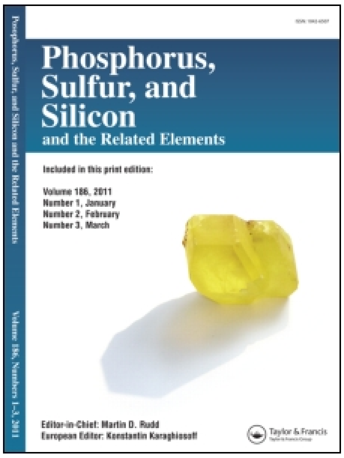


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis and Characterization of Novel Phospholane Heterocycles

Vijaya Kabra[a]; Arpana Meel[a]; Ritu Mathur[a]; Priti Kaushik[a]
[a] Department of Chemistry, University of Rajasthan, Jaipur, India

To cite this Article Kabra, Vijaya , Meel, Arpana , Mathur, Ritu and Kaushik, Priti(2007) 'Synthesis and Characterization of Novel Phospholane Heterocycles', Phosphorus, Sulfur, and Silicon and the Related Elements, 182: 6, 1403 — 1412

To link to this Article: DOI: 10.1080/10426500601161056

URL: http://dx.doi.org/10.1080/10426500601161056

Phosphorus, Sulfur, and Silicon, 182:1403–1412, 2007
Copyright © Taylor & Francis Group, LLC
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500601161056

Synthesis and Characterization of Novel Phospholane Heterocycles

Vijaya Kabra
Arpana Meel
Ritu Mathur
Priti Kaushik
Department of Chemistry, University of Rajasthan, Jaipur, India

Phospholanes are a unique class of cyclic organophosphorus compounds, which have marked applicability in medicinal science, agroscience, and catalytical chemistry. Using phosphorus trichloride as a phosphorylating agent, fourteen novel chiral cyclic organophosphorus derivatives were achieved using different 2-aminocycloimines as starting material. The resulting five-membered cyclic derivatives have shown the $ABCX_3$ *system associated with one phosphorus nucleus in* ^1H *NMR. The present study thus describes a novel synthetic strategy for phospholanes, which are analogous to cyclophosphamides.*

Keywords Bifunctional nucleophiles; cyclophosphamides; phospholane; phosphorylation

INTRODUCTION

A novel synthetic strategy for five-membered cyclophosphamide analogous has been developed using 2-aminocycloimines as starting material this piece of research work is the extension of our previous work, which has furnished different series of organophosphorus derivatives incorporating different heterocyclic nuclei.[1–5] As has been reported, cyclophosphamides and its analogous are of continuing interest based upon their chemical use in the treatment of cancer,[6] hence, this research will be of general application to scientists.

Different synthetic routes have been described in the literature, where cyclic organophosphorus compounds including dioxaphosphorinane and related phosphoramides were synthesized by Wadsworth and

Received October 30, 2006; accepted December 4, 2006.

We are highly grateful to the Head, Department of Chemistry, University of Rajasthan, for recording a number of spectra and for providing all of the necessary facilities.

Address correspondence to Vijaya Kabra, Department of Chemistry, University of Rajasthan, Jaipur, 302004, India. E-mail: sgkabra@sancharnet.in

Emmons[7] and Edmundson and Mitchell.[8] The basic idea for our recent developed synthetic route has been developed from the synthetic procedure of Mundt and Riese;[9] these scientists have used phosphorus trichloride as a phosphorylating agent, which has been reacted with bifunctional nucleophiles and thus successfully generated a variety of cyclic and heterocyclic dichlorophosphanyl compounds.[9–11] Interesting ^{31}P NMR spectrum has been described by these workers. Wink et al. using a different technology generated a new chiral auxillaries. The author has suggested the important use of these molecules in asymmetric catalysis.[12]

