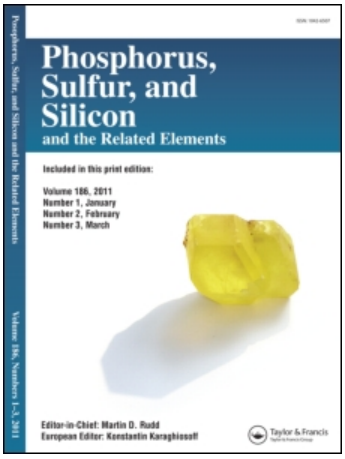
This article was downloaded by:
On: *27 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

Tributylphosphine-Catalyzed Stereoselective *O*-Vinylation of 2-Hydroxybenzaldehyde Derivatives

Ali Ramazani[a]; Vahid Azizkhani[a]; Farideh Gouranlou[b]
[a] Chemistry Department, Payam Noor University (PNU), Abhar, Zanjan, Iran [b] Chemistry Department, Malek Ashtar University of Technology, Tehran, Iran

Online publication date: 23 March 2010

To cite this Article Ramazani, Ali , Azizkhani, Vahid and Gouranlou, Farideh(2010) 'Tributylphosphine-Catalyzed Stereoselective *O*-Vinylation of 2-Hydroxybenzaldehyde Derivatives', Phosphorus, Sulfur, and Silicon and the Related Elements, 185: 4, 719 — 724
To link to this Article: DOI: 10.1080/10426500902922941
URL: http://dx.doi.org/10.1080/10426500902922941

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, 185:719–724, 2010
Copyright © Taylor & Francis Group, LLC
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500902922941

Taylor & Francis
Taylor & Francis Group

TRIBUTYLPHOSPHINE-CATALYZED STEREOSELECTIVE *O*-VINYLATION OF 2-HYDROXYBENZALDEHYDE DERIVATIVES

Ali Ramazani,[1] Vahid Azizkhani,[1] and Farideh Gouranlou[2]
[1]*Chemistry Department, Payam Noor University (PNU), Abhar, Zanjan, Iran*
[2]*Chemistry Department, Malek Ashtar University of Technology, Tehran, Iran*

Protonation of the highly reactive 1:1 intermediates, produced in the reaction between tributylphosphine and alkyl acetylenecarboxylates by 2-hydroxybenzaldehyde derivatives, leads to vinyltributylphosphonium salts, which undergo a Michael addition reaction with conjugate base to produce corresponding phosphorus ylides. The phosphorus ylides convert to electron-poor* O*-vinyl ether derivatives under reaction conditions.

Keywords Acetylenic ester; electron-poor *O*-vinyl ether; 2-hydroxybenzaldehyde; phosphorus ylide; tributylphosphine; vinyltributylphosphonium salt

Downloaded At: 16:44 27 January 2011

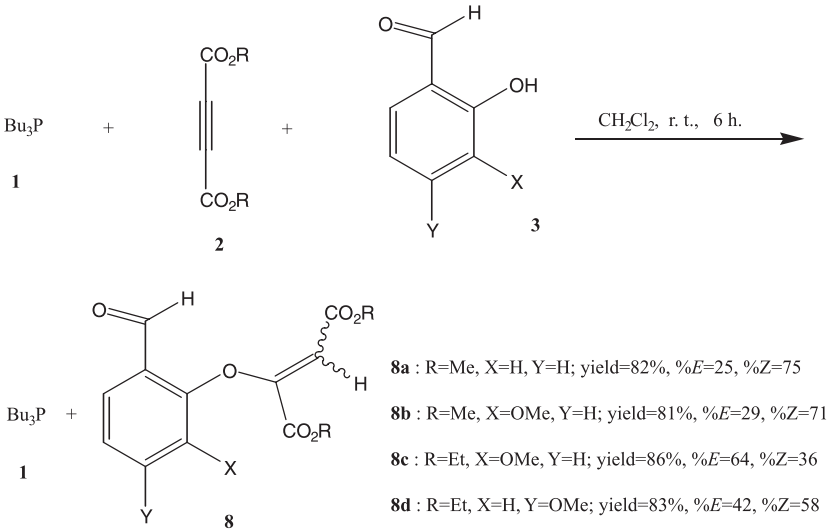
INTRODUCTION

The development of the modern chemistry of natural and physiologically active compounds would have been impossible without the phosphorus ylides.[1–16] The phosphorus ylides represent an outstanding achievement of the chemistry of the 20th century.[1–16] They have found use in a wide variety of reactions of interest to synthetic chemists.[1–16] Phosphorus ylides are important reagents in synthetic organic chemistry,[1–16] especially in the synthesis of naturally occurring products, and compounds with biological and pharmacological activity.[6] These compounds have attained great significance as widely used reagents for linking synthetic building blocks with the formation of carbon–carbon double bonds, and this has aroused much interest in the study of the synthesis, structure, and properties of P-ylides and their derivatives.[1–6]

