Cent. Eur. J. Chem. • 10(1) • 2012 • 47-53
DOI: 10.2478/s11532-011-0122-7

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Central European Journal of **Chemistry**

Mukaiyama-Michael vinylogous additions to nitroalkenes under solvent-free conditions

Invited Paper

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Received 22 June 2011; Accepted 17 September 2011

Abstract: The first Mukaiyama-Michael vinylogous reaction of a dioxinone-derived silyl ether to nitroalkenes is reported. The conjugate addition is performed in absence of any catalyst under solvent-free conditions, proceeding with satisfactory efficiency with variously substituted nitroalkenes.

Moreover, the first organocatalyzed Mukaiyama-Michael vinylogous reaction of trimethylsilyloxyfuran to nitroalkenes is described. The reaction is promoted by Brønsted acids under solvent-free conditions, taking place in moderate to good yield with variously substituted nitroalkenes..

Keywords: *Organocatalysis • Trimethylsilyloxyfuran • Dioxinone-derived silyl ether • Brønsted acids • Nitroalkenes*

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1. Introduction

Michael addition is widely recognized as one of the most important organic reactions for C-C bond construction [1] and allows to obtain highly functionalized building blocks for the total synthesis of organic compounds. Many activating groups [2] can promote the formation of C-C bond, but the strong electron-withdrawing character of the nitro group makes nitroalkenes very good acceptors for conjugate addition [3]. Moreover, the availability of a consistent number of transformations, after the addition has taken place, contributes to the always increasing interest and development of its related chemistry.

In fact, as well known, the presence of nitro group in an organic compound represents a powerful tool from a preparative point of view for its easily manipulation that permits the generation of different functionalities [3b,4]. As reported in Fig. 1, the Nef reaction [5], the nucleophilic displacement [6], the reduction to amino group [7], the Meyer reaction [8], and the conversion into a nitrile oxide [9], are only some examples of the possible interconversions that nitro group can undergo.

Recently, the development of organocatalytic asymmetric Michael additions to nitro olefins has received growing attention, so that many efficient metal-free synthetic methods have been developed for enantioselective addition of aldehydes [3c,10] and ketones [10], malonate esters and ketoesters [11] to nitroalkenes.

The alternative approach, based on Lewis acid-catalyzed addition of silyl enol ethers (known as Mukaiyama-Michael reaction) has found broad application in the case of α,β-unsaturated carbonyl derivatives [12]. Conversely, nitroalkenes, in spite of their enhanced reactivity as Michael acceptors, have only been occasionally used in Mukaiyama-Michael reactions [13], especially with regard to the vinylogous version.

Recent investigations have widely pointed out the significant nucleophilic properties of the masked acetoacetate ester **1** (Fig. 2), as confirmed by its involvement in many procedures for vinylogous aldol and imino-aldol reactions [14], taking place with very high γ-selectivity both under metal- and organo-catalytic conditions. It must be pointed out, that, in the case of silyl dienolates of type **1**, the control of regioselectivity is the main difficulty to circumvent, since the presence of two nucleophilic sites may result in the formation of α- and/or γ-products (Fig. 1) [15].

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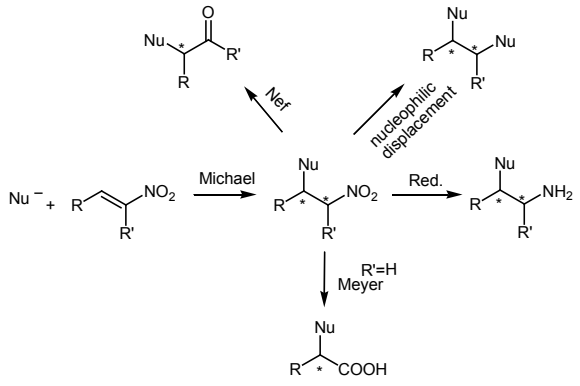


Figure 1. Possible trasformations of nitro group.

