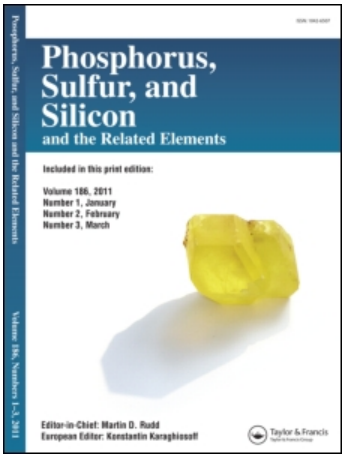


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

MICROWAVE IRRADIATION IN ORGANOPHOSPHORUS CHEMISTRY 1: THE MICHAELIS-ARBUZOV REACTION

James J. Kiddle[a]; Alison F. Gurley[a]
[a] Department of Chemistry, University of North Carolina at Wilmington, Wilmington, North Carolina

To cite this Article Kiddle, James J. and Gurley, Alison F.(2000) 'MICROWAVE IRRADIATION IN ORGANOPHOSPHORUS CHEMISTRY 1: THE MICHAELIS-ARBUZOV REACTION', Phosphorus, Sulfur, and Silicon and the Related Elements, 160: 1, 195 — 205
To link to this Article: DOI: 10.1080/10426500008043680
URL: http://dx.doi.org/10.1080/10426500008043680

Phosphorus, Sulfur and Silicon, 2000, Vol. 160, pp. 195-205
Reprints available directly from the publisher
Photocopying permitted by license only

MICROWAVE IRRADIATION IN ORGANOPHOSPHORUS CHEMISTRY 1: THE MICHAELIS-ARBUZOV REACTION

JAMES J. KIDDLE* and ALISON F. GURLEY

Department of Chemistry, University of North Carolina at Wilmington Wilmington, North Carolina 28403

(Received September 07, 1999; In final form October 21, 1999)

A diverse series of phosphonate esters have been prepared using a domestic microwave oven. The microwave enhanced Michaelis-Arbuzov reaction shows remarkable rate acceleration under microwave irradiation and allows the facile synthesis, and in certain cases easy workup, of alkyl, α-substituted and aryl phosphonates.

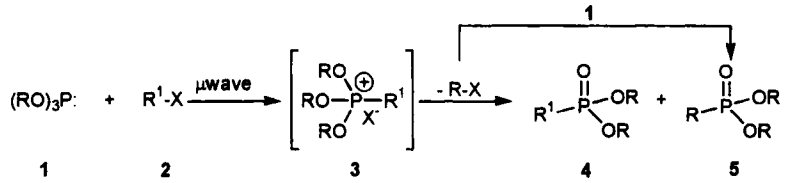
Keywords: Arbuzov reaction; alkylphosphonates; alpha-substituted phosphonates; arylphosphonates; microwave irradiation

INTRODUCTION

Phosphonates are one of several pentavalent phosphorus compounds of considerable synthetic interest due to their utility as reagents in the Wadsworth-Emmons reaction[1] and their applications in bioorganic chemistry.[2] Although several synthetic methods exist for the preparation of phosphonates, one of the most versatile is the Michaelis-Arbuzov reaction (Scheme 1).[3],[4] Unfortunately, some limitations exist in the classical Michaelis-Arbuzov reaction of a trivalent phosphorus ester and an alkyl halide. Although general limitations are imposed on the reaction since it follows an S_N2 mechanism, one condition which is extremely difficult to avoid is the length of time the reaction must remain at high temperature. The majority of Michaelis-Arbuzov reactions require the heating of the two starting materials, neat, at high temperatures for several hours and in

* Corresponding Author.

some cases for days.[4] These harsh conditions can produce low yields or side reactions, as well as limiting the utility of the reaction with sensitive starting materials.[3] Therefore, it would be synthetically useful to develop a modification of the Michaelis-Arbuzov reaction which would allow for the synthesis of phosphonates using considerably shorter times at elevated temperatures.



