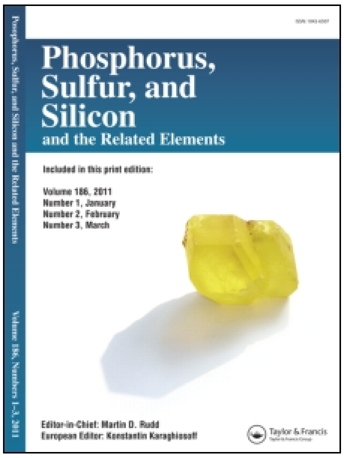
This article was downloaded by:
On: *28 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Lithium Perchlorate Diethyl Ether Solution: A Highly Efficient Media for the Abramov Reaction

Najmedin Azizi[a]; Mohammad R. Saidi[a]
[a] Sharif University of Technology, Tehran, Iran

Online publication date: 27 October 2010

To cite this Article Azizi, Najmedin and Saidi, Mohammad R.(2003) 'Lithium Perchlorate Diethyl Ether Solution: A Highly Efficient Media for the Abramov Reaction', Phosphorus, Sulfur, and Silicon and the Related Elements, 178: 6, 1255 — 1259
To link to this Article: DOI: 10.1080/10426500307904
URL: http://dx.doi.org/10.1080/10426500307904

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phosphorus, Sulfur, and Silicon, 178:1255–1259, 2003

ISSN: 1042-6507 print
DOI: 10.1080/10426500390200530

LITHIUM PERCHLORATE DIETHYL ETHER SOLUTION: A HIGHLY EFFICIENT MEDIA FOR THE ABRAMOV REACTION

Najmedin Azizi and Mohammad R. Saidi
Sharif University of Technology, Tehran, Iran

(Received October 22, 2002; accepted November 19, 2002)

The α-hydroxy phosphonates are readily prepared by treating aromatic or aliphatic aldehydes and ketones with trialkylphosphite in the presence of trimethylsilylchloride in a very short time and in almost quantitative yields.

Keywords: Abramov reaction; α-hydroxy phosphonates; lithium perchlorate

Phosphonic acids and their phosphonate derivatives are of great interest in the literature of organic chemistry due to their biological activity.[1] They are employed in synthetic operations leading to carbon-carbon bond formation[2] and as transition state analogues in the production of antibody catalyst for a wide variety of reactions.[3] α-Hydroxy phosphonates, specially enantiomerically pure α-functionalized phosphonates,[4] have been used for generating α-substituted phosphonates such as α-halophosphonates, synthesis of halosubstituted alkenes, and alkynes which are important intermediates in organic synthesis,[5,6] preparation of α-keto phosphonates,[7] synthesis of 1,2-diketons from acyl chlorides, for preparation of α-aminophosphonates and widely used for pharmaceutical applications.[8] A number of synthetic methods for the preparation of α-hyroxyphosphonates have been reported during the past two decades.[3,4,8] But these methods have the disadvantage of long reaction time or difficult conditions.

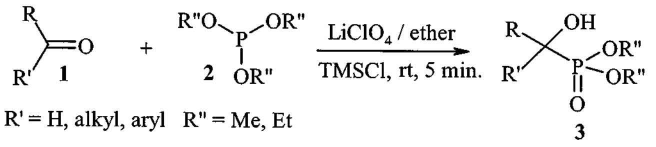
We are grateful to the Ministry of Science, Research and Technology for financial support of this research. We also thank Volkswagen-Stiftung, Federal Republic of Germany for financial support toward the purchase of equipment and chemicals.

Address correspondence to Mohammad R. Saidi, Department of Chemistry, Sharif University of Technology, PO Box 11365-9516, Tehran, Iran.

RESULTS AND DISCUSSION

During the course of our effort using a 5 M ethereal solution of lithium perchlorate, LPDE, for one-pot three-components method for aminoalkylation of aldehydes with different nucleophiles such as organolithium, organomagnesium, organosilicon, and functionalized organozinc compounds,[9] we found that the reaction of aldehydes or ketones with trialkylphosphite in the presence of trimethylsilylchloride, TMSCl, proceeded smoothly at ambient temperature to give α-hydroxy phosphonates with very high yields in a few minutes.