Several methods have been developed for preparation of phosphorus ylides.[7–10] These ylides are most often prepared by the treatment of a phosphonium salt with a base. Most of the phosphonium salts are usually made from phosphine and an alkyl halide,[10–16] and they are also obtained by the Michael addition of phosphorus nucleophiles to activated olefins.[10–16] β-Additions of nucleophiles to the vinyl group of vinylic phosphonium salts leading to the formation of new alkylidenephosphoranes have attracted much attention as a very convenient and synthetically useful method in organic synthesis.[17–30] Phosphorus

Received 7 February 2009; accepted 24 March 2009.
This work was supported by the Payam Noor University (PNU), Abhar, Zanjan, Iran.
Address correspondence to Chemistry Department, Payam Noor University (PNU), P O Box 97, Abhar, Zanjan, Iran. E-mail: aliramazani@gmail.com

ylides are a class of special type of zwitterions, which bear strongly nucleophilic electron-rich carbanions. The electron distribution around the P^+–C^- bond and its consequent chemical implications had been probed and assessed through theoretical, spectroscopic, and crystallographic investigations.[30] The proton affinity of these ylides can be used as a molecular guide to assess their utility as synthetic reagents and their function as ligands in coordination and organometallic chemistry.[17,30] In the past we have established a convenient, one-pot method for preparing stabilized phosphorus ylides utilizing an in situ generation of the phosphonium salts.[18–28] Stabilized phosphorus ylides, versatile intermediates in synthetic organic chemistry, can be prepared by the novel reaction of dialkyl acetylenedicarboxylates (DAAD), triphenylphosphine (TPP), and acids such as phenols, imides, amides, enols, oximes, and alcohols.[18–28] The reaction[31] involves an intermediate formed by the 1:1 conjugate addition reaction of the TPP to DAAD, and concomitant protonation of the intermediate by an acid leads to vinyltriphenylphosphonium salts.[18–28] The salts are unstable intermediates and converted to stabilized phosphorus ylides via a Michael addition reaction.[18–28] The stabilized phosphorus ylides are able to take part in the intramolecular Wittig reactions, but they are not generally able to participate in the intermolecular Wittig reactions.[18–28] The intermolecular Wittig reactions of the ylides are observed only with highly electron-poor carbonyl groups such as indane-1,2,3-trione.[31] The ylides are converted to electron-poor alkenes via elimination of TPP in solvent-free conditions.[31] Almost all of the final products are valuable families of compounds.[31] In this article, we wish to describe a simple, one-pot method for the preparation of electron-poor *O*-vinyl ethers from tributylphosphine **1**, dialkyl acetylenedicarboxylates **2**, and 2-hydroxybenzaldehyde derivatives **3** (Scheme 1).