SCHEME 1 Michaelis-Arbuzov Reaction

Since the appearance of the first papers[5] on the application of microwave irradiation in organic synthesis, the field has seen a steady growth to the point where a variety of transformations are now possible with microwave heating.[6] The advantage to microwave assisted organic chemistry is rapid reaction heating with a significant decrease in reaction time, which often leads to cleaner reactions and thus, easier work up than seen with other forms of laboratory heating. Whereas microwave heating has been applied to a wide range of organic reactions, a survey of the literature revealed only a few papers on its application in organophosphorus chemistry. Although sparse papers have shown the application of microwave heating with a limited scope to the synthesis of carbon-carbon double bonds[7] using organophosphorus reagents, only three papers have applied this method to the synthesis of pentavalent organophosphorus compounds. In the first case, a variety of aryl phosphonates were synthesized using a complicated mixture of reagents (triethylamine, $HSiEt_3$ $PdCl_2[P(C_6H_5)_3]_2$) and diethyl phosphite under microwave irradiation to provide the target compounds in yields ranging from 0–97%.[8] The second report was the first example of the application of microwave irradiation in a Michaelis-Arbuzov reaction, which detailed the synthesis of a single phosphine oxide compound, allyldiphenylphosphine oxide.[9] Recently, a third paper on the application of microwaves in the Michaelis-Arbuzov reaction has appeared demonstrating the application of this

method in the synthesis of diethyl alkylphosphonates.[10] However, there are two obstacles to the general applicability of this method in synthetic organic chemistry. One, the reactions were all conducted using a focused microwave cavity, and two, only diethyl alkylphosphonates were synthesized. Although the method demonstrates the utility of this route to phosphonates, the microwave equipment and the limited examples of phosphite/alkyl halide combinations do not fully illustrate the application of this method for use by practicing synthetic chemists. Therefore, a comprehensive examination of the Michaelis-Arbuzov reaction under microwave irradiation seemed to warrant further study of the scope of this method applied to phosphonates of practical synthetic interest. Herein, we report the results of such a study.

RESULTS AND DISCUSSION

In an effort to develop a more convenient method for effecting the Michaelis-Arbuzov reaction, we initially undertook several studies of the conditions of this transformation in a domestic microwave oven. Consistent with previous findings,[3] reacting iodopropane with triethyl phosphite in molar ratios ranging from 1:1 to 5:1, for 5 minutes on high power, indicated an excess of alkyl halide was necessary to retard the formation of phosphonate **5**which results from the Michaelis-Arbuzov reaction of the alkyl halide eliminated from the phosphonium intermediate **3** during the reaction (Scheme 1). The latter ratio showed the best results providing the phosphonates **4** and **5** as a 4.5:1 mixture of the two compounds as determined by ^{31}P NMR. Further increases in the amount of alkyl halide failed to improve this ratio significantly. Also, in conformity with the accepted S_N2 mechanism for the reaction under microwave heating on high power, iodopropane showed complete consumption of the triethylphosphite after five minutes by ^{31}P NMR, while ^{31}P NMR of reactions of bromopropane and chloropropane under identical conditions indicated increasing amounts of unreacted triethylphosphite present which was consistent with the normal order of reactivity observed for an S_N2 mechanism.

To fully examine the scope of the microwave assisted Michaelis-Arbuzov reaction several representative alkyl halides were reacted with phosphites under microwave irradiation to afford the corresponding

phosphonates in excellent yields (Table I). The conversion of all alkyl halides to phosphonates proceeded in a straight-forward fashion, requiring heating for five minutes or less on high power at the 5:1 molar concentration in threaded Teflon capped pressure tubes.[11]

