Int. J. Chem. Sci. : 1 (3), 2003, 245–254

SYNTHESIS AND CHARACTERISATION OF SOME NEW 1,3,4–THIAZAPHOSPHOLES THROUGH (4 + 1) CYCLOCONDENSATION AND ITS (2 + 4) CYCLOADDITION REACTION WITH 2,3–DIMETHYL–1,3–BUTADIENE

SANJAY SHARMA

Department of Chemistry
Institute of Engineering & Technology, MIA, ALWAR 301001 (Raj.) INDIA

ABSTRACT

Three new 1,3,4–Thiazaphospholes (**4**) have been synthesized by (4 + 1) cyclocondensation of S–alkylthiocarboxamidinium halides (**3**) with PCl_3 in presence of triethylamine. These compounds have been characterized by elemental analyses, molecular weight determinations, and on the basis of ^{31}P, ^{1}H, ^{13}C–NMR studies. All the compounds are pale yellow solids, having low melting points, soluble in polar solvents and very much air sensitive. (2 + 4) Cycloaddition of 5–methoxycarbonyl–2–phenyl–1,3,4–thiazaphosphole (**4a**) with 2,3–dimethyl–1,3–butadiene has been investigated and the adduct (**6**) obtained has been characterized on the basis of ^{31}P and ^{1}H–NMR spectroscopy.

Key words : Heterophosphole, 1,3,4–Thiazaphosphole, (4 + 1) Cyclocondensation, NMR–studies, (2 + 4) Cycloaddition.

INTRODUCTION

Heterophospholes are five membered 6π – electron heterocyclic compounds having a two–coordinate, tervalent (σ^2, λ^3) phosphorus. Besides this sp^2 – hybridized phosphorus, which contributes one λ – electron to the aromatic sextet, there is atleast one more heteroatom like NR, O, S etc., which contributes two π – electrons. However, there can be more than one hetero atoms in the ring.

Chemistry of heterophosphole has developed much during last two decades[1–5]. In our research group, the phospha–analogues of indolizines[6–8], azaindolizines[9], diazaindolizines[10], pyrrolo (2.1–b) thiazoles, imidazo (2,1–b) thiazoles and their derivatives[11], pyrollo (2,1–b) , oxazoles[12], have been synthesized. For this purpose, both (4 + 1) as well as (3 + 2) cyclocondensation approaches have been used.

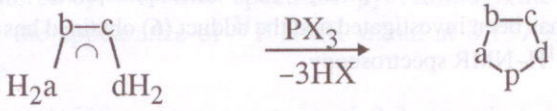
Azaphospholes represent a special subclass of heterophospholes which have atleast one three–coordinate nitrogen in the five membered ring, thus contributing 2π–electrons to the aromatic sextat. Besides three coordinate nitrogen, there may be more two–coordinate nitrogen,

*Address for Correspondence : Anukampa, C–195b, HKM Nagar, Alwar (India)

oxygen, sulphur, or even additional phosphorus atom (besides two–coordinate phosphorus in he ring). The literature survey indicates that thiazoles have been mainly synthesized from the reaction of thioamides with chloroacetaldehyde involving (3 + 2) cyclocondensation[13]. Synthesis of 2–aminothiazole involving cyclocondensation of thiourea with ethyl α–chloroacetate has been found to proceed through initial S–alkylation followed by ring clousre[14]. It has also been found that depending upon the number and positions of heteroatoms in the five membered ring, in total twenty azaphospholes have been reported so far[15]. Of these, fourteen have been synthesized through (4 + 1) cyclocondensation; 1,3,4–thiazaphosphole is one of these[2].

Two preliminary reports[2,16] pertaining to the synthesis of 1,3,4–thiazaphospholes have appeared so far in the literature. A limited number of 1,3,4–thiazaphosphole derivatives have been obtained through (4 + 1) cyclocondensation of S–alkylthicarboxamidinium halides with PCl_3. Unsubstituted 2–phenyl–1,3,4–thiazaphosphole has been prepared from (3 + 2) cyclocondensation of thiobenzamide with chloromethyldichlorophosphine[17]. The (4 + 1) cyclocondensation method involves condensation of an unsaturated four membered chain having reactive methylene, amino, hydroxy, mercapto, or phosphine groups at at the terminals with a phosphorus donating reagent like PCl_3, $P(NR_2)_3$, $P(SiMe_3)_3$. While using PCl_3, the presence of a base like triethylamine is necessary (Scheme 1).

