13** was prepared following literature;[18] flasks and all equipment used for its preparation were dried by electric heat gun under Ar; THF was distilled from Na/benzophenone ketyl. Acetal **13a** was prepared following a previously optimized procedure.[9b] Structure and purity of all isolated products were confirmed by comparison of their physical and spectral data (IR, MS and ^{1}H NMR) with those reported in literature. See Supplementary Electronic Information for details.

General procedure for Mukaiyama aldol reaction

A mixture of aldehyde **4** (2.0 mmol), trimethylsilyl enol ether **2** (0.68 g, 4.0 mmol) or **3** (0.50 g, 2.6 mmol), and *o*-benzenedisulfonimide (**1**, mol % as in Table 2) was stirred at r.t. in a vial until TLC and GC analyses showed almost complete conversion of **4**. The reaction mixture was then treated with 2 N HCl (2 mL) and stirred at rt for 5-20 min. After TLC analyses showed complete hydrolysis of **5** or **6** (or **8** to **9**), the mixture was extracted with CH_2Cl_2 (3 x 10 mL). The organic extracts were washed with aqueous $NaHCO_3$ (20 mL), dried with Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by flash chroma-tography on a short column of silica gel (eluent reported in footnote of Table 2).

Representative experimental data:
2-[(4-Chlorophenyl)(hydroxy)methyl]cyclohexan-1-one (**6a**).
White solid, 68% yield; dr (*syn*/*anti*) = 50:50, determined by ^{1}H NMR analysis of title compound isolated partially as pure *syn* and *anti* diastereomers, and partially as a mixture.
syn-**6a**:[19] ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.13–1.25 (m, 1H), 1.40–1.88 (m, 5H), 1.98–2.10 (m, 1H), 2.30–2.50 (m, 3H), 5.29 (d, *J* = 2.4 Hz, 1H), 7.12–7.28 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 24.7, 25.8, 27.7, 42.5, 56.8, 69.9, 127.0 (2C), 128.1 (2C), 132.1, 139.8, 214.4. FT-IR ($CHCl_3$, cm^{-1}): 3584, 3539, 3016, 2946, 2870, 1698, 1494, 1208, 1091, 702.
anti-**6a**:[19] ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.11–1.40 (m, 1H), 1.42–1.80 (m, 5H), 1.98–2.10 (m, 1H), 2.15–2.55 (m, 3H), 4.70 (d, *J* = 8.8 Hz, 1H), 7.14–7.29 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 24.5, 27.5, 30.5, 42.4, 57.1, 73.8, 128.2 (2C), 128.3 (2C), 133.3, 139.4, 215.1. FT-IR ($CHCl_3$, cm^{-1}): 3584, 3539, 3025, 2946, 2869, 1697, 1491, 1211, 1089, 781.
2-(4-Chlorobenzylidene)cyclohexan-1-one (**7a**).[20]
Yield 5%. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.64–1.74 (m, 2H), 1.78–1.90 (m, 2H), 2.45 (t, *J* = 6.8 Hz, 2H), 2.71 (td, *J* = 6.4 and 2.2 Hz, 2H), 7.20–7.30 (m, 4H), 7.34 (t, *J* = 2.2 Hz, 1H). MS m/z (%): 220 [M+] (88), 129 (100).

3-(4-Chlorophenyl)-3-hydroxy-1-phenylpropan-1-one (**9a**).[3d,21]
White needles, mp 99.4–100.4 °C (CH_2Cl_2–PE) [lit.[22] 96–96.5 °C]. Yield 87%.
^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.20 (br s, 1H), 3.28 (d, *J* = 6.0 Hz, 2H), 5.20–5.31 (m, 1H), 7.26–7.32 (m, 4H), 7.35–7.45 (m, 2H), 7.48–7.55 (m, 1H), 7.80–7.93 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 47.1, 69.2, 127.0 (2C), 128.0 (2C), 128.5 (2C), 128.6 (2C), 133.1, 133.6, 136.2, 141.3, 199.8. FT-IR ($CHCl_3$, cm^{-1}): 3584, 3550, 3010, 2905, 1677, 1598, 1582, 1494, 1450, 1093, 1014, 800, 668.

General procedure for Mukaiyama aldol-type reaction

A mixture of aldehyde dimethyl acetal **13** (2.0 mmol), trimethylsilyl enol ether **3** (0.50 g, 2.6 mmol), and *o*-benzenedisulfonimide (**1**, mol % as in Table 3) was stirred at rt in a vial until TLC and GC analyses showed almost complete conversion of **13**. The mixture was extracted with CH_2Cl_2 (3 x 10 mL). The organic extracts were dried with Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by flash chromatography on a short column of silica gel (eluent reported in footnote of Table 3).

Representative experimental data:
3-Cyclohexyl-3-methoxy-1-phenylpropan-1-one (**14b**).[10b]
Colorless oil, 61% yield.
^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.90–1.18 (m, 5H), 1.45–1.72 (m, 6H), 2.84 (dd, *J* = 16.2 and 4.0 Hz, 1H), 3.13 (overlapped dd, *J* = 16.2 and 7.8 Hz, 1H), 3.23 (s, 3H), 3.59–3.68 (m, 1H), 7.32–7.46 (m, 3H), 7.85–7.92 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 26.1 (2C), 26.4, 28.3, 28.42, 40.6, 41.7, 58.1, 81.6, 128.0 (2C), 128.3 (2C), 132.7, 137.3, 199.2. MS m/z (%): 246 [M^+] (2), 231 [M^+-15] (10), 105 (100). FT-IR ($CHCl_3$, cm^{-1}): 3013, 2905, 2856, 1684, 1598, 1582, 1450, 1232, 1095.

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Notes and references

[a] *Dipartimento di Chimica Generale e Chimica Organica, Università degli Studi di Torino, Via Pietro Giuria, 7, 10125 Torino, Italy,*
Fax: +390116707642; Tel: +390116707645; E-mail: margherita.barbero@unito.it

† Electronic Supplementary Information (ESI) available: General procedures, ^{1}H and ^{13}C NMR spectra of products 6a-e, 9a-i, 10, 12, 13a, 14a-c

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