TABLE I Synthesis of Alkyl Phosphonates Under Microwave Irradiation

entry	R^1	*R*	*X*	*time (min)*	^{31}P *NMR* δ *4*[a]	*ratio 4/5*[b]	*yield (%)*
a	CH_3	CH_3	I	5	32.1	100/0	95
b	CH_3	C_2H_5	I	5	29.4	100/0	89
c	CH_3	$(CH_3)_3Si$	I	1	17.9	76/24	64
d	CH_3CH_2	CH_3	I	5	34.8	46/54	31
e	CH_3CH_2	C_2H_5	I	5	33.9	100/0	91
f	$CH_3CH_2CH_2$	C_2H_5	I	5	31.2	82/18	93
g	$CH_3CH_2CH_2$	$CH(CH_3)_2$	I	5	30.9	100/0	98
h	$CH_3CH_2CH_2CH_2$	C_2H_5	I	5	31.6	86/14	72
i	$CH_3CH_2CH_2CH_2$	$CH(CH_3)_2$	I	5	30.6	100/0	96

a. Determined in $CDCl_3$ solutions
b. Ratios were determined from crude reaction mixtures by integration of the ^{31}P NMR signals

Table II presents the results from a study to examine the synthesis of α-substituted phosphonates under microwave irradiation. In each of these reactions the 5:1 molar ratio of starting material was not essential for complete reaction of the alkyl halides **2j – 2o** which, when reacted in a 1:1 molar ratio with phosphite, produced the desired phosphonates in quantitative yields. Additionally, these phosphonates (**4j – 4o**) were easily purified by rotary evaporation to remove the eliminated alkyl halide furnishing pure products as indicated by GC/MS.

In view of the tendency of triethyl phosphite to undergo the microwave assisted Michaelis-Arbuzov reaction, it was not surprising to find that a variety of phosphites would also react under these conditions. However, as previously seen, in reactions employing triisopropyl phosphite the formation of a second phosphonate product (**5**) is not observed from the eliminated secondary alkyl halide.[4] It is also interesting to note that triphenyl phosphite did not undergo Michaelis-Arbuzov reaction under microwave irradiation conditions. This is not surprising since dealkylation of interme-

diate **3** does not readily occur for aromatic esters of trivalent phosphorus, even though the phosphonium salt is easily formed.[4] However, aryl halides can be reacted with alkyl esters of trivalent phosphorus in the presence of a suitable catalyst ($NiCl_2$) to yield the corresponding aryl phosphonates **4p – 4s** (Table III). Additionally, benzyl and cinnamyl bromides also readily undergo the microwave assisted Michaelis-Arbuzov reaction to yield the corresponding phosphonates in quantitative yields (**4t – 4w**).

TABLE II Synthesis of α-Substituted Phosphonates Under Microwave Irradiation

entry	R^1	R	X	*time (min)*[a]	^{31}P *NMR* δ *4*[b]	*ratio 4/5*[c]	*yield (%)*
j	$(CH_3CH_2O)_2P(O)CH_2$	C_2H_5	I	3	19.3	93/7	91
k	$CH_3CH_2OC(O)CH_2$	C_2H_5	Br	2	20.5	100/0	98
l	$CH_3CH_2OC(O)CHF$	C_2H_5	Br	2	8.6	100/0	94
m	$NCCH_2$	C_2H_5	Br	2	13.6	100/0	95
n	$NCCH_2$	$(CH_3)_3Si$	Br	1	–4.7	95/5	82
o	$H_2NC(O)CH_2$	C_2H_5	Br	1	21.9	100/0	94

a. 1:1 Ratio of alkyl halide and phosphite
b. Determined in $CDCl_3$ solutions
c. Ratios were determined from crude reaction mixtures by integration of the ^{31}P NMR signals

TABLE III Synthesis of Aryl Phosphonates Under Microwave Irradiation

entry	R^1	R	X	*time (min)*	^{31}P *NMR* δ *4*[a]	*ratio 4/5*[b]	*yield (%)*
p	Ph	CH_3	I	5[c]	20.3	68/32	49
q	Ph	C_2H_5	I	5[c]	19.1	100/0	86
r	Ph	$CH(CH_3)_2$	I	5[c]	16.6	100/0	83
s	Ph	$(CH_3)_3Si$	I	4[c]	4.6	91/9	78
t	$PhCH_2$	C_2H_5	Br	2	25.5	100/0	95
u	$PhCH_2$	$CH(CH_3)_2$	Br	4	24.5	100/0	93
v	$PhCH_2$	$(CH_3)_3Si$	Br	1	10.1	95/5	84
w	$PhCH{=}CHCH_2$	C_2H_5	Br	1	27.4[d]	100/0	95

a. Determined in $CDCl_3$ solutions
b. Ratios were determined from crude reaction mixtures by integration of the ^{31}P NMR signals
c. Reactions require 5 mol % $NiCl_2$ as a catalyst
d. ^{31}P NMR indicated the presence of only the *E*-isomer[25]

