$HClO_4$–SiO_2 as a Novel and Recyclable Catalyst for the Phospha-Michael Addition of Phosphorous Nucleophiles to α,β-Unsaturated Malonates

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Received 19 December 2009

Abstract: An efficient synthesis of β-phosphono malonates via phospha-Michael addition of phosphorous nucleophiles to α,β-unsaturated malonates in the presence of $HClO_4$–SiO_2 as a new and recyclable catalyst is described.

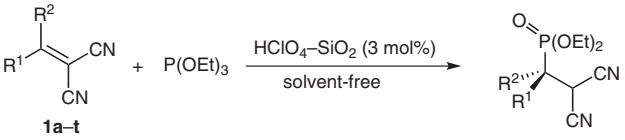
Key words: silica-supported perchloric acid, phospha-Michael addition, β-phosphono malonates

Phosphonates are fascinating and versatile compounds in organic synthesis. They also have unique properties which expand their applications as enzyme inhibitors, metabolic probes,[1] peptide mimetics,[2] antibiotics, and pharmacologic agents[3] besides their traditional roles as intermediates in organic synthesis.[4] Direct phosphorus–carbon bond formation represents one of the most versatile and powerful tools for the synthesis of phosphonates. Amongst these methods, phospha-Michael addition, the addition of a phosphorous nucleophile to an electron-deficient alkene, has invoked considerable attention.[5] This kind of phosphorus–carbon bond formation has been promoted by bases,[5,6] Brønsted/Lewis acids,[7,8] microwaves,[9] transition metals[10] and radical initiators such as AIBN.[11] Although these methods are valuable, they suffer from disadvantages such as requiring high temperatures, long reaction times, tedious workup protocols, using a large amount of unrecyclable catalyst or resulting in low yields. Hence, the development of a new procedure with more efficiency for this important transformation is still in demand.

Reusable solid-supported reagents have advantages such as low toxicity, low cost and moisture and air tolerance.[12] They have also shown better activity and selectivity than the corresponding unsupported reagents.[12b]

Silica-supported perchloric acid ($HClO_4$–SiO_2)[13] has recently received considerable attention as a recyclable solid-supported catalyst for various organic transformations,[14–20] including Knoevenagel condensations, Michael additions, cyclodehydration,[14] synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes,[15] Friedländer synthesis of quinolines,[16] synthesis of enaminones and enaminoesters,[17] synthesis of quinoxalines and dihydropyrazines[18] and chemoselective carbon–sulfur bond formation.[19]

As part of our continued interest in the synthesis of phosphonate derivatives, we have recently concentrated on the development of new environmentally benign procedures for the synthesis of these important scaffolds.[21] In this connection, herein, we wish to introduce an eco-friendly method for the efficient synthesis of β-phosphono malonates via phospha-Michael addition of phosphorous nucleophiles to α,β-unsaturated malonates in the presence of $HClO_4$–SiO_2 (Scheme 1, Table 1). In this procedure, $HClO_4$–SiO_2 was applied as a recyclable heterogeneous catalyst at room temperature and under solvent-free conditions.



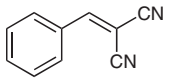
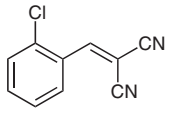
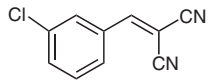
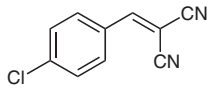
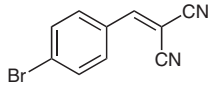
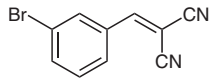
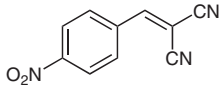
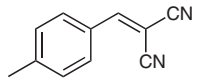
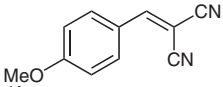
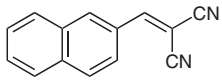
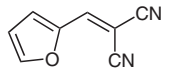
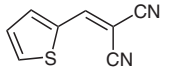
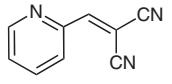
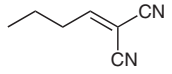
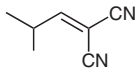
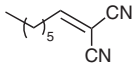
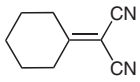
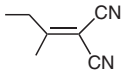
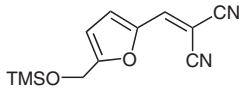
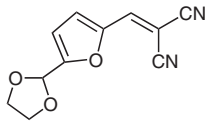
R^1 = aryl, heteroaryl, alkyl
R^2 = alkyl, H