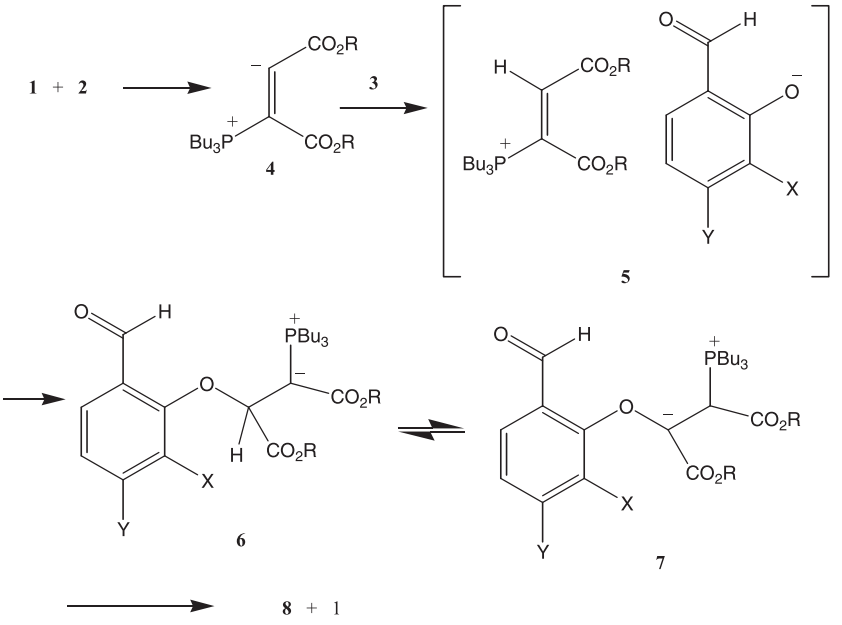
Scheme 1

RESULTS AND DISCUSSION

Tributylphosphine **1**, dialkyl acetylenedicarboxylates **2**, and 2-hydroxybenzaldehyde derivatives **3** were reacted in a 1:1:1 ratio in dichloromethane at room temperature to give

Downloaded At: 16:44 27 January 2011

electron-poor *O*-vinyl ethers **8** (Scheme 1). TLC indicated the formation of products. The reaction proceeded smoothly and cleanly under mild conditions, and no side reactions were observed. In the reaction, tributylphosphine **1** acts as catalyst (Scheme 1). Reactions are known in which an α,β -unsaturated carbonyl compound is produced from a phosphorane and a carbonyl compound such as an aldehyde or ketone.[19–21] Thus, compounds **8** may be regarded as the product of an addition–elimination reaction. Such addition–elimination products may result from an initial addition of tributylphosphine **1** to the acetylenic ester **2** and concomitant protonation of the 1:1 adduct, followed by attack of the anion of 2-hydroxybenzaldehyde derivative **3** on the β-carbon atom of the vinylphosphonium cation **5** to form intermediates **6** and **7**. Elimination of tributylphosphine **1** from intermediate **7** would lead to stereoselective formation of electron-poor *O*-vinyl ethers (**8**) in fairly high yields (Scheme 2). However, in the presence of triphenylphosphine, chromene derivatives have been reported previously.[31] The mechanism of the reaction outlined above has not been established experimentally. However, a possible explanation[19] is proposed in Scheme 2.



Scheme 2

The structure of products **8** was proved by their IR, ^{1}H NMR, and ^{13}C NMR spectral data (see the Experimental section). The NMR spectra indicated that solutions of compounds **8a**, **8b**, and **8d** ($CDCl_3$ as solvent) contain the **Z** isomer as a major product[19] that may result from the easy formation of the ***Z*** isomer to ***E*** isomer. However, in the case of **8c**, ***E*** isomer as a major product was observed. Increasing of steric strain in the Et group in comparison with Me group may be a plausible factor for the formation of ***E*** isomer, as a major product in the case of **8c**. Because of the closing of spot distances of the stereoisomers in TLC and even using simple flash column chromatography, separations of stereoisomers are not possible. The use of HPLC techniques may be suitable for the separation of them. The ratio of the stereoisomers was determined from their ^{1}H NMR spectra. The ^{1}H NMR spectrum of

Downloaded At: 16:44 27 January 2011

the major (*Z*) stereoisomer of **8a** exhibited five signals readily recognized as arising from two OMe groups [$\delta = 3.71$ and 3.76 (6 H, 2 s, 2 OCH_3)], =CH [$\delta = 6.75$ (1 H, s, =CH)], aromatic moieties [$\delta = 6.80$–8.00 (4 H, m, arom.)], and [$\delta = 10.54$ (1 H, s, aldehyde)]. The ^{13}C NMR spectrum of the major (*Z*) stereoisomer of **8a** showed 13 distinct resonances, as expected. Partial assignment of these resonances is given in the Experimental section. The ^{1}H and ^{13}C NMR signals of the minor stereoisomer (*E*) of **8a** are similar to those of the major stereoisomer (*Z*) of **8a** (see the Spectral Analysis section).[28,32]

CONCLUSION

In summary, we have found a new and efficient method for the stereoselective synthesis of electron-poor *O*-vinyl ethers (**8**) from dialkyl acetylenedicarboxylates (**2**) and 2-hydroxybenzaldehyde derivatives (**3**) in the presence of tributyphosphine (**1**) as catalyst (Scheme 1 and Scheme 2). We believe the reported method offers a simple and efficient route for the preparation of the electron-poor *O*-vinyl ethers **8** (Scheme 1). Its ease of workup and high yields make it a useful method.[33–36] Possible extensions are under investigation.