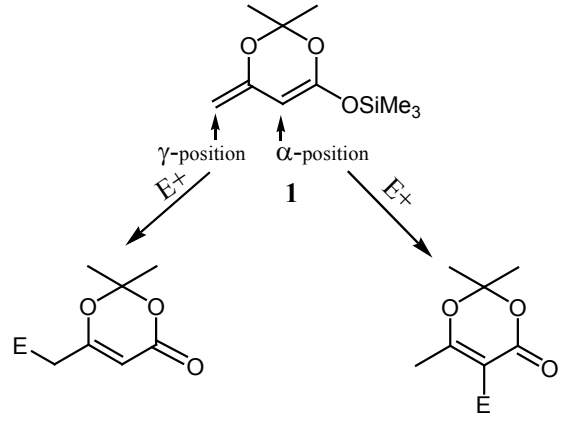
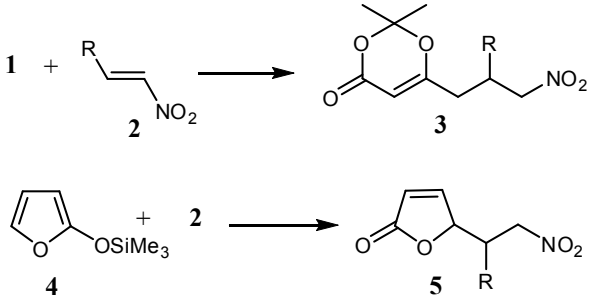


Figure 2. Nucleophilic sites of silyl dienolate **1**.



Scheme 1. Vinylogous Mukaiyama-Michael addition of **1** and **6** to nitroalkenes.

Rather surprisingly, **1** has been rarely used in vinylogous Mukaiyama-Michael additions. The few available reports concern the addition of **1** to particularly activated Michael acceptors, such as 2-acyl-naphthoquinones,[16] and at present no procedure for the addition to nitroalkenes, neither metal nor organo-catalytic, is described.

Consequently, in order to evidence how synthetic equivalent of the γ−anion can give a complete γ-selective vinylogous addition to appropriate acceptors, we decided to focus our attention on the possible use of the masked acetoacetate ester **1** and trimethyl-silyloxyfuran **6** as Michael donors, in vinylogous Mukaiyama- Michael addition to nitroalkenes **2**

2. Experimental procedure

All the chemicals were purchased from Sigma-Aldrich and used without any further purification. TLC was performed on silica gel 60 F_{254} 0.25 mm on glass plates (Merck) and non-flash chromatography was performed on silica gel (0.063-0.200 mm) (Merck). All ^{1}H NMR and ^{13}C NMR spectra were recorded with a DRX 400 MHz Bruker instrument, by using $CDCl_3$ (δ=7.26 ppm in ^{1}H NMR spectra and δ=77.0 ppm in ^{13}C NMR spectra) as solvent (400.135 MHz for ^{1}H and 100.03 MHz for ^{13}C). Data for ^{1}H are reported as follows: chemical shift (δ in ppm), multiplicity (s singlet, d doublet, t triplet, dd doublet of doublets, m multiplet) and coupling costant (J in Hz). Mass spectrometry analysis was carried out using an electrospray spectrometer Waters 4 micro quadrupole. The elemental analyses were performed with FLASH EA 1112 Thermo equipment

2.1. General Procedure

The reaction was carried out in a dry vial. Nitroalkene **2** (149 mg, 1mmol) and silyloxydiene **1** (342 mg, 1.6 eq.) were added and the resulting mixture stirred at room temperature for the time indicated. After completion of the reaction, the crude was purified by chromatography on silica gel in gradient elution with *n*-Hexane/Ethyl acetate to obtain the pure product.

2,2-dimethyl-6-(3-nitro-2-phenylpropyl)-4H-1,3-dioxin-4-one 3a : Yellow oil. MS: *m/z* 292 [M+H$^+$], 314 [M+Na$^+$]; IR (KBr neat): 1725, 1635, 1554, 1378; ^{1}H NMR (400 MHz, $CDCl_3$): 7.34-7.25 (m, 3 H), 7.18 (d, 2 H, J = 8.3 Hz), 5.13 (s, 1 H), 4.58 (d, 2 H, J = 7.5 Hz), 3.86-3.78 (m, 1 H), 2.74-2.61 (m, 2 H), 1.58 (s, 3 H), 1.40 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 167.8 161.0, 137.5, 129.7, 129.0, 127.9, 107.4, 96.1, 80.4, 41.6, 37.3, 25.9, 24.9 ppm. Anal. Calcd for $C_{15}H_{17}NO_5$: C, 61.85; H, 5.88; N, 4.81. Found C, 61.73; H, 5.75; N, 4.69.