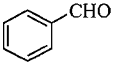
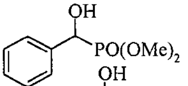
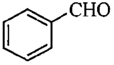
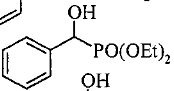
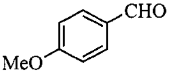
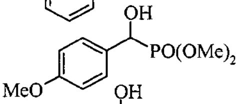
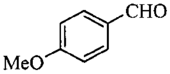
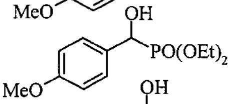
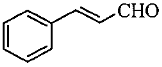
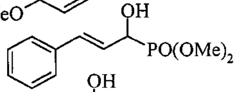
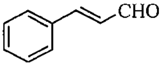
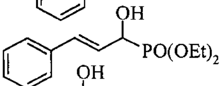
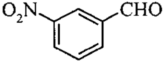
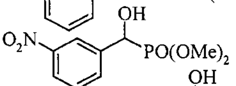
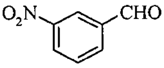
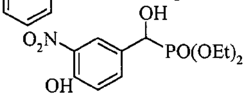
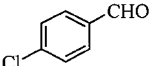
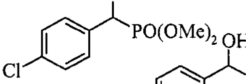
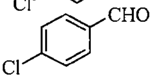
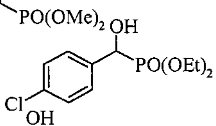
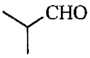
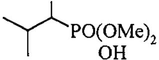
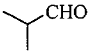
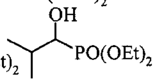
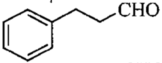
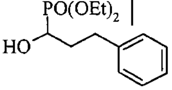
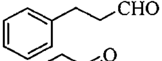
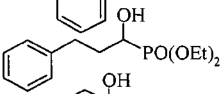
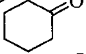
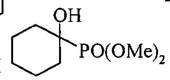
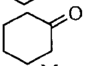
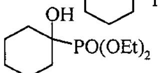
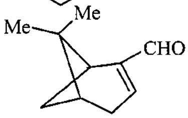
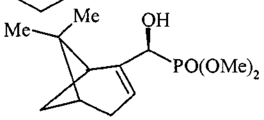
By the addition of aldehyde **1** (1.0 equiv.), to an excess of freshly distilled trialkylphosphite (1.25 equiv.) and 1 equiv. of TMSCl in a concentrated ethereal solution of lithium perchlorate, α-hyroxyphosphonate was formed within 5 min. The transformation was carried out at room temperature with easy work-up and without any by-products. This procedure has been followed for the preparation of all α-hyroxyphosphonates listed in Table I. Although the lithium perchlorate mediated aminoalkylation of enolizable aldehydes proceeds in low yields, and the aminoalkylation reaction of ketones has not been reported in ethereal solution of lithium perchlorate, this procedure can be applied for both enolizable (entry 11–14, Table I) and nonenolizable aldehydes and ketones (entry 15–16, Table I), Scheme 1. The crude products were obtained in a high purity.



SCHEME 1

By using chiral aldehyde such as (*1R*)-(-)-myrtenal, α-hyroxyphosphonate of (*1R*)-(-)-myrtenal (entry 17, Table I) was produced with the same procedure. The ^{1}H NMR spectra of the crude product showed a mixture of two diastereomers for **3s** with the ratio of 82 to18.[11] The configuration and the ratio of the major diasereomer was determined by ^{1}H NMR spectra of the crude product and comparison of the chemical shift and coupling constant of the proton attached to the carbon bearing the phosphonate group with similar compounds reported in the literature. Each diasereomer shows a doublet with different chemical shift and coupling constant. The upfield doublet was assigned to the major diasereomer (*R*, *S*)-**3**.

TABLE I α-Hydroxyphosphonates Obtained from the Abramov Reaction in Ethereal Solution of Lithium Perchlorate[a]

Entry	Aldehyde or Ketone	Product	%	Yield
1			**3a**	98
2			**3b**	95
3			**3c**	93
4			**3d**	90
5			**3e**	95
6			**3f**	95
7			**3g**	97
8			**3h**	97
9			**3i**	98
10			**3j**	95
11			**3k**	97
12			**3l**	95
13			**3m**	95
14			**3n**	95
15			**3p**	90
16			**3r**	90
17			**3s**	95

[a] Reaction time: 5 min.

EXPERIMENTAL

All products were identified with their NMR and IR spectroscopic data. The starting materials were used as received without further purification. Trimethy phosphite and triethyl phosphite were distilled before use. Lithium perchlorate was dried according to the procedure described in the literature.[9a]