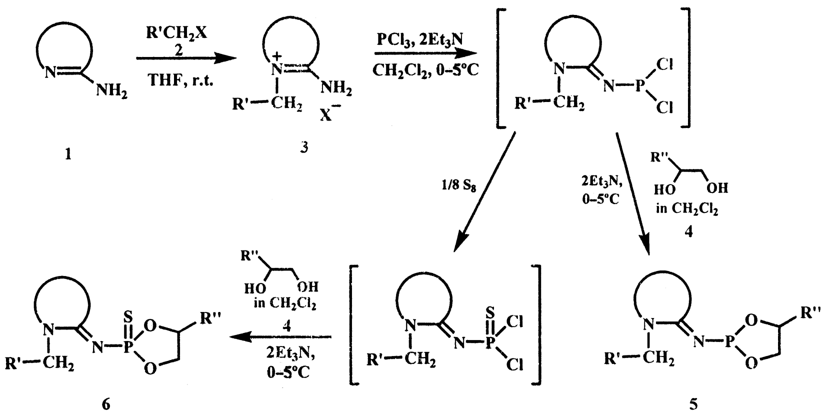
Ramirez et al.[13] has described the another synthetic route and the geometry of dioxaphosphorane. Detailed stereochemistry has also been discussed in his article.

RESULTS AND DISCUSSION

Under a nitrogen atmosphere, the N-alkyl-2-aminopyridinium/thiazolium/benzothiazolium halides (**3**) have been reacted with an equimolar amount of phosphorus trichloride and two equivalents of triethylamine at 0–5°C in methylene chloride to generate corresponding iminodichlorophosphines. These intermediates have been oxidized in situ with elemental sulfur (1/8 equivalents) at ambient temperature generating cycloiminylidenamidothiophosphoryl dichlorides, which, on substitution with racemic 1,2-propanediol/1-phenyl-1,2-ethanediol, gave corresponding phospholanes (**6a–j**) in which phosphorus was in its more stable tetracoordinated state. While in the synthesis of **5a–d**, the corresponding iminodichlorophosphines directly reacted with diol moiety (**4**) without oxidation with sulfur; thus in **5a–d**, the phosphorus was in its comparatively less stable tricoordinated state (Scheme 1).

The products were white crystalline solids with sharp melting points. All the products were characterized by ^{1} H and ^{31}P NMR techniques. The results have been reported in Table I.

Compouds **6a–j** were obtained as diastereomers in which sulfur at position 2 and methyl/phenyl at position 4 were in *trans* configuration, which has provided more stability to these molecules. The most interesting feature in ^{1} H NMR spectra of **6a**, **6c**, **6e**, **6f**, **6j**, **5b**, and **5d** was the appearance of protons from the diol component as $ABCX_3$ system associated with a phosphorus nucleus. Here 5-CH_2 and 4-H protons of the phospholane ring comprised the ABC part of the system, and 4-CH_3 group formed the X_3 part (Figure 1).

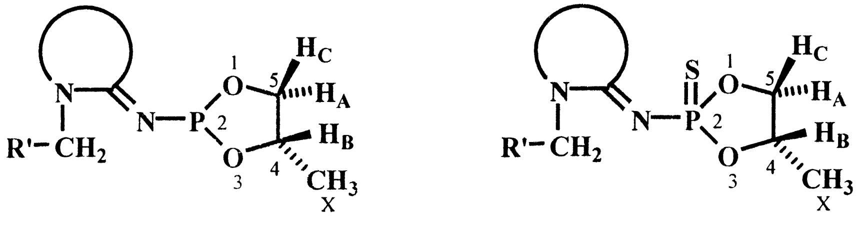


6	R'	R"	X	Nuclei
a	C_6H_5	CH_3	Br	Pyridine
b	C_6H_5	C_6H_5	Br	Pyridine
c	H	CH_3	Br	Pyridine
d	H	C_6H_5	I	Pyridine
e	CH_3	CH_3	I	Pyridine
f	H	CH_3	I	Benzothiazole
g	H	C_6H_5	I	Benzothiazole
h	C_6H_5	C_6H_5	Br	Thiazole
i	H	CH_3	I	Thiazole
j	C_6H_5	CH_3	Br	Thiazole