Downloaded At: 16:44 27 January 2011

EXPERIMENTAL

IR spectra were recorded on a Mattson 1000 FT-IR spectrometer. ^{1}H and ^{13}C NMR spectra were measured with a Bruker Spectrospin spectrometer at 250.0 and 62.5 MHz, respectively. The ratio of the stereoisomers was determined from their ^{1}H NMR spectra.

General Procedure for the Preparation of Electron-Poor *O*-Vinyl Ethers 8a–d

To a magnetically stirred solution of tributylphosphine **1** (0.260 mL, 1.00 mmol) and 2-hydroxybenzaldehyde derivative **3** (1.0 mmol) in CH_2Cl_2 (10 mL), a mixture of dialkyl acetylenedicarboxylate **2** (0.13 mL, 1.0 mmol) in CH_2Cl_2 (5 mL) was added dropwise at –10 °C over 15 min. The mixture was allowed to warm up to room temperature and stirred for 6 h. The solvent was removed under reduced pressure, and the viscous residue was purified by flash column chromatography (silica gel; petroleum ether:ethyl acetate, 10:1). The solvent was removed under reduced pressure to give products **8a–d**.

Dimethyl 2-(2-Formyl phenoxy)-2-butenedioate (8a)

Light yellow oil; yield: 82%.%*Z* = 75%; ^{1}H NMR ($CDCl_3$) δ_H: 3.71 and 3.76 (6 H, 2 s, 2 OCH_3); 6.75 (1 H, s, =CH); 6.80–8.00 (4 H, m, arom.); 10.54 (1 H, s, aldehyde). ^{13}C NMR ($CDCl_3$) δ_C: 52.22 and 53.32 (2 OCH_3); 115.32, 116.75, 123.75, 128.55 and 135.54 (5 CH); 125.64, 149.06 and 158.86 (3 C); 162.11 and 163.46 (2 C=O of 2 CO_2Me); 189.07 (C=O of aldehyde).%*E* = 25%; ^{1}H NMR ($CDCl_3$) δ_H: 3.67 and 3.92 (6 H, 2 s, 2 OCH_3); 5.22 (1 H, s, =CH); 6.80–8.00 (4 H, m, arom.); 10.28 (1 H, s, aldehyde). ^{13}C NMR ($CDCl_3$) δ_C: 52.02 and 53.12 (2 OCH_3); 101.63, 121.61, 126.92, 127.72 and 136.06 (5 CH); 129.06, 155.11 and 159.86 (3 C); 162.27 and 165.21 (2 C=O of 2 CO_2Me); 187.77 (C=O of aldehyde).

Dimethyl 2-(2-Formyl-6-methoxyphenoxy)-2-butenedioate (8b)

Light brown oil; yield: 81%. IR (υ_{max}, cm^{-1}): 2928 (CH); 2853 (CH); 1723 (C=O, carbonyl); 1276 (C-O).*%Z* = 71%; ^{1}H NMR ($CDCl_3$) δ_H: 3.65, 3.77 and 3.80 (9 H, 3 s, 3 OCH_3); 6.33 (1 H, s, =CH); 7.10–7.55 (3 H, m, arom.); 10.49 (1 H, s, aldehyde). ^{13}C NMR ($CDCl_3$) δ_C: 51.82, 52.99 and 56.51 (3 OCH_3); 108.57 (=CH); 118.43, 124.42 and 127.61 (3 CH, arom.); 148.07, 127.86, 149.55 and 152.05 (4 C); 162.35 and 164.02 (2 C=O of 2 CO_2Me); 189.37 (C=O of aldehyde).*%E* = 29%; ^{1}H NMR ($CDCl_3$) δ_H: 3.68, 3.91 and 3.95 (9 H, 3 s, 3 OCH_3); 5.04 (1 H, s, =CH); 7.10–7.55 (3 H, m, arom.); 10.25 (1 H, s, aldehyde). ^{13}C NMR ($CDCl_3$) δ_C: 51.90, 53.27 and 56.45 (3 OCH_3); 98.91 (=CH); 188.02 (C=O of aldehyde).