6-(2-(4-chlorophenyl)-3-nitropropyl)-2,2-dimethyl-4H-1,3-dioxin-4-one 3b : Yellow oil. MS: *m/z* 348 [M+Na$^+$]; IR (KBr neat): 1726, 1635, 1554, 1378; ^{1}H NMR (400 MHz, $CDCl_3$): 7.31 (d, 2 H, J = 8.3 Hz), 7.13 (d, 2H, J = 8.3 Hz), 5.14 (s, 1 H), 4.61-4.51 (m, 2 H), 3.85-3.77 (m, 1 H) 2.70 (dd, 1 H, J = 14.6, 6.4 Hz), 2.60 (dd, 1 H, J = 14.6, 9.5 Hz), 1.60 (s, 3 H), 1.46 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 167.4, 160.9,

136.1, 134.9, 129.7, 129.3, 107.5, 96.2, 90.1, 40.9, 37.2, 25.8, 25.0 ppm. Anal. Calcd for $C_{15}H_{16}ClNO_5$: C, 55.31; H, 4.95; N, 4.30. Found C, 55.42; H, 4.83; N, 4.42.

2,2-dimethyl-6-(3-nitro-2-p-tolylpropyl)-4H-1,3-dioxin-4-one 3c : Yellow oil. MS: *m/z* 306 [M+H$^+$], 328 [M+Na$^+$]; IR (KBr neat): 1726, 1636, 1555, 1378; ^{1}H NMR (400 MHz, $CDCl_3$): 7.12 (d, 2 H, J = 8.0 Hz), 5.11 (s, 1 H), 4.55 (d, 2 H, J = 7.6 Hz), 3.80-3.76 (m, 1 H), 2.68 (dd, 1 H, J = 14.6, 6.0 Hz), 2.62 (dd, 1 H, J = 14.6, 9.6 Hz), 2.30 (s, 3 H), 1.59 (s, 3 H), 1.44 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 167.9, 161.5, 138.7, 134.4, 130.4, 127.8, 107.4, 96.0, 80.6, 41.2, 37.3, 25.9, 24.9, 21.6 ppm. Anal. Calcd for $C_{16}H_{19}NO_5$: C, 62.94; H, 6.27; N, 4.59. Found C, 62.82; H, 6.14; N, 4.46.

4-(3-(2,2-dimethyl-6-oxo-6H-1,3-dioxin-4-yl)-1-nitropropan-2-yl)benzonitrile 3d : Yellow oil. MS: *m/z* 317 [M+H$^+$], 339 [M+Na$^+$]; IR (KBr neat): 2230, 1725, 1555, 1378 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 7.67 (d, 1 H, J = 8.5 Hz), 7.34 (d, 1 H, J = 8.5 Hz), 5.17 (s, 1 H), 4.67-4.57 (m, 2 H), 3.95-3.88 (m, 1 H), 2.75 (dd, 1 H, J = 14.7, 6.4 Hz), 2.65 (dd, 1 H, J = 14.7, 9.1 Hz), 1.62 (s, 3 H), 1.49 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 166.7, 160.7, 143.0, 133.5, 128.9, 118.5, 113.2, 107.6, 96.4, 79.5, 41.4, 37.1, 25.7, 25.2 ppm. Anal. Calcd for $C_{16}H_{16}N_2O_5$: C, 60.75; H, 5.10; N, 8.86. Found C, 60.61; H, 5.22;N, 8.72.

