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PII: S0040-4039(15)30171-4
DOI: http://dx.doi.org/10.1016/j.tetlet.2015.09.129
Reference: TETL 46801

To appear in: *Tetrahedron Letters*

Received Date: 8 April 2015
Revised Date: 24 August 2015
Accepted Date: 26 September 2015

Please cite this article as: Kaboudin, B., Kazemi, F., Habibi, F., Fe_3O_4@MgO nanoparticles as an efficient recyclable catalyst for the synthesis of phosphoroamidates *via* the Atherton-Todd reaction, *Tetrahedron Letters* (2015), doi: http://dx.doi.org/10.1016/j.tetlet.2015.09.129

Tetrahedron Letters
journal homepage: www.elsevier.com

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ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

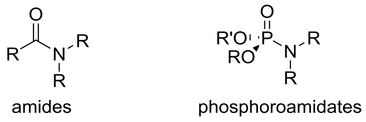
Keywords:
Phosphoroamidate
Fe_3O_4@MgO nanoparticles
H-Dialkyl phosphite
Atherton-Todd reaction

ABSTRACT

A simple and efficient method is presented for the synthesis of phosphoroamidates in moderate to good yield *via* the Atherton-Todd coupling of primary amines with *H*-dialkyl phosphites using Fe_3O_4@MgO nanoparticles as a recyclable catalyst.

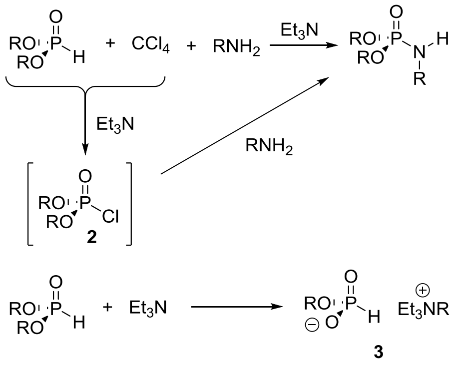
Dedicated to Professor Tsutomu Yokomatsu from Tokyo University of Pharmacy and Life Sciences on the occasion of his 65th birthday

Phosphorus-heteroatom bond formation is an active and important research area for the preparation of organophosphorus compounds.[1] Many investigations have been conducted in order to develop new procedures and methods for the synthesis of biologically and materially important organophosphorus compounds.[2] Among organophosphorus compounds, phosphoroamidates (phosphorus analogues of amides containing a tetrahedral pentavalent phosphorus atom) are particularly important (Scheme 1). They are stable analogues of the high-energy tetrahedral transition states for many enzyme-catalyzed reactions.[3] Phosphoroamidate containing peptides and lipid chains are used as inhibitors of HIV protease[4] and nucleoside reverse transcriptase.[5] These compounds have also been applied as a flame retardant for rigid polyureathane foams.[6] Recently chiral phosphoroamidates have been used as chiral catalysts in asymmetric transformations.[7]



Scheme 1: Structures of amides and phosphoroamidates

One-pot, multi-step and multi-component reactions are attractive since they can significantly lower the cost of synthetic routes by reducing the number of separation and purification steps.[8] The Atherton-Todd reaction, which involves the one-pot reaction of a dialkyl phosphite with a primary amine and carbon tetrachloride (CCl_4) in the presence of base, is a typical method for the synthesis of phosphoroamidates.[9,10] The key step is the *in-situ* formation of a dialkyl chlorophosphate *via* the reaction of dialkylphosphites with CCl_4. This is then followed by nucleophilic addition of an amine to the resulting dialkyl chlorophosphate **2** (Scheme 2).[11]
However, the use of triethylamine as the base has associated problems that include harsh reaction conditions, long reaction times and the formation of side-products. Additionally, it is well-known that the formation of salt **3** accompanies the formation of dialkyl chlorophosphate in the presence of a base (Scheme 2).[12]



Scheme 2: The Atherton-Todd reaction *via* the formation of intermediate **2** and as well as potential side product **3**

In the past decade, numerous publications have been reported for organic transformations regarding the development of catalysts bound to inorganic solids, due to environmental and economical considerations.[13] Magnetic nanoparticles have great potential in view of their easy recovery and accessibility, and can be prepared