5	R'	R"	X	Nuclei
a	H	C_6H_5	I	Benzothiazole
b	H	CH_3	I	Benzothiazole
c	C_6H_5	C_6H_5	Br	Thiazole
d	C_6H_5	CH_3	Br	Thiazole

SCHEME 1

In the ABC part, the most upfield signal at δ 2.14–3.99 ppm corresponding to H_A was assigned to that proton of the 5-CH_2 moiety, which is *cis* to CH_3 group. This signal was a typical doublet of a doublet of a doublet due to the geminal coupling with H_C, vicinal coupling with *trans* H_B, and three bond coupling with phosphorus, but in some compounds



5

6

FIGURE 1

TABLE I Physical and Spectral Data of Compounds

Compound	Mol. Formula (Mol. Wt.)	Yield (%)	M.P. (°C)	Elemental Analysis			^{31}P NMR	^{1}H NMR δ(ppm)*J*(Hz)
				%C	%H	%N		
5a	$C_{16}H_{15}O_2N_2SP$ (330.35)	71	216	58.17 58.16	4.58 4.56	8.48 8.47	171.7	3.12–3.21 (ddd, 1H, $^2J_{AC} = 14.8$, $^3J_{CB} = 7.3$, $^3J_{PC} = 7.3$, H_C); 3.47–3.73 (ddd, 1H, $^3J_{BC} = 7.2$, H_B); 3.73 (s, 1H, H_A); 4.02 (s, 3H, NCH_3); 7.26 (dd, 1H, $^3J_{HH} = 7.5$, $^4J_{HH} = 5.2$, H-7); 7.37 (t, 2H, $^3J_{HH} = 7.5$, H-5, H-6); 7.6 (d, 1H, $^3J_{HH} = 7.5$, H-4)
5b	$C_{11}H_{13}O_2N_2SP$ (298.27)	61	Syrup	49.25 49.22	4.88 4.86	10.44 10.42	170.0	1.16–1.25 (dd, 3H, $^3J_{HB} = 6.9$, $^4J_{HC} = 5.8$, 4-CH_3); 3.42–3.51 (dd, 1H, $^2J_{AC} = 4.8$, $^3J_{PA} = 6.9$, H_A); 3.63–3.65 (d, 1H, $^3J_{BP} = 7.6$, H_B); 3.65 (s, 1H, H_C); 3.92 (s, 3H, NCH_3); 2.76 (m, 4H, Ar)
5c	$C_{18}H_{17}O_2N_2SP$ (356.39)	60	Syrup	60.66 60.63	4.81 4.80	7.86 7.82	152.6	3.46–3.49 (m, 1H, H_C); 3.78–3.92 (m, 1H, H_B); 4.15–4.29 (m, 1H, H_A); 6.47 (d, 1H, $^3J_{HH} = 7.1$, H-5); 6.7 (s, 1H, H-4); 7.26–7.43 (m, 12H, Ar)
5d	$C_{13}H_{15}O_2N_2SP$ (294.30)	50	Syrup	53.05 53.00	5.14 5.11	9.52 9.50	141.0	1.26–1.35 (dddd, 3H, $^4J_{HA} = 2.2$, $^3J_{HE} = 6.2$, $^4J_{HC} = 2.3$, $^4J_{PH} = 2.1$, 4-CH_3,); 3.05–3.20 (d, 1H, $^2J_{HC} = 2.3$, H_A); 4.51–4.60 (d, 1H, $^3J_{HC} = 6.2$, $^3J_{HP} = 4.2$, H_B); 4.68–4.75 (ddd, 1H, $^2J_{HA} = 2.3$, $^3J_{HP} = 6.0$, $^3J_{HB} = 6.2$, H_C); 5.69 (s, 2H, NCH_2); 7.26–7.38 (m, 7H, Ar)
6a	$C_{15}H_{17}O_2N_2SP$ (320.35)	71	106	56.24 56.20	5.35 5.33	8.74 8.71	47.1	1.37–1.47 (dddd, 3H, $^3J_{HB} = 6.4$, $^4J_{HC} = 2.8$, $^4J_{HC} = 2.0$; 4-CH_3); 3.40–3.49 (ddd, 1H $^2J_{AC} = 15.6$, $^3J_{AB}) = 8.2$, $^3J_{PA} = 3.2$, H_A); 3.90–4.07 (ddd, 1H, $^3J_{HA} = 6.9$, $^3J_{HC} = 6.7$, $^3J_{PH} = 10.8$, H_B); 4.67 (s, H_C); 5.39 (s, 2H, NCH_2); 6.73 (dt, 1H, $^3J_{HH} = 6.5$, $^4J_{HH} = 1.6$, H-5); 7.33 (d, 1H, $^3J_{HH} = 6.1$, H-3); 7.35–7.38 (m, 5H, Ar); 7.39 (dd, 1H, $^3J_{HH} = 6.0$); $^4J_{HH} = 1.2$, H-4); 7.67 (dd, 1H, $^3J_{HH} = 6.7$, $^4J_{HH} = 2.3$, H-6)