6-(2-(4-methoxyphenyl)-3-nitropropyl)-2,2-dimethyl-4H-1,3-dioxin-4-one 3e : Yellow oil. MS: *m/z* 344 [M+Na$^+$]; IR (KBr neat): 1723, 1634, 1555, 1378, 1016; ^{1}H NMR (400 MHz, $CDCl_3$): 7.09 8d, 1 H, J = 8.1 Hz), 6.85 (d, 1 H, J = 8.1 Hz), 5.12 (s, 1 H), 4.55-4.53 (m, 1 H), 3.80-3.73 (m, 4 H), 2.68 (dd, 1 H, J = 14.6, 5.9 Hz), 2.60 (dd, 1 H, J = 14.6, 9.7 Hz), 1.59 (s, 3 H), 1.44 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 168.0, 161.0, 130.0, 128.9, 115.1, 107.0, 96.1, 80.7, 55.8, 40.9, 37.4, 30.2, 25.9, 25.0 ppm. Anal. Calcd for $C_{16}H_{19}NO_6$: C, 59.81; H, 5.96; N, 4.36. Found C, 59.78; H, 5.83; N, 4.25.

2,2-dimethyl-6-(3-nitro-2-(thiophen-2-yl)propyl)-4H-1,3-dioxin-4-one 3f : Yellow-orange oil. MS: *m/z* 344 [M+Na$^+$]; IR (KBr neat): 1725, 1636, 1555, 1378; ^{1}H NMR (400 MHz, $CDCl_3$): 7.25 (d, 1 H, J = 5.0 Hz), 6.94 (dd, 1 H, J = 5.04, 3.5 Hz), 6.90 (d, 1 H, J = 3.5 Hz), 5.20 (s, 1 H), 4.59 (d, 2 H, J = 7.2 Hz), 4.21-4.12 (m, 1 H), 2.76 (dd, 1 H, J = 14.7, 5.7 Hz), 2.67 (dd, 1 H, J = 14.7, 9.5 Hz), 1.64 (s, 3 H), 1.51 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 167.3, 140.3, 129.7, 126.6, 125.9, 116.4, 107.5, 96.4, 80.6, 38.4, 30.1, 25.9, 24.9 ppm. Anal. Calcd for $C_{13}H_{15}NO_5S$: C, 52.51; H, 5.09; N, 4.71. Found C, 52.39; H, 5.21;N, 4.83.

6-(2-(furan-2-yl)-3-nitropropyl)-2,2-dimethyl-4H-1,3-dioxin-4-one 3g :Yellow orange oil. MS: *m/z* 282 [M+H$^+$], 304 [M+Na$^+$]; IR (KBr neat): 1726, 1637, 1556, 1378 cm^{-1} ; ^{1}H NMR (400 MHz, $CDCl_3$): 7.36 (d, 1 H, J = 1.88 Hz), 6.30 (dd, 1 H, J = 3.2, 1.88 Hz), 6.18 (d, 1 H, J = 3.2 Hz), 5.19 (s, 1 H), 4.65 (dd, 1 H, J = 12.5, 7.5), 4.58 (dd, 1 H9, J = 12.5, 6.9); 4.01-3.94 (m, 1 H), 2.72 (dd, 1 H, J = 14.5, 9.04 Hz), 2.65 (dd, 1 H, J = 14.5, 5.96 Hz), 1.66 (s, 3 H), 1.57 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 167.3, 161.0, 150.7, 143.4, 110.5, 108.7, 96.1, 35.5, 30.8, 25.1, 23.4 ppm. Anal. Calcd for $C_{13}H_{15}NO_6$: C, 55.51; H, 5.38; N, 4.98. Found C, 55.64; H, 5.50; N, 5.10

6-(2-cyclohexyl-3-nitropropyl)-2,2-dimethyl-4H-1,3-dioxin-4-one 3h :Yellow oil. MS: *m/z* [M+Na$^+$]; IR (KBr neat): 1730, 1636, 1553, 1377 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 5.29 (s, 1 H), 4.44 (dd, 1 H, J = 12.5, 6.2 Hz), 4.29 (dd, 1 H, J = 12.5, 7.0 Hz), 2.51-2.41 (m, 3 H), 2.23 (dd, 1 H, J = 14.1, 7.3 Hz), 1.69 (s, 6 H), 1.25-0.89 (m, 11 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 169.2, 161.1, 125.3, 107.3, 95.7, 40.5, 39.5, 33.9, 30.2, 30.0, 29.7, 26.7, 26.4, 25.6, 25.5 ppm. Anal. Calcd for $C_{15}H_{13}NO_5$: C, 60.59; H, 7.80; N, 4.71. Found C, 60.47; H, 7.69; N, 4.83.