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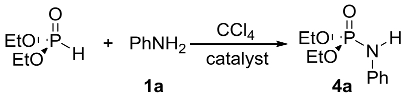
from inexpensive materials, and easily supported on organic and inorganic materials.[14] For example, Fe_3O_4 nanoparticles (NPs) supported on metal oxides have been extensively studied in the fields of chemical catalysis,[15a-e] environmental protection,[15f] sensors[15g] and magnetic storage medias.[15h] Recently, Marquina and co-workers reported the preparation and characterization of Fe_3O_4 NPs supported on magnesium oxide (MgO) using the sol-gel method.[16] As part of our efforts to explore the utility of solid phase reactions for the synthesis of organophosphorus compounds,[17] we recently reported Fe_3O_4 NPs supported on MgO (Fe_3O_4@MgO) as a novel, recyclable solid base catalyst for the synthesis of 1-hydroxyphosphonates.[18] To the best of our knowledge, there are no reports on conducting the Atherton-Todd reaction in the presence of a recyclable solid base catalyst. Therefore, we decided to study the feasibility of the Atherton-Todd reaction in the presence of Fe_3O_4@MgO NPs as a base catalyst.

The superparamagnetic Fe_3O_4@MgO NPs were prepared according to Marquina's method and our previous report (see the literature[16,18] and ESI for preparation). The Fe_3O_4/MgO mol ratio of the catalyst was calculated from chemical analysis by atomic absorption spectroscopy giving a mole ratio of 2.78 Fe_3O_4 to 1.0 MgO. The NPs size were determined from the XRD pattern using Scherrer equation (the NPs sizes evaluted by Scherrer's equation were 9.2 nm). Initially, the one-pot reaction of aniline **1a** with diethylphosphite in the presence of carbon tetrachloride was chosen as a model reaction to be studied under various conditions (Scheme 3 and Table 1).



Scheme 3 Reaction of aniline (1 equiv.) with diethylphosphite (1 equiv.) and CCl_4

Table 1. Reaction of aniline (1 equiv.) with diethylphosphite (1 equiv.) and CCl_4

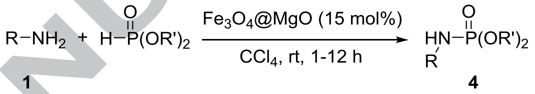
Entry	Catalyst loading (mol%)	Temp.	Time (h)[a]	Yield of **4a** (%)[b]
1	-	rt	8	15
2	5	rt	8	55
3	10	rt	8	63
4	15	rt	8	72
5	20	rt	8	73
6	15	rt	24	72
7	15	reflux	24	36
8	15	rt	6[c]	70
9	15[d]	rt	24	54
10	15[e]	rt	24	20
11	15	rt	3[f]	80

[a] 2 equiv. of CCl_4; [b] isolated yield; [c] 1 equiv. of CCl_4; [d] Reaction carried out in the presence of Fe_3O_4 nanoparticles; [e] Reaction carried out in the presence of MgO powder; [f] Dropwise addition of a mixture of diethylphosphite and CCl_4 to aniline **1a**

Treatment of **1a** with a mixture of diethylphosphite and CCl_4 (2 equiv.) at room temperature in the absence of base gave the corresponding phosphoroamidate **4a** in 15% yield after 8 h (Entry 1). The yield of the reaction increased to 55% yield in the presence of 5 mol% Fe_3O_4@MgO (Entry 2). When the catalyst loading was raised from 5% to 15%, the yield of **4a** increased to 72% (Entries 3 and 4) however this did not increase futher upon increasing the catalyst loading or reaction time (Entries 5 and 6). Heating diethyl phosphite, aniline (**1a**), and CCl_4 (as solvent) at reflux for 24 hours led to the formation of the desired product **4a** in 36% yield (Table 1, Entry 7). The reaction yield also decreased when the reaction was carried out in the presence of only 1 equiv. of carbon tetrachoride (Entry 8). Treatment of **1a** with a mixture of diethylphosphite and CCl_4 at room temperature in the presence of Fe_3O_4 NPs or MgO powder gave the corresponding phosphoroamidate **4a** in 54% and 20% yield respectively (Entries 9, 10). Finally, we found that the dropwise addition of a mixture of diethylphosphite and CCl_4 to aniline **1a** at ambient temperature in the presence of 15 mol% catalyst led to an acceleration of the reaction rate and an increase in the yield of **4a** (Entry 11).