6b	$C_20H_{19}O_2N_2SP$ (382.42)	72	102	62.82 62,80	5.01 5.00	7.33 7.31	47.2	3.44–3.49 (dd, 1H, $^2J_{HA} = 13.6$ $^3J_{HB} = 6.9$, H_C); 3.68–3.73 (dd, 1H, $^3J_{HA} = 6.7$, $^3J_{HC} = 6.9$, H_B); 3.75–5.20 (dd, 1H, $^2J_{AC} = 3.2$, $^3J_{HH} = 6.4$, H_A); 5.29 (d, 2H, $^5J_{PH} = 6.9$, NCH_2); 6.72 (dt, 1H, $^3J_{HH} = 6.6$ $^4J_{HH} = 2.1$, H-5); 7.29–7.42 (m, 11H, H-3, Ar); 7.66 (d, 1H, $^3J_{HH} = 6.3$, H-4); 7.70 (dd, 1H, $^3J_{HH} = 6.5$, $^4J_{HH} = 2.1$, H-6)
6c	$C_9H_{13}O_2N_2SP$ (244.25)	72	105	44.26 44.22	5.36 5.34	11.47 11.46	43.4	1.15–1.28 (d, 3H, $^3J_{HB} = 6.3$ 4-CH_3); 3.37–3.51 (dddq, 1H, $^2J_{HC} = 17.5$, $^3J_{HB} = 7.6$, $^4J_{HCH} = 6.9$, $^3J_{HP} = 3.4$, H_A); 3.6–13.66 (dd, 1H, $^3J_{HCH3}$ 7.3, $^3J_{HP} = 3.1$, H_B); 3.88–3.94 (dddq, 1H, $^2J_{HA} = 14.1$, $^3J_{HB} = 6.2$, $^4J_{HCH_3}$ 4.4, $^3J_{HP} = 3.1$, H_C); 5.42 (d, 3H $^5J_{PH} = 6.7$, NCH_3); 6.71 (dt, 1H, $^3J_{HH}$, 6.4, $^3J_{HH} = 2.0$ H-5), 7.27 (d, 1H, $^3J_{HH} = 6.0$, H-3); 7.38(d, 1H, $^3J_{HH} = 6.0$, H-4); 7.68 (dd, 1H, $^3J_{HH} = 6.3$, $^4J_{HH} = 1.4$, H-6)
6d	$C_{14}H_{15}O_2N_2SP$ (306.33)	56	103	54.89 54.88	4.94 4.90	9.14 9.11	39.1	3.08–3.17 (ddd, 1H, $^2J_{HA} = 14.2$, $^3J_{HB} = 7.1$, $^3J_{HP} = 7.1$, HC); 3.49–3.64 (d, 1H, $^3J_{HA} = 7.6$, H_B); 4.05 (s, 1H, H_C); 5.53 (s,3H, NCH_3); 7.27 (m, 9H, Ar)
6e	$C_{10}H_{15}O_2N_2SP$ (258.28)	61	110	46.50 46.46	5.85 5.84	10.85 10.81	42.9	1.10–1.25 (dd, 3H, $^3J_{HB} = 6.9$, $^4J_{HH} = 6.5$, 4-CH_3); 1.41–1.45 (t, 3H, $^3J_{HH} = 6.7$, $CH_2\underline{CH_3}$); 2.14–2.24 (ddd, 1H, $^{23}J_{HC} = 16.1$, $^4J_{HCH} = 2.9$, $^3J_{HB} = 7.1$, H_A); 2.95–3.40 (m, 1H, H_B); 3.46–3.49 (d, 1H, $^3J_{HB} = 7.1$, H_C); 5.39 (s, 2H, NCH_2); 6.73 (dt, 1H, $^3J_{HH} = 6.6$, $^4J_{HH} = 1.6$, H-5); 7.27 (d, 1H, $^3J_{HH} = 6.3$, H-3); 7.36 (dd, 1H, $^3J_{HH} = 6.7$, $^4J_{HH} = 1.4$, H-4); 7.67 (dd, 1H, $^3J_{HH} = 7.6$, $^4J_{HH} = 2.1$, H-6)