In conclusion, we have demonstrated that very rapid Michaelis-Arbuzov reaction can be accomplished using a variety of reagents with heating in a domestic microwave oven. In addition to the short reaction times, the phosphonate products are often produced in good to excellent yields with high selectivity and in some cases, with extremely simple work up procedures.

EXPERIMENTAL SECTION

General Methods

All reactions were conducted in a domestic microwave oven (Panasonic) at 2450 MHz on high power (1100 watts). The threaded Teflon capped pressure tubes were purchased from Ace Glass and had a capacity of approximately 15 mL, but reaction volumes were never allowed to exceed 5 mL. All reagents were purchased from Aldrich Chemical Co, except diethyl iodomethylphosphonate which was purchased from Lancaster, and used without further purification.

General Procedure for the Synthesis of Phosphonates

Halide (5 equiv. or 1 equiv.) and phosphite (1 equiv.) were added neat to the pressure tube and the threaded Teflon cap sealed finger tight. The pressure tube was placed in a beaker and was surrounded by glass wool. The glass wool not only serves to evenly heat the tube, but to absorb the reaction mixture if the tube were to shatter. The tube and beaker are then placed in the microwave oven and heated for the appropriate time on high power (1100 watts). Once the heating cycle is complete and the beaker and tube have cooled to ambient temperature, the tube is opened and the mixture purified by fractional distillation or rotary evaporation.

***Caution*! It is hazardous to rapidly heat organic reactions in closed vessels by either traditional means or with microwave irradiation. Therefore, caution should be exercised when conducting reactions of this type.**

Dimethyl methylphosphonate (4a)

^{1}H NMR δ 3.74 [d, 6H, J = 11.1 Hz], 1.47 [d, 3H, J = 17.5 Hz]; ^{31}P NMR δ 32.1. ^{1}H and ^{31}P NMR data were consistent with an authentic sample.[12]

Diethyl methylphosphonate (4b)

^{1}H NMR δ 4.10 [m, 4H], 1.46 [d, 3H, J = 17.6 Hz], 1.33 [t, 6H, *J* = 7.1 Hz]; ^{31}P NMR δ 29.4. ^{1}H and ^{31}P NMR data were consistent with an authentic sample.[12]

Bis(trimethylsilyl) methylphosphonate (4c)

^{1}H NMR δ 1.79 [d, 3H, J = 18.2], 0.39 [s, 18H]; ^{31}P NMR δ 17.9. ^{1}H and ^{31}P NMR data were consistent with a sample prepared according to a literature procedure.[13]

Dimethyl ethylphosphonate (4d)

^{1}H NMR δ 3.74 [d, 6H, J = 11.3], 1.78 [m, 2H], 1.18 [dt, 3H, *J* = 20.0, 7.3 Hz]; ^{31}P NMR δ 34.8. ^{1}H and ^{31}P NMR data were consistent with those previously reported.[14]

Diethyl ethylphosphonate (4e)

^{1}H NMR δ 4.10 [m, 4H], 1.75 [m, 2H], 1.33 [t, 6 H, J = 7.1 Hz], 1.16 [dt, 3H, *J* = 19.8, 7.4 Hz]; ^{31}P NMR δ 33.9. ^{1}H and ^{31}P NMR data were consistent with those previously reported.[15]

Diethyl propylphosphonate (4f)