This process was successfully applied to other amines as summarized in Table 2. Substituted anilines reacted with a mixture of diethylphosphite and CCl_4 in the presence of 15 mol% of Fe_3O_4@MgO NPs as the basic catalyst to afford the desired products **4b-4k** in moderate to good yields. Benzylamine and cyclohexyl amine also reacted to give compounds **4l** and **4m** in 70% and 85% yield respectively.

Table 2. Reaction of amines (1 equiv.) with a mixture of dialkyl phosphite (1 equiv.) and CCl_4 (2 equiv.) in the presence of Fe_3O_4@MgO NPs (15 mol%).

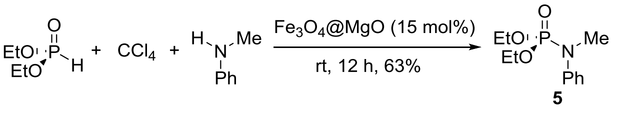


Entry	R	R'	Time (h)	Product	Yield (%)[a]
1	C_6H_5	C_2H_5	3	**4a**	80
2	*p*-MeC_6H_4	C_2H_5	2	**4b**	78
3	*p*-$MeOC_6H_4$	C_2H_5	1	**4c**	85
4	*p*-$NO_2C_6H_4$	C_2H_5	12	**4d**	52
5	*p*-ClC_6H_4	C_2H_5	12	**4e**	70
6	*p*-BrC_6H_4	C_2H_5	12	**4f**	71
7	*m*-$MeOC_6H_4$	C_2H_5	8	**4g**	65
8	*m*-$NO_2C_6H_4$	C_2H_5	10	**4h**	65
9	*o*-MeC_6H_4	C_2H_5	12	**4i**	75
10	*o*-EtC_6H_4	C_2H_5	12	**4j**	70
11	*o*-$NO_2C_6H_4$	C_2H_5	12	**4k**	68
12	$PhCH_2$-	C_2H_5	1	**4l**	70
13	cyclohexyl	C_2H_5	1	**4m**	85
14	*p*-MeC_6H_4	$(CH_3)_2CH$-	3	**4n**	50
15	*p*-$MeOC_6H_4$	$(CH_3)_2CH$-	3	**4o**	67
16	$PhCH_2$-	$(CH_3)_2CH$-	3	**4p**	67

[a] Yield (based on amine equiv. with regard to phosphite) refers to yield after column chromatography

The Atherton-Todd reaction of amines with a mixture diisopropyl phosphite and CCl_4 was also studied (entries 14-16). The reaction of aromatic and aliphatic amines with a mixture of diisopropyl phosphite and CCl_4 at ambient temperature, gave the desired products **4n-4p** in moderate yields.

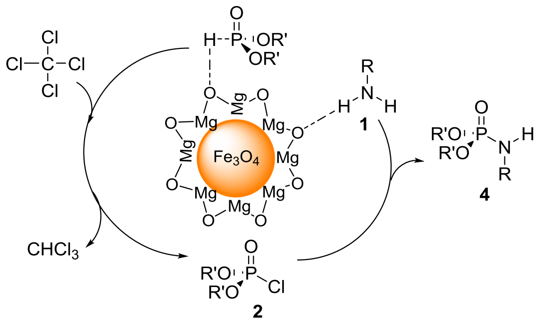
We found that it was also possible to carry out this reaction using *N*-methylaniline to give the corresponding phosphoroamidate **5** in 63% yield (Scheme 4).



Scheme 4: Reaction of *N*-methylaniline (1 equiv.) with a mixture of diethylphosphite (1 equiv.) and CCl_4 (2 equiv.) in the presence of Fe_3O_4@MgO NPs (15 mol%).

The reusability of the Fe_3O_4@MgO NPs was also studied for the reaction of **1a** with diethylphosphite in the presence of CCl_4. The NPs were collected using a magnet and washed four times with deionized water and methanol and reused after drying at 60 °C for 3 h for further reactions. The catalytic activity did not considerably decrease after four catalytic cycles (5% decreases after four catalytic cycles).