X = Cl, NR_2, $SiMe_3$
a,d = N, CR, O, S, P
b,c = CR, N



Scheme–1

As in our research group, the (4 + 1) cyclocondensation approach has been used for the synthesis of a variety of annulated azaphospholes, it was decided to prepare some new representatives of 1,3,4–thiazaphosphole from the reaction of S–alkylthiocarboxamidinium bromide with PCl_3 involving (4 + 1) cyclocondensation. In this manner, three new 1,3,4–thiazaphospholes have been prepared and well characterized by NMR studies. In this article, we report the synthesis and characterization of these new 1,3,4–thiazaphospholes.

A survey of the literature reveals that the reactivity of 1,3,4–thiazaphosphole (**4**) has been investigated to a limited extent and some scanty reports have appeared in a review[2]. In this regard, (2 + 4) cycloaddition of one representative 5–methoxycarbonyl–2–phenyl–1,3,4–thiazaphosphole (**4a**) with 2,3–dimethyl–1,3–butadiene has been investigated and results are reported here, which reveals interesting reactivity of C = P moiety in these systems.

EXPERIMENTAL

All reactions were carried out under dry nitrogen or argon atmosphere using the Schlenk technique; NMR spectra have been recorded on a Bruker ARX300 (^{1}H NMR at 300 MHz, and

^{13}C NMR at 75.5 MHz) spectrometer or JEOL FX 90Q(^{1}H NMR at 89.55 MHz) spectrometer. The Chemical shifts refer to 85% H_3PO_4 (taking external) or TMS as an internal standard.

S–Alkylthiocarboxamidinium bromides : A general procedure

A general procedure was followed. To a solution of suitably substituted methyl bromide (0.025 mol) in THF or dry diethyl ether (60 mL), a solution of the thiocarboxamide (**1**) (0.025 mol) in THF or diethylether (10 mL) was added slowly at room temperature with continuous stirring. After stirring for 24–30 hours, colourless to cream coloured solid separated, which was filtered, washed with dietylether (2 x 30 mL) and dried under reduced pressure. The S–alkylthiocarboxamidinium bromides (**3**) thus obtained were used without further purification for NMR studies.

3a. *Yield 70%* mp 104–107; ^{1} H NMR ($CDCl_3$): δ = 1.26 (t, 3H, $^{3}J_{HH}$ = 7.1Hz, $OCH_2\underline{CH_3}$; 2.76 (s, 3H, CH_3); 4.06 (q, 2H, $^{3}J_{HH}$ = 7.1, OCH_2); 4.43 (s, 2H, SCH_2).

3b. *Yield 83%*, mp 178–180; ^{1}H NMR ($CDCl_3$): δ = 3.22 (s, 3H,CH_3); 7.9 (s, 2H, SCH_2); 7.42–8.03 (m, 5H, Ar–H)

^{13}C NMR ($CDCl_3$); δ = 16.63 (s, CH_3); 115.66 (s, SCH_2); 126.28 (s, C–i); 127.25 (s, C–o); 129.26 (s, C–*m*); 130.83 (s, C–*p*); 147.41 (s, C–NH_2); 173.03 (s, CO).

3c. *Yield 81%*, mp 107–109, ^{1}H NMR ($CDCl_3$): δ = 3.7 (s, 3H, CH_3); 4.7 (s, 2H, SCH_2); 7.42–8.03 (m, 5H, Ar–H); 10.99 and 11.70 (bs,2H, NH_2).

3d. *Yield 90%*, mp 98–100; ^{1}H NMR ($CDCl_3$): δ = 1.25 (t, 3H, ^{3} J_{HH} = 7.08, $OCH_2\underline{CH_3}$); 4.22 (q, 2H, ^{3} J_{HH} = 7.08 $O\underline{CH_2}CH_3$); 4.44 (s, 2H, SCH_2); 7.5–8.04 (m, 5H, Ar–H); 12.51 and 13.13 (bs 2H, NH_2).

3e. *Yield 67%*, mp 143–145; ^{1}H NMR ($CDCl_3$ + DMSO–d_6): δ = 3.84 (s, 2H, SCH_2), 7.37–8.13 (m, 5H, Ar–H); 10.72 (d, 2H, NH_2).

3f. *Yield 52%*, mp 140–143; ^{1}H NMR ($CDCl_3$): δ = 4.35 (d, 2H, ^{2} J_{HH} = 6.1 Hz, SCH_2); 5.36 (d, H_A, J_{AC} = 18); 5.62 (d, H_B, J_{BC} = 11); 5.89 (m, H_c); 7.7–8.41 (m, 5H, Ar–H); 12.12 (bs, 2H, NH_2).

^{13}C NMR ($CDCl_3$): δ = 36.4 (s, SCH_2); 122.16 (s, = CH_2); 127.79 (s, C–*p*); 128.88 (s, C–*m*); 129.26 (s, C–*o*); 129.80 (s, C–*i*) 135.65 (s, =CH–); 187.01 (s, C=NH_2).