Diethyl 2-(2-Formyl-6-methoxyphenoxy)-2-butenedioate (8c)

Light brown oil; yield: 86%. IR (υ_{max}, cm^{-1}): 2928 (CH); 2853 (CH); 1730 (C=O, carbonyl); 1276 (C—O).*%Z* = 36%; ^{1}H NMR ($CDCl_3$) δ_H: 1.00–1.50 (6 H, m, 2 Me); 3.76 (3 H, s, OCH_3); 4.10–4.45 (4 H, m. OCH_2); 6.31 (1 H, s, =CH); 7.10–7.53 (3 H, m, arom.); 10.49 (1 H, s, aldehyde). ^{13}C NMR ($CDCl_3$) δ_C: 13.90 and 14.07 (2 Me of 2 Et); 56.50 (OCH_3); 60.74 and 62.17 (2 OCH_2); 108.56 (=CH); 118.36, 124.26 and 129.26 (3 CH, arom.); 127.90, 148.25, 149.74 and 152.26 (4 C); 161.78 and 163.67 (2 C=O of 2 CO_2Et); 189.43 (C=O of aldehyde).*%E* = 64%; ^{1}H NMR ($CDCl_3$) δ_H: 1.00–1.50 (6 H, m, 2 Me); 3.84 (3 H, s, OCH_3); 4.10–4.45 (4 H, m. OCH_2); 5.03 (1 H, s, =CH); 7.10–7.53 (3 H, m, arom.); 10.26 (1 H, s, aldehyde). ^{13}C NMR ($CDCl_3$) δ_C: 13.88 and 14.05 (2 Me of 2 Et); 56.42 (OCH_3); 60.80 and 62.56 (2 OCH_2); 99.18 (=CH); 118.43, 119.58 and 127.49 (3 CH, arom.); 127.84, 143.66, 151.57 and 160.14 (4 C); 162.17 and 164.96 (2 C=O of 2 CO_2Et); 188.08 (C=O of aldehyde).

Diethyl 2-(2-Formyl-5-methoxyphenoxy)-2-butenedioate (8d)

Brown oil; yield: 83%.*%Z* = 58%; ^{1}H NMR ($CDCl_3$) δ_H: 0.80–1.42 (6 H, m, 2 Me); 3.73 (3 H, s, OCH_3); 3.78–3.95 (4 H, m. OCH_2); 6.28 (1 H, s, =CH); 6.60–7.90 (3 H, m, arom.); 10.39 (1 H, s, aldehyde). ^{13}C NMR ($CDCl_3$) δ_C: 11.10 and 13.89 (2 Me of 2 Et); 52.24 (OCH_3); 55.79 and 57.32 (2 OCH_2); 101.26, 109.00, 119.55 and 129.44 (4 CH); 128.59, 148.85, 160.47 and 161.17 (4 C); 163.78 and 165.67 (2 C=O of 2 CO_2Et); 187.73 (C=O of aldehyde).*%E* = 42%; ^{1}H NMR ($CDCl_3$) δ_H: 0.80–1.42 (6 H, m, 2 Me); 3.70 (3 H, s, OCH_3); 3.78–3.95 (4 H, m. OCH_2); 5.27 (1 H, s, =CH); 6.60–7.90 (3 H, m, arom.); 10.11 (1 H, s, aldehyde). ^{13}C NMR ($CDCl_3$) δ_C: 11.10 and 13.89 (2 Me of 2 Et); 52.02 (OCH_3); 55.70 and 57.39 (2 OCH_2); 101.55, 106.44, 116.96 and 129.14 (4 CH); 125.95, 157.19, 160.15 and 161.20 (4 C); 163.11 and 165.87 (2 C=O of 2 CO_2Et); 188.08 (C=O of aldehyde).

REFERENCES

1. O. I. Kolodiazhnyi, *Russ. Chem. Rev.*, **66,** 225 (1997).
2. K. M. Pietrusiewiz and M. Zablocka, *Chem. Rev.*, **94,** 1375 (1994).
3. J. I. G. Cadogan, *Organophosphorus Reagents in Organic Synthesis*, J. I. G. Cadogon, ed. (Academic Press, New York, 1979).
4. B. E. Maryanoff and A. B. Reitz, *Chem. Rev.*, **89,** 863 (1989).