For general procedure, analytical and spectroscopic data of compounds **5a-d** and **5f-l** see [30].

5-(1-nitroundecan-2-yl)furan-2(5H)-one 5e : 284 (M+H$^+$), 306 (M+Na$^+$). IR (KBr, neat)1755, 1641, 1554, 1382 cm^{-1}. 1H NMR (400 MHz, $CDCl_3$): 7.51-7.41 (m, 1 H_{anti} + 1H_{syn}), 6.26, (dd, 1 H_{syn}, J = 5.7, 2.1), 6.18 (dd, 1 H_{anti}, J = 5.7, 2.1), 5.20-5.16 (m, 1 H_{anti} + 1H_{syn}), 4.52 ((dd, 1H_{anti}, J = 13.4, 7.9), 4.39 (dd, 1 H_{syn}, J = 13.4, 5.4), 4.35-4.30 (m, 1 H_{anti} + 1H_{syn}), 2.65-2-40 (m, 1 H_{anti} + 1H_{syn}), 1.65-1.29 (m, 16 H), 0.85-0.90 (m, 3H). ^{13}C NMR, (100 MHz, $CDCl_3$): 172.9, 154.4, 154.0, 124.0, 123.6, 83.0, 76.1, 74.7,40.5, 40.6, 40.3, 32.0, 29.7, 29.4, 27.5, 27.1, 26.8, 26.5, 25.9, 23.1,14.8 ppm. Anal. Calcd for $C_{15}H_{25}NO_4$.C, 63.58; H, 8.89; N, 4.94; Found C, 63.48; H, 8.95 N, 4.87

3. Results and discussion

Preliminarly, β-nitrostyrene **2a** (R=Ph) was chosen as the representative substrate, and, as is in our habit, a control experiment was carried out in absence of any catalyst under solvent-free conditions. The combination of the nucleophilic/electrophilic properties of the reagents **1** and **2a** proved to be particularly successful since the formation of the Michael γ-vinylogous adduct **3a** occurred in good yield, complete selectivity and rather reduced reaction time (Table 1, entry 1).

Furthermore, we were delighted to observe a rather satisfactory level of general validity, since the conjugate addition was found to take place under the same conditions as in entry 1 (Table 1) with complete

Table 1. Vinylogus Mukaiyama-Michael addition of **1** to nitroalkenes **2**.

Entry	R	2	Time (h)	Product	Yield (%)[a]
1	Ph	2a	1.40	3a	82
2	4-ClC_6H_4	2b	3.00	3b	67
3	4-MeC_6H_4	2c	24.00	3c	64
4	4-CNC_6H_4	2d	24.00	3d	69
5	4-MeOC_6H_4	2e	24.00	3e	77
6	2-thienyl	2f	5.00	3f	61
7	2-furyl	2g	3.30	3g	54
8	c-C_6H_{11}	2h	23.00	3h	40

[a] *All the yield refer to isolated, chromatographically pure compounds whose structures were assigned by analytical and spectroscopic data.*

Table 2. Conjugate addition of 6 to nitrostyrene 2a (R=Ph) catalysed by Bronsted Acids.

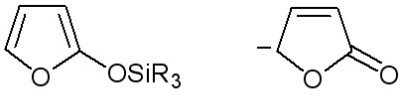
Entry	Catalyst (mol%)	Time (h)	Temp (°C)	Yield (%)[a]	Syn/anti[b]
1	-	1.5	r.t.	12	57/43
2	PhCOOH(5)	1.5	r.t.	20	57/43
3	PhCOOH (10)	48.0	-20	40	58/42
4	Rac-8 (10)	24.0	r.t.	25	58/42
5	9 (10)	22.0	-20	60	66/34
6	9 (20)	20.0	-20	60	75/25
7	10 (10)	17.0	-20	56	65/35
8	10 (20)	18.0	-20	75	75/25
9	Rac-11 (10)	0.5	r.t.	70	60/40
10	Rac-11 (5)	6.0	-20	82	75/25
11[c]	Rac-11 (10)	24.0	r.t.	27	70/30