3g. *Yield 72%*, mp 155–157; ^{1}H NMR ($CDCl_3$ + DMSO–d_6): δ = 7.21 (s, 5H, COPh). 7.92 (s, 2H, SCH_2); 7.73–8.31 (m, 5H, Ar–H).

3h. *Yield 63%*, mp 185–187; ^{1}H NMR ($CDCl_3$): δ = 1.47 (s, 9H, $(CH_3)_3$);7.57–8.44 (m, 7H, Ar–H and SCH_2).

3i. *Yield 46%*, mp 95–97; ^{1} H NMR ($CDCl_3$): δ = 1.40(t,3H, $^{3}J_{HH}$ = 7.1, $\underline{CH_2}CH_3$); 3.69 (q, 2H, $^{3}J_{HH}$ = 7.1; $\underline{CH_2}CH_3$) 7.5–8.17 (m, 5H, Ar–H); 10.05 (bs, 2H, NH_2).

1,3,4–Thiazaphospholes : A general procedure

A general procedure was adopted. A solution of S–alkylthiocarboxamidinium bromide (**3**) (0.008 mol) in acetonitrile (40 mL) was allowed to stir at 0–5°C under inert atmosphere of nitrogen. Then phosphorus trichloride (0.008 mol, 1.13 g, 0.7 mL) was added through side tube. After 10–15 minutes, a solution of triethylamine (0.032 mol, 3.32 g, 4.6 mL) in acetonitrile (10 mL) was added dropwise. The reaction mixture turned yellow and then to orange. After stirring for about 4–5 hours. ^{31} P–NMR signal of phosphorus trichloride (δ 220) disappeared and a new signal appeared at δ ~ 300. The solvent was removed under reduced pressure and extracted with diethyl ether (3 x 50 ml). The etheral extract was concentrated to about 10 mL and left in refrigerator, when yellow to orange solid deposited, which was separated and dried under vacuo.

(2 + 4) Cycloaddition reaction of 5–methoxycarbonyl–2–phenyl–1,3,4–thiazaphosphole (4a) with 2,3–dimethyl–1,3–butadiene

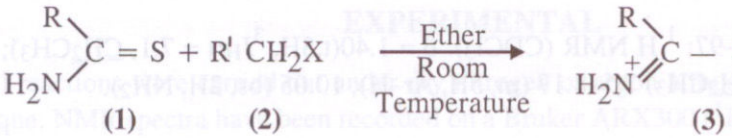
5–methoxycarbonyl–2–phenyl–1,3,4–thiazaphosphole (**4a**) (2.8 mmol, 670 mg) was dissolved in toluene (20 mL) under nitrogen atmosphere. To the stirred solution, 2,3–dimethyl–1, 3–butadiene (2.8 mmol, 232 mg, 0.3 ml) in toluene was added at room temperature. The progress of the reaction was monitored by ^{31} P NMR spectroscopy. Although the formation of cycloadduct (**5**) was indicated by the appearance of ^{31}P NMR signal at δ 137.9; the product could not be obtained in pure state.

In other experiment, **4a** (2.1 mmol, 520 mg) was reacted with 2,3–dimethyl–1,3–butadiene (2.1 mmol, 70 mg) in presence of sulfur (1 equiv.), under nitrogen atmosphere at room temperature. After stirring for four hours, a ^{31}P NMR signal at δ 132.2 accompanied by the disappearance of the ^{31}P NMR signal of **4a** indicated the formation of the (2 + 4) cycloadduct (**6**). The solvent was removed under reduced pressure and the resulting residue was stirred with hexane for two hours. After removal of the hexane solution, the solid was recrystallized from acetonitrile, when cream colored fine crystals were obtained.

RESULTS AND DISCUSSION

Synthesis of 1,3,4–Thiazaphospholes (4)

Thiobenzamide or thioacetamide (**1**) on stirring with equimolar quantity of appropriately substituted methyl halide (**2**) in diethyl ether at room temperature gives the corresponding S–alkylthiocarboxamidinium salt (**3**) in quantitative yield (Scheme 2).



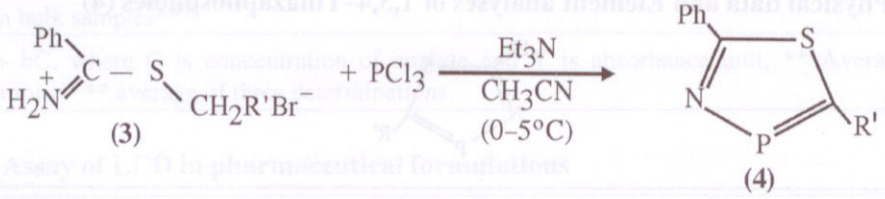
(1) (2) (3)

Compd.	R	R^1	X
3a	CH_3	COOEt	Br
3b	CH_3	COPh	Br
3c	Ph	COOMe	Br
3d	Ph	COOEt	Br
3e	Ph	CN	Br
3f	Ph	$CH = CH_2$	Br
3g	Ph	COPh	Br
3h	Ph	$COC(CH_3)_3$	Br
3i	Ph	CH_3	I

Scheme–2

The compounds (**3**) so obtained are stable, white or light brown, high melting solids, soluble in polar solvents like chloroform, methylene chloride, acetonitrile but insoluble in nonpolar solvents like diethyl ether, toluene, etc. They have been well characterized on the basis of ^1H and ^{13}C–NMR studies.