(Continued on next page)

Physical and Spectral Data of Compounds *(Continued)*

Compound	Mol. Formula (Mol. Wt.)	Yield (%)	m.p. (°C)	Elemental Analysis			^{31}P NMR	^{1}H NMR δ(ppm)J(Hz)
				%C	%H	%N		
6f	$C_{11}H_{13}O_2N_2S_2P$ (300.34)	59	135	43.99 43.96	4.36 4.33	9.33 9.32	83.5	1.42 (dd, 3H, $^3J_{HB} = 6.1$, $^4J_{HC} = 2.9$, 4-CH_3); 3.53 (d, 3H, $^5J_{PH} = 2.7$, NCH_3); 3.90–3.99 (ddd, 1H, $^2J_{AC} = 16.9$, $^3J_{HB} = 8.3$, $^3J_{PA} = 4.8$, H_A); 4.33–4.47 (ddqd, 1H, $^3J_{BA} = 8.3$, $^3J_{BC} = 6.1$; $^3J_{HCH_3}$ 6.1 $^3J_{PB} = 5.8$, H_B); 4.70–4.79 (dddq, 1H, $^2J_{AC} = 16.9$, $^3J_{CB} = 6.1$, $^3J_{PC} = 6.1$, $^{43}J_{HCH_3}$ 2.9, H_C); 7.13 (dd, 1H, $^3J_{HH} = 6.3$, $^4J_{HH} = 4.9$, H-6) 7.18(d, 1H, $^3J_{HH} = 8.9$, H-7); 7.30(d, 1H, $^3J_{HH} = 7.6$, H-5); 7.44 (d, 1H, $^3J_{HH} = 7.7$, H-4)
6g	$C_{16}H_{15}O_2N_2S_2P$ (362.41)	70	Syrup	53.03 53.01	4.17 4.15	7.73 7.71	51.3	2.10–2.16 (m, 1H, H_C); 3.06–3.08 (d, 1H, $^3J_{HP} = 4.3$, H_B), 3.42 (s, 1H, H_A); 3.68 (d, 3H, $^5J_{PH} = 3.2$, NCH_3); 7.15–7.28 (m, 9H, Ar)
6h	$C_{18}H_{17}O_2N_2S_2$ (388.45)	62	70	55.66 55.62	4.41 4.40	7.21 7.20	58.2	3.00–3.06 (ddd, 1H, $^2J_{HA} = 13.4$, $^3J_{HB} = 7.1$, $^3J_{HP} = 5.6$, H_C); 3.12–3.16 (ddd, 1H, $^3J_{HC} = 7.2$, $^3J_{HA} = 7.2$, $^3J_{PH} = 4.9$, H_B); 3.44–3.51 (ddd, 1H, $^2J_{HC} = 13.9$, $^3J_{HB} = 7.1$, $^3J_{PA} = 7.1$, H_A); 5.15 (d, 2H, $^5J_{PH} = 6.9$, NCH_2); 6.59 (dd, 1H, $^3J_{HH} = 4.7$, H-5); 6.90 (dd, 1H, $^3J_{HH} = 4.7$, H-4); 7.33 (m, 12H, Ar)
6i	$C_7H_{11}O_2N_2S_2P$ (250.28)	69	Syrup	33.59 33.56	4.43 4.42	11.19 11.17	51.3	1.08–1.42 (ddd, 3H, $^3J_{HB} = 7.7$, $^4J_{HA} = 6.2$; $^4J_{HP} = 6.9$, 4-CH_3); 2.98–3.14 (m, 1H, H_A); 3.40–3.55 (q, 1H, $^3J_{HCH_3}$ 7.6, H_B); 3.76–3.96 (m, 1H, H_C); 4.39 (d, 3H, $^5J_{PH} = 3.3$, NCH_3); 6.39 (s, 1H, H-5); 7.26 (d, 1H, H-4)