Scheme 1

As indicated in Table 1, different substituted benzylidenemalonitriles with electron-donating and electron-withdrawing groups underwent successful phospha-Michael addition with triethyl phosphite and gave the corresponding β-phosphono malonates in 83–93% yields (entries 1–9). The catalyst was compatible with functional groups such as Cl, Br and OMe. No competitive nucleophilic methyl ether cleavage was observed for the substrate which possessed an aryl methoxy group (entry 9), despite the strong nucleophilicity of phosphites.[22] This method is also applicable for the synthesis of β-phosphono malonates from the reaction of triethyl phosphite with α,β-unsaturated malonates substituted with polyaromatic, heteroaromatic and aliphatic groups (entries 10–16). By this method, the reaction of triethyl phosphite with β,β-disubstituted malonates **1q** and **1r** proceeded well and the corresponding products (**2q** and **2r**) were obtained in good yields. α,β-Unsaturated malonates which contain acid-labile functionalities such as trimethylsilyl ether or acetal groups (**1s** and **1t**) also underwent smooth reaction with triethyl phosphite and produced the desired products in 80% and 85% yields, respectively (entries 19 and 20), with the protecting groups being unaffected during the reaction.

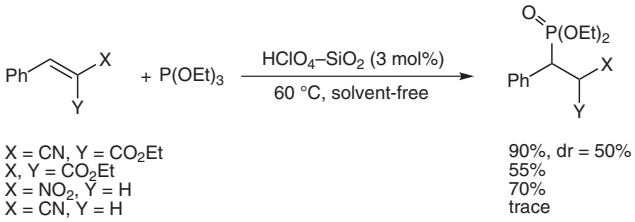
SYNLETT 2010, No. 10, pp 1485–1488
Advanced online publication: 25.05.2010
DOI: 10.1055/s-0029-1220069; Art ID: D37309ST

Table 1 Synthesis of Different Types of β-Phosphono Malonates Catalyzed by $HClO_4$–SiO_2 under Solvent-Free Conditions at Room Temperature

Entry	Substrate	Product	Time (min)	Yield[a] (%)
1	 **1a**	**2a**	60	93
2	 **1b**	**2b**	30	83
3	 **1c**	**2c**	45	85
4	 **1d**	**2d**	60	87
5	 **1e**	**2e**	20	93
6	 **1f**	**2f**	30	85
7	 **1g**	**2g**	5	90
8	 **1h**	**2h**	150	90
9	 **1i**	**2i**	180	83
10	 **1j**	**2j**	60	85
11	 **1k**	**2k**	90	88
12	 **1l**	**2l**	180	87
13	 **1m**	**2m**	5	95
14[b]	 **1n**	**2n**	15	80
15[b]	 **1o**	**2o**	60	75
16[b]	 **1p**	**2p**	5	83
17[c]	 **1q**	**2q**	120	85
18[c]	 **1r**	**2r**	120	78
19	 **1s**	**2s**	180	80
20	 **1t**	**2t**	120	85

[a] Isolated yield. Conditions: catalyst (0.03 mmol), α,β-unsaturated malonate (1 mmol), triethyl phosphite (1 mmol). All the products were characterized by spectroscopic methods and compared with the authentic spectra.[23]
[b] Reaction temperature: 60 °C.
[c] Reaction temperature: 80 °C.

We have also examined the applicability of this method for the phospha-Michael addition reaction to some other activated alkenes. As shown in Scheme 2, the reactions proceeded in one hour affording the desired products in 55–90% yields, although only a trace of the desired product was obtained with acrylonitrile after 24 hours.



Scheme 2

After performing the phospha-Michael addition reaction of triethyl phosphite with benzylidenemalonitrile (**1a**) under the present conditions, EtOAc was added to the reaction mixture. Then the catalyst was separated by a simple filtration from the resulting heterogeneous mixture, dried at 100 ºC and was reused for a consecutive run under the

same reaction conditions. The average isolated yield of **2a** for five consecutive runs was 90%, which clearly demonstrates the recyclability of this catalyst (Figure 1).