Downloaded At: 16:44 27 January 2011

5. R. A. Cherkasov and M. A. Pudovik, *Russ. Chem. Rev.*, **63,** 1019 (1994).
6. O. I. Kolodiazhnyi, *Phosphorus ylides, Chemistry and Application in Organic Synthesis* (Wiley-VCH, New York, 1999).
7. H. J. Bestmann, *Angew. Chem.*, **89,** 361 (1977).
8. A. W. Johnson, *Ylide Chemistry* (Academic Press, London, 1966).
9. G. Keglevich, H. Forintos, T. Körtvélyesi, and L. Tőke, *J. Chem. Soc., Perkin Trans.*, **1,** 26 (2002).
10. G. Keglevich, T. Körtvélyesi, H. Forintos, Á. Gy. Vaskó, V. Izvekov, and L. Tőke, *Tetrahedron*, **58,** 372 (2002).
11. G. Keglevich, T. Körtvélyesi, H. Forintos, and S. Lovas, *J. Chem. Soc., Perkin Trans.*, **2,** 1645 (2002).
12. G. Keglevich, H. Forintos, A. Ujvári, T. Imre, K. Ludányi, Z. Nagy, and L. Tőke, *J. Chem. Res.*, 432 (2004).
13. G. Keglevich, T. Körtvélyesi, A. Ujvári, and E. Dudás, *J. Organomet. Chem.*, **690,** 2497 (2005).
14. G. Keglevich, E. Dudás, M. Sipos, D. Lengyel, and K. Ludányi, *Synthesis*, 1365 (2006).
15. G. Keglevich, H. Forintos, and T. Körtvélyesi, *Current Org. Chem.*, **8,** 1245 (2004).
16. V. Nair, C. Rajesh, A. U. Vinod, S. Bindu, A. R. Sreekanth, J. S. Mathess, and L. Balagopal, *Acc. Chem. Res.*, **36,** 899 (2003).
17. W. C. Kaska, *Coord. Chem. Rev.*, **48,** 1 (1983).
18. A. Ramazani, A. Abbasi Motejadded, and E. Ahmadi, *Phosphorus, Sulfur, and Silicon*, **181,** 233 (2006), and references cited therein.
19. I. Yavari and A. Ramazani, *Synth. Commun.*, **27,** 1449 (1997).
20. A. Ramazani and A. Bodaghi, *Tetrahedron Lett.*, **41,** 567 (2000).
21. I. Yavari, A. Ramazani, and A. Yahya-Zadeh, *Synth. Commun.*, **26,** 4495 (1996).
22. I. Yavari and A. Ramazani, *Phosphorus, Sulfur, and Silicon*, **130,** 73 (1997).
23. A. Ramazani, A. Momeni-Movahhed, and F. Gouranlou, *Phosphorus, Sulfur, and Silicon*, **177,** 903 (2002).
24. A. Ramazani, B. Mohammadi, and N. Noshiranzadeh, *Phosphorus, Sulfur, and Silicon*, **178,** 545 (2003).
25. A. Ramazani, B. Mohammadi, and N. Noshiranzadeh, *Phosphorus, Sulfur, and Silicon*, **178,** 767 (2003).
26. A. Ramazani, N. Noshiranzadeh, and B. Mohammadi, *Phosphorus, Sulfur, and Silicon*, **178,** 761 (2003).
27. A. Ramazani, N. Noshiranzadeh, and B. Mohammadi, *Phosphorus, Sulfur, and Silicon*, **178,** 539 (2003).
28. A. Ramazani and H. Ahani, *Phosphorus, Sulfur, and Silicon*, **170,** 181 (2001).
29. K. Becker, *Tetrahedron*, **36,** 1717 (1980).
30. D. E. C. Cobridge, *Phosphorus: An Outline of Chemistry, Biochemistry and Uses*, 5th ed. (Elsevier, Amsterdam, 1995).
31. A. Ramazani, A. R. Kazemizadeh, E. Ahmadi, N. Noshiranzadeh, and A. Souldozi, *Curr. Org. Chem.*, **12,** 59 (2008).
32. A. Ramazani, A. R. Kazemizadeh, E. Ahmadi, K. Ślepokura, and T. Lis, *Z. Naturforsch.*, **61b,** 1128 (2006).
33. M. A. Alavi and A. Morsali, *Ultrason. Sonochem.*, **17,** 132 (2010).
34. N. Soltanzadeh and A. Morsali, *Ultrason. Sonochem.*, **17,** 139 (2010).
35. M. Mohammadi and A. Morsali, *Mater. Lett.*, **63,** 2349 (2009).
36. Z. R. Ranjbar and A. Morsali, *J. Mol. Struct.*, **936,** 206 (2009).

Downloaded At: 16:44 27 January 2011