6j	$C_{13}H_{15}O_2N_2S_2P$ (326.38)	66	Syrup	47.84 47.83	4.63 4.60	8.58 8.56	52.4	1.20–1.48 (ddd, 3H, $^3J_{HB} = 6.0$, $^4J_{HA} = 2.2$, $^4J_{PA} = 2.7$, 4-CH_3); 2.17 (s, 2H, NCH_2); 3.12–3.16 (dd, 1H, $^2J_{HC} = 12.4$, $^3J_{HB} = 7.3$, H_A); 3.99–4.0 (dd, 1H, $^3J_{HA} = 6.2$, $^3J_{HC} = 6.0$, H_B); 5.11 (s, 1H, H_C); 7.26 (m, 7H, Ar)

it was a typical multiplet due to four-bond coupling also with the 4-CH_3 group.

The other proton H_C of the 5-CH_2 group formed the C-part, and its signal appeared at δ 3.46–4.79 ppm and could be identified as a doublet of a doublet of a doublet of a quartet due to geminal coupling with 5-H_A, vicinal coupling with H_B, three-bond coupling with phosphorus, and four-bond coupling with *trans* 4-CH_3 protons.

The 4-H_B proton appeared at δ 2.95–4.60 ppm and formed the B part of the system. This could be identified as a doublet of a doublet of a quartet of a doublet. It showed vicinal coupling with *trans* H_A and *cis* H_C, three-bond coupling with 4-CH_3 protons, and three-bond coupling with phosphorus.

The 4-CH_3 group (the X_3 part) appeared as a multiplet and could be identified as a doublet of a doublet at δ 1.08–1.47 ppm due to three-bond coupling with H_B and long range coupling with H_C.

In **6b**, **6d**, **6g**, **5a**, **5c**, and **6h**, the phenyl ring was present in place of the methyl group, and hence less multiplicity was observed. Instead these phenyl protons appeared in the aromatic region. The effect of deshielding due to this phenyl ring on H_A, H_B, and H_C was also observed, and H_A proton was most deshielded and appeared in the most downfield region, while H_C appeared in most upfield region.

All the aromatic protons of the heterocyclic ring appeared in the expected aromatic region with expected multiplicities. The ^{31}P NMR values were observed in a particular range for tri- and tetracoordinated phosphorus depending upon the nature of the nuclei (Table I).