[a] *All the yield refer to isolated, chromatographically pure compounds whose structures were assigned by analytical and spectroscopic data.*
[b] *Diastereoisomeric ratios were determined by ^1H NMR analysis (400 MHz) on the crude products.*
[c] *The reaction was performed in CH_2Cl_2 solution.*

γ-selectivity and moderate to good yields in the case of α,β-unsaturated nitro-compounds bearing aromatic groups, irrespective of the electronic properties of the substituents on the aromatic nucleus (entries 2-5). Slightly lower efficiency was observed for substrates **2f-h** bearing a heteroaromatic (entries 6 and 7) and, most of all, an aliphatic substituent (entry 8).

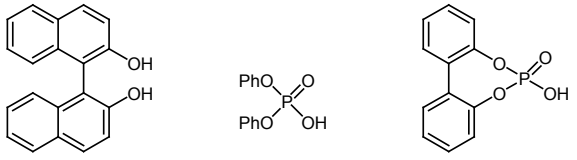
It has to be noted that this new protocol, allowing an easy access to polyfunctional adducts of type **3** under simple and cheap conditions, can be considered of relevant synthetic value because of the broad possibility of elaboration both of the $-NO_2$ group and dioxinone moiety. In a recent report, for example, the vinylogous addition of an acylsilane-derived dienol ether to nitroalkenes under Lewis acid catalysis represented the key-step for an easy approach to 3-substituted azepanes [17].

In the past two decades 2-trialkylsilyloxy furans of type **6** (Fig. 2) have shown to be valuable starting materials for the synthesis of a lot of variously substituted and/or functionalized 2-(5*H*)-furanone derivatives

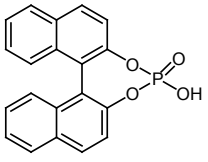


6 **7**

Figure 3. Common starting materials for the synthesis of various functionalized 2-(5H)-furanone derivatives.

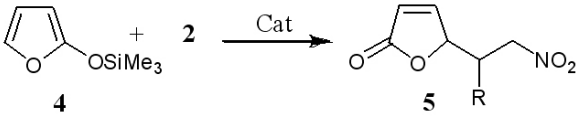


Rac-**8** **9** **10**



Rac-**11**

Figure 4. Phenol and BINOL-based phosphoric acids.



4 **5**

Scheme 2. Conjugate addition of 6 to nitroalkenes **2**.

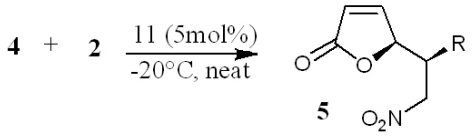
[18]. In fact, their reactivity, as synthetic equivalents of the γ-anion of 2-(5*H*)-furanone **7**, has been widely exploited for the direct introduction of a γ-butenolide core, which represents the main structural feature of a thickly populated class of bioactive compounds.

However, while many important preparative processes, such as alkylation [19], alkenylation [20], arylation [21], aldol and imino-aldol reactions [22,23], have benefited from the use of compounds of type **6**, rather modest attention was devoted to the conjugate addition of **6** to electron deficient alkenes.

In fact, most of the reported procedures are based on the use of α,β-unsaturated carbonyl compounds as Michael acceptor, and they involve carbonyl activation by Lewis Acids [24] or enolate activation by F- sources [25]. Very interestingly, an organocatalytic approach has recently proven to be successful in the asymmetric addition of **6** to α,β-unsaturated aldehydes through iminium ion activation [26].

However, although nitroalkenes are considered among the best Michael acceptor, at present no procedure is available for the conjugate addition of 2-silyloxyfuran of type **6** to give the adducts **5**.

Table 3. Conjugate addition of **6** to nitroalkene **2** catalyzed by Phosphoric acid **11**.