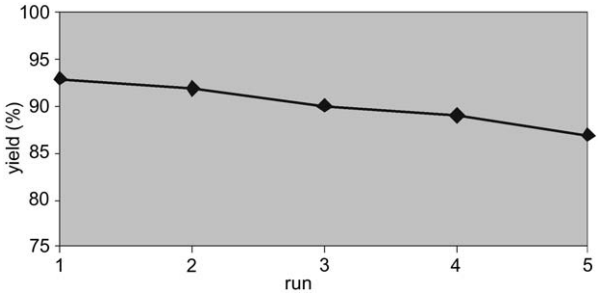


Figure 1 Reusability of $HClO_4$–SiO_2 as a catalyst for the synthesis of β-phosphono malonate **2a**

In order to show the unique catalytic behavior of supported perchloric acid in these reactions, we performed the phospha-Michael addition of triethyl phosphite to benzylidenemalonitrile (**1a**) in the presence of a catalytic amount (3 mol%) of $HClO_4$, $LiClO_4$, metal triflates [e.g., $Al(OTf)_3$, $Ce(OTf)_4$, $Zn(OTf)_2$, $Mg(OTf)_2$, LiOTf], Lewis acids (e.g., $AlCl_3·6H_2O$, $ZrCl_4$, $FeCl_3$, $ZnCl_2$), metal oxides (e.g., Sb_2O_3, SnO_2, ZnO) and a Brønsted acid (NH_2SO_3H) for comparison. As is evident from Table 2, supported perchloric acid is the most effective catalyst for this purpose leading to the formation of β-phosphono malonate (**2a**) in high yield. A similar reaction in the absence of the catalyst led to the formation of the desired product (**2a**) in low yield after 24 hour (Table 2, entry 17).

Finally, we evaluated the generality of this method for the phospha-Michael addition of different phosphite esters to benzylidenemalonitrile (**1a**) under the standard reaction conditions (Table 3).

The catalytic phospha-Michael addition of trimethyl phosphite and triisopropyl phosphite with **1a** proceeded well and the desired products were isolated in 77% and 60% yields (entries 1 and 2). A similar reaction in the presence of triphenyl phosphite or diethyl phosphite as a phosphorus nucleophile led to the formation of the desired product in low yields (entries 3 and 4).

In conclusion, $HClO_4$–SiO_2 has been shown to be a reusable and efficient catalyst for the synthesis of a variety of β-phosphono malonates by phospha-Michael addition of phosphite esters to different α,β-unsaturated malonates.[24] Good to high yields, short reaction times, simple workup, ease of catalyst recovery, lack of by-products, and recyclability of the catalyst without appreciable loss of activity make this method an attractive and useful contribution to the present methodologies.

Acknowledgment

We are thankful to the Birjand University Research Council for its support of this work.

Table 2 Comparison of the Catalytic Efficiency of $HClO_4$–SiO_2 with Various Catalysts[a]

Entry	Catalyst	Time (h)	Yield[b] (%)
1	$HClO_4$–SiO_2	1	93
2	$HClO_4$	14	72
3	$LiClO_4$	15	75
4	$Al(OTf)_3$	24	83
5	$Ce(OTf)_4$	24	65
6	$Zn(OTf)_2$	24	70
7	$Mg(OTf)_2$	24	70
8	LiOTf	24	70
9	$AlCl_3·6H_2O$	24	85
10	$ZrCl_4$	16	80
11	$FeCl_3$	24	78
12	$ZnCl_2$	24	65
13	Sb_2O_3	24	75
14	SnO_2	4	85
15	ZnO	24	75
16	NH_4SO_3H	6	83
17	–	24	50

[a] Reaction conditions: catalyst (0.03 mmol), **1a** (1 mmol), phosphite (1 mmol), r.t., solvent-free.
[b] Isolated yield.

Table 3 Phospha-Michael Addition of Various Phosphite Esters to Benzylidenemalonitrile (**1a**) Catalyzed by $HClO_4$–SiO_2[a]

Entry	Phosphite	Time (h)	Yield[b] (%)
1	$P(OMe)_3$	2	77
2	$P(O\text{-}i\text{-}Pr)_3$	4	60
3	$P(OPh)_3$	5	8
4	$HP(O)(OEt)_2$	16	15

[a] Reaction conditions: catalyst (0.03 mmol), **1a** (1 mmol), phosphite (1 mmol), r.t., solvent-free.
[b] Isolated yield.

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(24) **General Procedure for the Synthesis of β-Phosphono Malonates (2a–t)**: $HClO_4$–SiO_2 (0.03 mmol, 0.057 g, 0.52 mmol/g) was added to a mixture of α,β-unsaturated malonates **1a–t** (1 mmol) and $P(OEt)_3$ (1 mmol). The mixture was stirred and monitored by TLC. After completion of the reaction, the reaction mixture was diluted with EtOAc and filtered. Evaporation of the solvent under reduced pressure gave the crude products. The pure products, **2a–t**, were obtained by chromatography on silica, eluting with *n*-hexane–EtOAc (1:1).