^{1}H NMR δ 4.09 [m, 4H], 1.73 [m, 4H], 1.32 [t, 6H, J = 7.0 Hz], 1.05 [t, 3H, *J* = 7.0 Hz]; ^{31}P NMR δ 31.2. ^{1}H and ^{31}P NMR data were consistent with those previously reported.[15]

Diisopropyl propylphosphonate (4g)

^{1}H NMR δ 4.68 [m, 2H], 1.89 [d, 12H, J = 6.7 Hz], 1.65 [m, 4H], 1.00 [t, 3H, *J* = 7.3 Hz]; ^{31}P NMR δ 30.9. ^{1}H and ^{31}P NMR data were consistent with a sample prepared by the Michaelis-Becker reaction.[4]

Diethyl butylphosphonate (4h)

^{1}H NMR δ 4.10 [m, 4H], 1.72 [m, 2H], 1.59 [m, 2H], 1.42 [m, 2H, J = 7.4 Hz], 1.32 [t, 6H, J = 7.2 Hz], 0.93 [t, 3H, J= 7.4 Hz]; ^{31}P NMR δ 31.6. ^{1}H and ^{31}P NMR data were consistent with those previously reported.[15]

Diisopropyl butylphosphonate (4i)

^{1}H NMR δ 4.68 [m, 2H], 1.89 [d, 12H, J = 6.8 Hz], 1.70 [m, 2H], 1.57 [m, 2H], 1.37 [m, 2H], 0.91 [t, 3H, J = 7.2 Hz]; ^{31}P NMR δ 30.6. ^{1}H and ^{31}P NMR data were consistent with a sample prepared by the Michaelis-Becker reaction.[4]

Tetraethyl methylenediphosphonate (4j)

^{1}H NMR δ 4.09 [m, 8H], 2.49 [t, 2H, J = 21.3 Hz], 1.32 [t, 12H, J = 6.9 Hz]; ^{31}P NMR δ 19.3. ^{1}H and ^{31}P NMR data were consistent with an authentic sample.[12]

Triethyl phosphonoacetate (4k)

^{1}H NMR δ 4.18 [m, 6H], 2.97 [d, 2H, J = 21.6 Hz], 1.35 [t, 6H, J = 7.1 Hz], 1.29 [t, 3H, J = 6.1 Hz]; ^{31}P NMR δ 20.5. ^{1}H and ^{31}P NMR data were consistent with an authentic sample.[12]

Triethyl-2-fluoro-2-phosphonoacetate (4l)

^{1}H NMR δ 5.21 [dd, 1H, J = 47.0, 12.5 Hz], 4.25 [m, 4H], 3.43 [q, 2H, J = 7.3 Hz], 1.67 [t, 3H, J = 7.3 Hz], 1.33 [t, 6H, J = 6.7 Hz]; ^{31}P NMR δ 8.7 [d, $^2J_{P\text{-}F}$ = 71.8 Hz]. ^{1}H and ^{31}P NMR data were consistent with an authentic sample.[16]

Diethyl cyanomethylphosphonate (4m)

^{1}H NMR δ 4.24 [m, 4H], 2.89 [d, 2H, J = 21.8 Hz], 1.40 [t, 6H, J = 7.2]; ^{31}P NMR δ 13.6. ^{1}H NMR data[17] and ^{31}P NMR data[18]were consistent with those previously reported.

Bis(trimethylsilyl) cyanomethylphosphonate (4n)

^{1}H NMR δ 2.88 [d, 2H, J = 21.5 Hz], 0.40 [s, 18H]; ^{31}P NMR δ –4.7. ^{1}H NMR data was consistent with those previously reported.[19]

Diethyl acetamidephosphonate (4o)

^{1}H NMR δ 6.99 [bs, 1H], 6.28 [bs, 1H], 4.16 [m, 4H], 2.89 [d, 2H, *J* = 21.0 Hz], 1.27 [t, 6H, *J* = 7.0 Hz]; ^{31}P NMR δ 21.9. ^{1}H, ^{31}P NMR data and the mp 78–81 °C (lit. 80–82 °C) were consistent with a sample prepared according to a literature procedure.[20]