Entry	R	Time (h)	5	Yield (%)[a]	Syn/anti[b]
1	Ph	6	5a	82	75/25
2	4-MeC_6H_4	20	5b	44	77/23
3	c-C_6H_{11}	23	5c	60	82/18
4	n-C_7H_{15}	23	5d	61	71/29
5	n-C_9H_{19}	23	5e	59	72/28
6	4-ClC_6H_4	23	5f	50	80/20
7	2-thienyl	23	5g	45	75/25
8	PhCH_2CH_2	23	5h	84	67/33
9	4-CNC_6H_4	23	5i	57	77/23
10	4-FC_6H_4	23	5j	67	80/20
11	2-naphthyl	23	5k	40	76/24
12	4-MeOC_6H_4	23	5l	27	67/33

[a] *All the yield refer to isolated, chromatographically pure compounds whose structures were assigned by analytical and spectroscopic data.*
[b] *Diastereoisomeric ratios were determined by ^{1}H NMR analysis (400 MHz) on the crude products.*

In recent reports the products of type **5** were obtained in good yield and high stereoselectivity through the direct use of furanone derivatives, as nucleophiles, in presence of a chiral dinuclear zinc complex [27a] or an axially chiral guanidine base [27b].

Therefore, we decided to focus our investigation on the achievement of an organocatalytic procedure for the conjugate addition of **4** to nitroalkenes as reported in Scheme 2. As usual, a preliminary experiment was performed on β--nitrostyrene **2a**, chosen again as the representative substrate, in the absence of any catalyst under solvent-free conditions (entry 1, Table 2). The attainment of adduct **5a** (R = Ph) in 12% yield after 1.5 hours pointed out the occurrence of a competing background reaction proceeding in rather poor diastereoselectivity (*syn/anti* ratio = 57/43) and confirmed the notable properties of nitroalkenes as Michael acceptors.

In an attempt to improve the efficiency and stereoselectivity of the reaction, the catalytic properties of some easily accessible H-donors, capable of lowering the LUMO of nitroalkenes through hydrogen bonding, were examined [28].

The use of benzoic acid and racemic BINOL, as H-donors, proved to be unsatisfactory both in terms of efficiency and diastereoselectivity (entries 2-4, Table 2).

Because of the ever increasing importance of organic phosphoric acids in organic synthesis [29], we decided to explore the catalytic properties of some easily available phenol and BINOL-based organocatalysts **8**-**11** (Fig. 4) under a variety of experimental conditions reported in [30].

In entries 5-10 (Table 2) we were pleased to observe a significant improvement of efficiency and diastereoselectivity. Solvent free conditions, catalyst loading and low temperature (-20°C), proved to be determining factors for the achievement of a successful process. Notably, the best results in terms of efficiency and diastereoselectivity were obtained in presence of catalyst *Rac*-**11** (5 mol%, entry 10, Table 1).

It has to be noted that a dramatic drop of efficiency was detected by performing the reaction in CH_2Cl_2 solution, obtaining the Michael adduct in rather poor yield after prolonged reaction times (entry 9 *vs* 11, Table 2). In order to verify the scope of the procedure, a variety of nitroalkenes were examined reacting with 2-trimethylsilyloxyfuran **6** under the optimized conditions.

As reported in Table 3, the conjugate addition took place in moderate to good yields with nitroalkenes bearing in β-position aromatic (entries 1,2,6,9-12), heteroaromatic (entry 7), aliphatic (entries 3,4,5,8) substituents.

4. Conclusions

In conclusion, the first vinylogous Mukaiyama-Michael addition of silyloxydiene 1 to nitroalkenes was described, representing a rapid and easy approach to the attainment of useful intermediates of relevant synthetic value for the possibility of further elaboration both of the –NO2 group and the dioxinone moiety. The absence of catalyst and the solvent free conditions make this procedure economically convenient, operationally simple and environmental friendly.

Moreover, the catalytic properties of phenyl and binaphthyl phosphoric acids have been conveniently exploited for the achievement of the first organocatalytic procedure for the Mukaiyama-Michael addition of silyloxyfuran to nitroalkenes, allowing an easy and direct access to variously substituted γ-butenolides.

In both protocols no solvent and no work-up are required and, after the completion of the reaction, the crude mixtures can be directly submitted to purification by column chromatography.

Acknowledgements

We are grateful to MIUR and University of Salerno for financial support.

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