(1-Phenyl-2,2-dicyanoethyl) Phosphonic Acid Diethyl Ester (2a)

^{1}H NMR ($CDCl_3$): δ = 1.11 (t, 3 H, $^3J_{HH}$ = 6.8 Hz), 1.33 (t, 3 H, $^3J_{HH}$ = 7.0 Hz), 3.65 (dd, 1 H, $^3J_{HH}$ = 8.0, $^2J_{HP}$ = 21.0 Hz), 3.91–4.21 (m, 4 H), 4.55 (t, 1 H, $^3J_{HH}$ = 8.3 Hz), 7.43 (s, 5 H). ^{13}C NMR ($CDCl_3$): δ = 16.1 (d, $^3J_{CP}$ = 5.6 Hz), 16.2 (d, $^3J_{CP}$ = 5.6 Hz), 25.5, 44.6 (d, $^1J_{CP}$ = 144.0 Hz), 63.4 (d, $^2J_{CP}$ = 7.5 Hz), 64.4 (d, $^2J_{CP}$ = 7.0 Hz), 111.1 (d, $^3J_{CP}$ = 12.5 Hz), 111.3 (d, $^3J_{CP}$ = 10.0 Hz), 129.2, 129.3, 129.4, 129.8. ^{31}P NMR ($CDCl_3$): δ = 20.04. MS (70 eV): *m*/*z* = 292 [M^+], 155 [$M^+ - P(O)(OEt)_2$].

[1-(2-Chlorophenyl)-2,2-dicyanoethyl] Phosphonic Acid Diethyl Ester (2b)

^{1}H NMR ($CDCl_3$): δ = 1.11 (t, 3 H, $^3J_{HH}$ = 7.0 Hz), 1.36 (t, 3 H, $^3J_{HH}$ = 7.0 Hz), 3.75–4.30 (m, 4 H), 4.46 (dd, 1 H, $^3J_{HH}$ = 8.2, $^2J_{HP}$ = 21.2 Hz), 4.61 (t, 1 H, $^3J_{HH}$ = 8.5 Hz), 7.35 (d, 2 H, $^3J_{HH}$ = 4.0 Hz), 7.47 (s, 1 H), 7.75 (d, 1 H, $^3J_{HH}$ = 5.3 Hz). ^{13}C NMR ($CDCl_3$): δ = 16.0 (d, $^3J_{CP}$ = 6.3 Hz), 16.2 (d, $^3J_{CP}$ = 5.6 Hz), 24.9, 39.4 (d, $^1J_{CP}$ = 144.6 Hz), 63.6 (d, $^2J_{CP}$ = 7.5 Hz), 64.4 (d, $^2J_{CP}$ = 6.9 Hz), 110.9 (d, $^3J_{CP}$ = 5.6 Hz), 111.1, 127.8, 128.6, 129.6, 130.6, 135.1. ^{31}P NMR ($CDCl_3$): δ = 19.47. MS (70 eV): *m*/*z* = 326 [M^+], 328 [$M^+ + 2$], 189 [$M^+ - P(O)(OEt)_2$], 191 [$(M^+ + 2) - P(O)(OEt)_2$].

[1-(4-Chlorophenyl)-2,2-dicyanoethyl] Phosphonic Acid Diethyl Ester (2d)

^{1}H NMR ($CDCl_3$): δ = 1.16 (t, 3 H, $^3J_{HH}$ = 7.0 Hz), 1.33 (t, 3 H, $^3J_{HH}$ = 7.0 Hz), 3.62 (dd, 1 H, $^3J_{HH}$ = 7.5 Hz, $^2J_{HP}$ = 21.5 Hz), 3.82–4.19 (m, 4 H), 4.55 (t, 1 H, $^3J_{HH}$ = 7.7 Hz), 7.42 (s, 4 H). ^{13}C NMR ($CDCl_3$): δ = 16.1 (d, $^3J_{CP}$ = 5.0 Hz), 16.2 (d, $^3J_{CP}$ = 5.6 Hz), 25.5, 43.9 (d, $^1J_{CP}$ = 144.7 Hz), 63.5 (d, $^2J_{CP}$ = 7.0 Hz), 64.4 (d, $^2J_{CP}$ = 7.0 Hz), 111.0 (d, $^3J_{CP}$ = 11.9 Hz), 111.2 (d, $^3J_{CP}$ = 11.3 Hz), 128.8, 129.6, 130.7, 135.7. ^{31}P NMR ($CDCl_3$): δ = 19.42. MS (70 eV): *m*/*z* = 326 [M^+], 328 [$M^+ + 2$], 189 [$M^+ - P(O)(OEt)_2$], 191 [$(M^+ + 2) - P(O)(OEt)_2$].