A proposed mechanism for the synthesis of phosphoroamidates *via* the Atherton-Todd coupling using Fe_3O_4@MgO NPs is outlined in Scheme 5. The process is thought to proceed *via* the reaction of dialkyl phosphite with CCl_4 to give dialkyl chlorophosphate **2**, a known intermediate, followed by nucleophilic substitution by the amine to give phosphoroamidate **4**. The reaction was carried out in an open flask and the generation of HCl gas was detected with wet pH paper test.



Scheme 5: Proposed mechanism for the synthesis of phosphoroamidate **4**

In conclusion, we have reported a simple, and convenient method for the synthesis of phosphoroamidates *via* the Atherton-Todd coupling reaction of amines with dialkyl phosphites. A simple work-up, mild reaction conditions, moderate to good yields, and clean reactions should make this method an attractive and a useful contribution to present methodologies.[19]

Acknowledgements

The authors thank the Institute for Advanced Studies in Basic Sciences for support of this work. Thanks are also given to Professor Behzad Haghighi for the atomic absorption analysis of the catalyst and Ms Shahla Heydari for assistance in the preparation of the paper.

Supplementary Material

Spectroscopic characterization data and copies of ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR for compounds **4a-4p**. Supplementary data associated with this article can be found, in the online version

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General procedure for the synthesis of phosphoroamidates: A mixture of dialkyl phosphite (5 mmol) and CCl_4 (1 mL, 10 mmol) were added dropwise to a stirred mixture of the amine (5 mmol) in the presence of Fe_3O_4@MgO NPs (15 mol%, 0.17 g, calculated according to molecular weight of Fe_3O_4-MgO) in an open flask. The resultant mixture was stirred for 1-12 h at room temperature (see Table 2). EtOAc (50 mL) was added to reaction mixture and stirred for 10 min.

The solution was decanted and the catalyst washed three times with EtOAc (10 mL). The combined organic solutions were washed with water, dried with $CaCl_2$, and the solvent evaporated to give the crude product. Chromatography on silica gel eluting with EtOAc/*n*-hexane (4:6 to 10:1) gave the products in 52-85% yield. The recovered catalyst was washed with H_2O (50 mL) and MeOH (30 mL) and reused after drying for the next reaction. All the products are known and gave satisfactory spectral data in accordance with the assigned structures and literature reports (see NMR spectra of products in the ESI).[17e,20,21] For example: ***O,O′*-diethyl phenylamidophosphate** (**4a**)*:* White crystal; mp: 94-96 °C [Lit. mp[17] 95-96 °C]; ^{1}H-NMR (400 MHz, $CDCl_3$): 1.35 (6H, t, J_{HH} = 7.2 Hz), 4.07-4.23 (4H, m), 6.95 (1H, t, J_{HH} = 7.8 Hz), 7.02 (1H, -NH, br), 7.06 (2H, d, J_{HH} = 7.8 Hz), 7.26 (2H, m); ^{31}P-NMR (162.0 MHz, $CDCl_3$, H_3PO_4): 2.77 ppm; ^{13}C-NMR (100.6 MHz, $CDCl_3$): 16.1 (d, J_{CP} = 7.0 Hz), 62.6 (d, J_{CP} = 4.0 Hz), 117.2 (d, J_{CP} = 8.0 Hz), 121.3, 129.2, 140.0. ***O,O′*-Diethyl methyl(phenyl)amidophosphate (5)**, colorless viscous oil.[20] ^{1}H-NMR (250 MHz, $CDCl_3$): δ 1.38 (t, 6H, J = 6.5 Hz), 3.15 (d, 3H, J_{PH} = 11.2 Hz), 3.85-4.15 (4H, m), 6.95-7.30 (5H, m); ^{31}P-NMR (101.2 MHz, $CDCl_3$, 85% H_3PO_4): δ 5.99; ^{13}C-NMR (62.9 MHz, $CDCl_3$): 16.0 (d, J_{PC} = 6.9 Hz), 36.7 (d, J_{PC} = 4.4 Hz), 62.5 (d, J_{PC} = 5.0 Hz), 121.8 (d, J_{PC} = 3.8 Hz), 123.4, 128.8, 143.9.

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