Dimethyl phenylphosphonate (4p)

^{1}H NMR δ 7.80 [m, 2H], 7.57 [t, 1H, J = 7.4 Hz], 7.45 [m, 2H], 1.48 [d, 6H, *J* = 17.5 Hz]; ^{31}P NMR δ 20.3. ^{1}H and ^{31}P NMR data were consistent with those previously reported.[21]

Diethyl phenylphosphonate (4q)

^{1}H NMR δ 7.80 [m, 2H], 7.55 [t, 1H, J = 7.4 Hz], 7.44 [m, 2H], 4.08 [m, 4H], 1.34 [t, 6H, *J* = 6.9 Hz]; ^{31}P NMR δ 19.1. ^{1}H and ^{31}P NMR data were consistent with those previously reported.[21]

Diisopropyl phenylphosphonate (4r)

^{1}H NMR δ 7.82 [m, 2H], 7.54 [m, 1H], 7.44 [m, 2H], 4.61 [m, 2H], 1.37 [d, 6H, *J* = 7.5 Hz], 1.25 [d, 6H, *J* = 7.5 Hz]; ^{31}P NMR δ 16.6 ^{1}H and ^{31}P NMR data were consistent with those previously reported.[21]

Bis(trimethylsilyl) phenylphosphonate (4s)

^{1}H NMR δ 7.71 [d, 2H, J = 7.9 Hz], 7.34 [m, 1H], 7.12 [t, 2H, *J* = 7.8 Hz], 0.37 [s, 18H]; ^{31}P NMR δ 4.7. ^{1}H and ^{31}P NMR data were consistent with a sample prepared according to a literature procedure.[22]

Diethyl benzylphosphonate (4t)

^{1}H NMR δ 7.35 [m, 5H], 4.03 [m, 4H], 3.15 [d, 2H, J = 21.6 Hz], 1.23 [t, 6H, *J* = 7.0 Hz]; ^{31}P NMR δ 25.5. ^{1}H and ^{31}P NMR data were consistent with an authentic sample.[12]

Diisopropyl benzylphosphonate (4u)

^{1}H NMR δ 7.33 [m, 5H], 4.59 [m, 2H], 3.11 [d, 2H, J = 21.6 Hz], 1.26 [d, 6H, *J* = 6.2 Hz], 1.15 [d, 6H, *J* = 6.2 Hz]; ^{31}P NMR δ 24.5. ^{1}H and ^{31}P NMR data were consistent with those previously reported.[23]

Bis(trimethylsilyl) benzylphosphonate (4v)

^{1}H NMR δ 7.30 [m, 5H], 3.24 [d, 2H, J = 16.6 Hz] 0.29 [s, 18H]; ^{31}P NMR δ 10.1. ^{1}H NMR data was consistent with those previously reported.[24]

Diethyl (E)-3-phenyl-2-propenylphosphonate (4w)

bp 267 °C (20 mmHg); ^{1}H NMR δ 7.30 [m, 5H], 6.52 [dd, 1H, *J* = 15.9, 5.2 Hz], 6.16 [m, 1H], 4.14 [m, 4H], 2.76 [ddd, 2H, *J* = 22.1, 7.4, 1.1 Hz], 1.32 [t, 6H, *J* = 7.0]; ^{31}P NMR δ 27.4. ^{1}H and ^{31}P NMR data were consistent with those previously reported.[25]

Acknowledgements

The author wishes to thank the North Carolina Biotechnology Center Institutional Development Grant Program (9610-IDG-1009) for the purchase of the Bruker 400 MHz NMR used in this study.