[1-(Naphthalen-2-yl)-2,2-dicyanoethyl] Phosphonic Acid Diethyl Ester (2j)

^{1}H NMR ($CDCl_3$): δ = 1.08 (t, 3 H, $^3J_{HH}$ = 7.0 Hz), 1.36 (t, 3 H, $^3J_{HH}$ = 7.0 Hz), 3.65–4.22 (m, 5 H), 4.66 (t, 1 H, $^3J_{HH}$ = 8.5 Hz), 7.52–7.58 (m, 3 H), 7.87–7.96 (m, 4 H). ^{13}C NMR ($CDCl_3$): δ = 16.1 (d, $^3J_{CP}$ = 5.6 Hz), 16.2 (d, $^3J_{CP}$ = 6.2 Hz), 25.7, 44.8 (d, $^1J_{CP}$ = 144.0 Hz), 63.4 (d, $^2J_{CP}$ = 7.5 Hz), 64.4 (d, $^2J_{CP}$ = 7.0 Hz), 111.2 (d, $^3J_{CP}$ = 13.2 Hz), 111.3 (d, $^3J_{CP}$ = 8.2 Hz), 125.9, 126,9, 127.2, 127.6, 127.7, 127.8, 128.2, 129.2, 129.4, 133.3. ^{31}P NMR ($CDCl_3$): δ = 19.95.

[1-(Furan-2-yl)-2,2-dicyanoethyl] Phosphonic Acid Diethyl Ester (2k)

^{1}H NMR ($CDCl_3$): δ = 1.24–1.37 (m, 6 H), 3.87 (dd, 1 H, $^3J_{HH}$ = 6.5 Hz, $^2J_{HP}$ = 22.7 Hz), 3.98–4.23 (m, 4 H), 4.51 (t, 1 H, $^3J_{HH}$ = 8.7 Hz), 6.44 (s, 1 H), 6.62 (s, 1 H), 7.49 (s, 1 H). ^{13}C NMR ($CDCl_3$): δ = 16.1, 16.2, 24.3, 39.1 (d, $^1J_{CP}$ = 147.1 Hz), 63.9 (d, $^2J_{CP}$ = 6.9 Hz), 64.2 (d, $^2J_{CP}$ = 6.9 Hz), 110.9 (d, $^3J_{CP}$ = 9.4 Hz), 111.1 (d, $^3J_{CP}$ = 11.9 Hz), 111.3, 111.7, 143.2, 144.0. ^{31}P NMR ($CDCl_3$): δ = 19.88. MS (70 eV): *m*/*z* = 282 [M^+], 145 [$M^+ - P(O)(OEt)_2$].

[1-(Pyridin-3-yl)-2,2-dicyanoethyl] Phosphonic Acid Diethyl Ester (2m)

^{1}H NMR ($CDCl_3$): δ = 1.18 (t, 3 H, $^3J_{HH}$ = 6.8 Hz), 1.33 (t, 3 H, $^3J_{HH}$ = 7.0 Hz), 3.65 (dd, 1 H, $^3J_{HH}$ = 6.8 Hz, $^2J_{HP}$ = 21.6 Hz), 3.92–4.21 (m, 4 H), 4.63 (t, 1 H, $^3J_{HH}$ = 8.5 Hz), 7.39 (t, 1 H, $^3J_{HH}$ = 6.5 Hz), 7.95 (d, 1 H, $^3J_{HH}$ = 6.5 Hz), 8.67 (s, 2 H). ^{13}C NMR ($CDCl_3$): δ = 16.1 (d, $^3J_{CP}$ = 5.0 Hz), 16.2 (d, $^3J_{CP}$ = 5.0 Hz), 25.3, 42.1 (d, $^1J_{CP}$ = 144.6 Hz), 63.8 (d, $^2J_{CP}$ = 7.0 Hz), 64.5 (d, $^2J_{CP}$ = 7.0 Hz), 110.8 (d, $^3J_{CP}$ = 10.7 Hz), 111.0 (d, $^3J_{CP}$ = 11.9 Hz), 124.0, 126,7, 136.5, 150.5, 150.8. ^{31}P NMR ($CDCl_3$): δ = 19.03. MS (70 eV): *m*/*z* = 293 [M^+], 156 [$M^+ - P(O)(OEt)_2$].