General Procedure for the Preparation of α-Hyroxyphosphonates

The aldehyde (2 mmol) and 3 ml of 5 M $LiClO_4$ in diethyl ether were placed in a 25 ml flask under argon and freshly distilled trialkyl phosphite (2/5 mmol) and TMSCl (2 mmol) were added via a syringe and the mixture was stirred for 5 min. Then, water (15 ml) and dichloromethane (15 ml) were added. The organic phase was separated and washed with water, dried with Na_2SO_4, and the solvent was removed in a rotary evaporator. All products gave satisfactory spectral data in accordance to the proposed structures and with those reported in the literature.[4,8] Spectral data of the new compounds are: **3a**, ^{1}H NMR, δ_H, ($CDCl_3$, 500 MHz), 3.58 (d, 3H, $J = 10.3$ Hz), 3.63 (d, 3H, $J = 10.3$ Hz), 5.03 (d, 1H, $J = 13.2$ Hz), 6.00 (br s, OH), 7.28–7.47 (m, 5H); ^{13}C NMR, δ_C, ($CDCl_3$, 125 MHz), 53.7 (d, $J_{CP} = 7.5$ Hz), 54.2 (d, $J_{CP} = 7.5$ Hz), 69.1 (d, $J_{CP} = 164$ Hz), 128.8, 129.4, 131.1, 133.8 (d, $J_{CP} = 2.9$ Hz); IR (KBr); 3430, 1030. **3i**, IR (KBr): 3430 (br, OH), 1030 cm^{-1}; ^{1}H NMR, δ_H, ($CDCl_3$, 500 MHz), 3.60–3.69 (m, 6H), 5.09 (d, 1H, $J = 13.4$ Hz), 6.2 (br s, OH), 7.42 (d, 2H, $J = 8.5$ Hz), 7.48 (d, 2H, $J = 8.5$ Hz); ^{13}C NMR, δ_C, ($CDCl_3$, 125 MHz), 53.7 (d, $J_{CP} = 7.1$ Hz), 54.2 (d, $J_{CP} = 7.5$ Hz), 69.1 (d, $J_{CP} = 161.1$ Hz), 128.8, 129.4, 133.1 (d, $J_{CP} = 3.9$ Hz), 138.2; IR (KBr); 3423, 1253, 1030. **3p**, IR (KBr): 3430 (braod, OH), 1030 cm^{-1}; ^{1}H NMR, δ_H, ($CDCl_3$, 500 MHz), 1.14–1.74 (m, 10H), 3.66 (d, 6H, $J = 10.1$ Hz), 5.22 (br s, 1H, OH); ^{13}C NMR, δ_C, ($CDCl_3$, 125 MHz), 20.4 (d, $J_{CP} = 11.5$ Hz), 27.3, 32.0 (d, $J_{CP} = 2.7$ Hz), 53.7 (d, $J_{CP} = 7.5$ Hz), 71.0 (d, $J_{CP} = 164.2$ Hz). **3s**, White solid, mp = 98–100°C; IR (nujol): 3423 (br, OH), 1661, 1053 cm^{-1}; ^{1}H NMR, δ_H, ($CDCl_3$, 500 MHz) for the major diastereoisomer, 0.80 (s, 3H), 1.07 (d, 1H, $J = 8.3$ Hz), 1.25 (s, 3H), 2.04–2.36 (m, 5H), 3.61 (d, 3H, $J = 11.4$ Hz), 3.67 (d, 3H, $J = 11.1$ Hz) 4.28 (d, 1H, $J = 13.6$ Hz), 5.45 (br s, 1H), 5.56 (s, 1H); ^{13}C NMR, δ_C, ($CDCl_3$, 125 MHz), for the major diastereoisomer, 21.8, 26.8, 31.8, 32.2, 38.2, 40.9, 43.2, 53.3 (d, $J_{CP} = 7.3$ Hz), 53.6 (d, $J_{CP} = 7.1$ Hz), 70.3 (d, $J_{CP} = 161.7$ Hz), 120.5 (d, $J_{CP} = 12.5$ Hz), 145.3 (d, $J_{CP} = 2.6$ Hz). Anal. Calcd. for $C_{12}H_{21}O_4P$: C, 55.37; H, 8.13. Found: C, 55.65; H, 8.25.

REFERENCES

[1] B. E. Maryanoff and A. B. Reitz, *Chem. Rev.*, **89,** 863 (1989).

[2] R. Engel, *Chem. Rev*., **77,** 349 (1977).

[3] R. A. Lerner, S., J. Benkovic, and P. G. Schultz, *Science*, **252,** 659 (1991).

[4] H. Groger and B. Hammer, *Chem. Eur. J.*, **6,** 9431 (2000).

[5] a) D. F. Wiemer, *Tetrahedron*, **53,** 16609 (1997); b) F. Eymery, B. Iorga, and P. Savignac, *Tetrahedron*, **55,** 13109 (1999).

[6] K. Praveen, *Tetrahedron Lett.*, **42,** 3219 (2001).

[7] B. Iorga, F. Eymery, and P. Savignac, *Tetrahedron*, **55,** 2671 (1999).

[8] a) H. Firouzabadi, N. Iranpoor, S. Sobhani, and A. Sardarian, *Tetrahedron Lett.*, **42,** 4369 (2001); b) G. O. Olah and A.-H. Wu, *J. Org.Chem.*, **56,** 902 (1991); c) T. Jeanmaire, Y. Hervaud, and B. Boutevin, *Phosphorus, Sulfur, and Silicon*, **177,** 1137 (2002).

[9] a) M. R. Saidi, H. R. Khalaji, and J. Ipaktschi, *J. Chem. Soc., Perkin Trans*. 1, 1983 (1997); b) M. R. Saidi and H. R. Khalaji, *J. Chem. Res. (S)*, 340 (1997); c) M. R. Naimi-Jamal, M. M. Mojtahedi, and J. Ipaktschi, *Eur. J. Org. Chem.*, 1735 (2000); d) M. R. Saidi, N. Azizi, and H. Zali-Boinee, *Tetrahedron*, **57,** 6829 (2001); e) M. R. Saidi, N. Azizi, and M. R. Naimi-Jamal, *Tetrahedron Lett.*, **42,** 8111 (2001); f) N. Azizi and M. R. Saidi, *Tetrahedron Lett.*, **43,** 4305 (2002); g) M. R. Saidi, R. Najjar, and M. M. Mojtahedi, *J. Sciences, I. R. Iran*, **13,** 39 (2002).