References

[1] B.E. Maryanoff, A.B. Reitz, *Chem. Rev.* **1989**, *89*, 863–927.
[2] For a leading reference see: R.L. Hilderbrand, *The Role of Phosphonates in Living Systems*; CRC Press: Boca Raton, FL, 1983.
[3] For a reviews see: A.K. Bhattacharya, G. Thyagarajan, *Chem. Rev.* **1981**, *81*, 415–430.
[4] R. Engel, *Synthesis of Carbon-Phosphorus Bonds*; CRC Press: Boca Raton, FL, 1988.
[5] (a) R. Gedye, F. Smith, K. Westaway, A. Humera, L. Baldisera, L. Laberge, J. Roussel, *Tetrahedron Lett.* **1986**, *27*, 279–282.
(b) R.J. Giguere, T.L. Bray, S.M. Duncan, G. Majetich, *Tetrahedron Lett.* **1986**, *27*, 4945–4948.

[6] For reviews see: (a) G. Majetich, K. Wheless, In *Microwave-Enhanced Chemistry Fundamentals, Sample Preparation, and Applications*; H.M. Kingston, S.J. Haswell, Eds., American Chemical Society: Washington D.C., 1997, pp 455–505.
(b) S. Caddick, *Tetrahedron* **1995**, *51*, 10403–10432.
[7] For use in the Wittig reaction see: (a) C.D. Xu, G.Y. Chen, X. Huang, *Chinese Chem. Lett.* **1995**, *6*, 467–468.
(b) C.D. Xu, G.Y. Chen, X. Huang, *Org. Prep. Proc.* **1995**, *27*, 559–561.
(c) C.D. Xu, G.Y. Chen, X. Huang, *Synth. Commun.* **1995**, *25*, 2229–2233.
(d) A. Spinella, T. Fortuanti, A. Soriente, *Synlett* **1997**, 93–94. For use in Wadswoth-Emmons and Knoevenagel reaction see: M. Hachiemi, M. Puciova-Sebova, S. Toma, D. Villemin, *Phosphorus Sulfur Silicon* **1996**, *113*, 131–136.
[8] D. Villemin, P-A Jaffrès, F. Siméon, *Phosphorus Sulfur Silicon* **1997**, *130*, 59–63.
[9] R.J. Giguere, B. Herberich, *Synth. Commun.* **1991**, *21*, 2197–2201.
[10] D. Villemin, F. Simeon, H. Decreus, P-A Jaffres, *Phosphorus Sulfur Silicon* **1998**, *133*, 209–213.
[11] D.R. Baghurst, D.M.P. Mingos, *J. Chem. Soc. Dalton Trans.* **1992**, 1151–1155.
[12] Authentic samples were purchased from Lancaster.
[13] R. Rabinowitz, *J. Org. Chem.* **1963**, *28*, 2975–2978.
[14] L. Evelyn. L.D. Hall, P.R. Steiner, D.H. Stokes, *Org. Mag. Reson.* **1973**, *5*, 141–145.
[15] C. Patois, P. Savignac, *Bull. Soc. Chim. Fr.* **1993**, *130*, 630–635.
[16] Authentic sample purchased from Aldrich.
[17] C.J. Wharton, R. Wrigglesworth, *J. Chem. Soc. Perkin Trans. I* **1981**, 433–436.
[18] T. Bottin-Strzalko, J. Seyden-Penne, M-J. Pouet, M-P. Simonnin, *J. Org. Chem.* **1978**, *43*, 4346–4351.
[19] T. Morita, Y. Okamoto, H. Sakurai, *Bull. Chem. Soc. Japan* **1978**, *51*, 2169–2170.
[20] A.J. Speziale, R.C. Freeman, *J. Org. Chem.* **1958**, *23*, 1883–1886.
[21] H. Duddeck, R. Lecht, *Phosphorus Sulfur Silicon* **1987**, *29*, 169–178.
[22] K. Issleib, A. Balszuweit, J. Kötz, St. Richter, R. Leutloff, *Z. Anorg. Allg. Chem.* **1985**, *529*, 151–156.
[23] D.A. Campbell, *J. Org. Chem.* **1992**, *57*, 6331–6335.
[24] T. Morita, Y. Okamoto, H. Sakurai, *Bull. Chem. Soc. Japan* **1981**, *54*, 267–273.
[25] J.J. Kiddle, J.H. Babler, *J. Org. Chem.* **1993**, *58*, 3572–3574.