CONCLUSION

A novel synthetic route has been developed for the synthesis of phospholanes including the pyridine/benzothiazole/thiazole nucleus. These molecules have resemblance with cyclophosphamides and hence should be highly bioactive and a potential antitumour agent.

EXPERIMENTAL

All the reactions were performed under an inert atmosphere of dry nitrogen using freshly dried solvents and reagents. Glasswares were also placed in oven before use for 2–3 h at a high temperature. The standard syringe technique was applied to transfer dry solvents and reagents. The diols 1,2-propanediol and 1-phenyl-1,2-ethanediol used in the reactions were racemates. The synthesized products were also stored under a nitrogen atmosphere until characterization. Their melting points were determined by the capillary method. ^{31}P spectra were recorded on Jeol AL300 at 121.50 MHz (Obset 156 KHz) using 85% H_3PO_4 as an external standard, and ^{1} H spectra were recorded on Jeol AL300 at 300.4 MHz (Obset 130 KHz) using TMS as an internal standard.

2-(N-Alkylpyridin-2′-ylidenamido)-4-methyl/phenyl-1,3,2-dioxaza-phospholanes-2-sulfides (6a–e): General Procedure

To the suspension of N-alkyl-2-aminopyridinium halides (12.7 mmoles) in methylene chloride, addition of triethylamine (25.4 mmoles) and phosphorus trichloride (12.7 mmoles) was done at 0–5°C. After continuous stirring of 2–4 h at ambient temperature, sulfur powder (12.7 mmoles) was added. After continuous stirring of 24 h, triethylamine (25.4 mmoles) and racemic 1,2-propanediol (12.7 mmoles)/1-phenyl 1,2-ethanediol (12.7 mmoles) in methylene chloride was added at 0–5°C. The stirring was allowed for 3 days. After that the solvent was removed under vacuo, and residue was extracted with ether and left in a refrigerator, whereupon a white solid separated out, which was filtered and dried.

2-(N-Alkylbenzothiazol-2′-ylidenamido)-4-methyl/phenyl-1,3,2-dioxaphospholanes-2-sulfides (6f–g): General Procedure

To a well-stirred suspension of N-alkyl-2-aminobenzothiazolium halides (10.3 mmoles) in methylene chloride (20 mL), at 0–5°C was added phosphorus trichloride (10.3 mmoles) followed by dropwise addition of a solution of triethylamine (20.5 mmoles) in methylene chloride (30 mL) under a nitrogen atmosphere. After 2–4 h of stirring at room temperature, sulfur powder (10.3 mmoles) was added to it. The resulting mixture was allowed to stir for 24 h, after which triethylamine (20.5 mmoles) and racemic 1,2-propanediol/(10.3 mmoles)/1-phenyl-1, 2-ehtanediol (10.3 mmoles) in methylene chloride were added dropwise at 0–5°C, and the stirring was allowed for the next three days. After that the solvent was removed under vacuo, and the residue was extracted with ether and kept in a refrigerator (0°C), whereupon a white solid was separated out, which was filtered and dried.

2-(N-Alkylthiazol-2′-ylidenamido)-4-methyl/phenyl-1,3,2-dioxaphospholanes-2-sulfides (6h–j): General Procedure

A very similar procedure for **6a–g** was followed. To the suspension of N-alkyl-2-aminothiazolium halide (12.4 mmoles) in methylene chloride (20 mL), at 0–5°C phosphorus trichloride (12.4 mmoles) was added followed by dropwise addition of triethylamines (24.8 mmoles), the resulting mixture was allowed to stir for the next 2–4 hours. After that sulfur powder (12.4 mmoles) was added to this at room temperature, and the stirring was continued for the next 24 h. After that triethylamine (24.8 mmoles) was added followed by dropwise addition of racemic 1,2-propanediol (12.4 mmoles)/1-phenyl-1,2-ethanediol (12.4 mmoles) in methylene chloride at 01–5°C, and stirring was continued for the next 3 days, after which the solvent was removed under vacuo, and the residue was extracted with ether and left in a refrigerator (0°C). A white solid was separated out and dried under vacuo.

2-(N-Alkylbenzothiazol-2′-ylidenamido)-4-methyl/phenyl-1,2,2-dioxaphospholane (5a–b): General Procedure

To the suspension of N-alkyl-2-aminobenzothiazolium halide (10.3 mmoles) in methylene chloride (20 mL), phosphorus trichloride (10.3 mmoles) was added, followed by a dropwise addition of triethylamine (20.5 mmoles) at 0–5°C. After 24 h of stirring, racemic 1,2-propanediol (10.3 mmoles)/1-phenyl-1,2-ethanediol (10.3 mmoles) in methylene chloride was added dropwise in the presence of triethylamine (20.5 mmoles) and left for stirring for the next two days. After that the solvent was dried under vacuo and residue was extracted with ether. A white solid was separated out and dried.

2-(N-Alkylthiazol-2′-ylidenamido)-4-methyl/phenyl-1,3,2-dioxaphospholanes (5c–d): General Procedure

To a well-stirred suspension of N-alkyl-2-aminothiazolium halide (12.4 mmoles) in methylene chloride (20 mL), phosphorus trichloride (12.4 mmoles) was added, followed by a dropwise addition of triethylamine (24.8 mmoles) in methylene chloride (10 mL) at 0–5°C. The resulting mixture was allowed to stirr for 24 h: after that, racemic 1,2-propanediol (12.4 mmoles)/1-phenyl-1,2-ehtanediol (12.4 mmoles) in methylene chloride (50 mL) was added dropwise in the presence of triethylamine (24.8 mmoles) at 0–5°C, and stirring was continued for the next two days. After that, the solvent was removed under vacuo, and residue was extracted with ether and left in a refrigerator. A solid was separated out, and it was dried.

REFERENCES

[1] R. K. Bansal, V. Kabra, R. Munjal, and N. Gupta, *Indian J. Chem.*, **33B,** 992 (1994).

[2] R. K. Bansal, V. Kabra, R. Munjal, and N. Gupta, *Phosphorus, Sulfur, and Silicon*, **97,** 141 (1994).

[3] V. Kabra, N. Gupta, S. Jain, and V. Saxena, *Heteroatom Chem.*, **14,** 498 (2003).
[4] N. Gupta, V. Kabra, V. Saxena, S. Jain, and K. Bhatnagar, *Phosphorus, Sulfur, and Silicon*, **178,** 851 (2003).
[5] V. Kabra, S. Ojha, P. Kaushik, and A. Meel, *Phosphorus, Sulfur, and Silicon*, **181,** 2337 (2006).
[6] R. F. Borch and G. W. Canute, *J. Med. Chem.*, **34,** 3044 (1991).
[7] W. D. Wadsworth and W. D. Emmons, *J. Am. Chem. Soc.*, **84,** 610 (1962).
[8] R. S. Edmundson and E. W. Mitchell, *J. Chem. Soc.* (C) 752 (1970).
[9] C. Mundt and L. Riesel, *Phosphorus, Sulfur, and Silicon*, **88,** 75 (1994).
[10] C. Mundt and L. Riesel, *Phosphorus, Sulfur, and Silicon*, **88,** 169 (1994).
[11] C. Mundt and L. Riesel, *Phosphorus, Sulfur, and Silicon*, **88,** 179 (1994).
[12] D. J. Wink, T. J. Kwok, and A. Yee, *Inorg. Chem.*, **29,** 5006 (1990).
[13] F. Remirez, A. V. Patwardhan, and C. P. Smith, *J. Am. Chem. Soc.*, **30,** 2575 (1965).