S–alkylthiocarboxamidinium bromides (**3c, 3d and 3e**) on reacting with phosphorus trichloride (1 equiv.) and triethylamine (4 equiv.) in acetonitrile at 0–5°C give 2–phenyl–1,3,4–thiazaphospholes (**4**) in quantitative yields (Scheme–3).



Scheme 3

The progress of the reaction is monitored with ^{31}P NMR spectroscopy and a downfield signal at $\delta \sim 300$ indicates formation of the desired compounds.

The corresponding reaction of S–ethoxycarbonylmethylthioacetamidinium bromide (**3a**) with phosphorus trichloride was not successful and there was no indication for the formation of the corresponding product. Reactions of other compounds (**3b, 3f, 3g, 3h, 3i**) with phosphorus trichloride are still under investigation in our laboratories.

All these compounds are pale yellow solids having low melting points, soluble in chloroform, methylene chloride and acetonitrile. They are stable under nitrogen but decompose

rapidly on exposure to air, particularly in moisture. They have been characterized on the basis of nuclear magnetic resonance (^{31}P, ^{1}H, and ^{13}C NMR) studies. The physical data and element analyses of (**4**) are given in *Table–1*. Spectral data of the synthesized 1,3,4–thiazaphospholes (**4**) are given in Table 2.

NMR–Studies

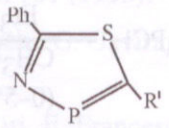
^{31}P–NMR : ^{31}P NMR chemical shift for these compounds is obtained characteristically downfield in the range δ~300–314 which compares well with that obtained in the case of other thiazaphospholes[15].

^{1}H – NMR : The structure has been confirmed by ^{1}H NMR spectra. In ^{1}H NMR spectrum of **4d**, a triplet at δ 1.32 ($^{3}J_{HH}$ = 7.3 Hz) and a quarter at δ 4.35 ($^{3}J_{HH}$ = 7.3 Hz) are obtained due to methyl and methylene protons of S–ethoxy group. In case of **4c**, a singlet at δ 3.85 is observed for OCH_3 group. The protons of the phenyl group absorb in the region δ 7.2–8.8.

^{13}C – NMR : The structure of **4d** has been confirmed unambiguously by recording its ^{13}C NMR and ^{1}H coupled ^{13}C NMR spectra.

The ring carbon C–2 gives a doublet at δ 181.6 due to its two bond coupling with phosphorus ($^{2}J_{PNC}$ = 21.2 Hz). Likewise, another downfield doublet at δ 167.7 is assigned to C–5 due to its one bond coupling with phosphorus (J_{PC} = 75.8 Hz). The observed values of the coupling constants accord well with the reported results[2]. The NMR chemical shifts of other carbons lie in the expected region. It may be mentioned here that the carbons of 2–phenyl group do not show any coupling with phosphorus.

Table 1. Physical data and Element analyses of 1,3,4–Thiazaphospholes (4)



Compd.	Colour	R	Yield (%)	M.Pt. (°C)	Mol. Formula (Mol. Wt.)	Element analyses (%)		Cal.: Found :
						C	H	N
4c	Pale yellow	CO_2Me	45	58–60	$C_{10}H_8NO_2SP$ (237.20)	50.59 50.32	3.37 3.67	5.9 5.4
4d	Light brown	CO_2Et	62	45–47	$C_{11}H_{10}NO_2SP$ (251.22)	52.6 52.2	4.01 4.45	5.57 5.48
4e	Pale yellow	CN	52	59–61	$C_9H_5N_2SP$ (204.18)	52.7 52.4	2.44 2.62	13.7 13.5

Table 2. Spectral (^{31}P, ^{1}H, ^{13}C–NMR) data of 1,3,4–Thiazaphospholes (4)

Compd.	R	^{31}P NMR δ (ppm)	^{1}H–NMR ($CDCl_3$) δ (ppm), J (Hz)	^{13}C NMR, δ (ppm), J(Hz)
4c	CO_2Me	301.1	3.85 (s. 3H, OCH_3); 7.5–8.71 (m, 5H, Ph)	—
4d	CO_2Et	300.2	1.32(t, 3H, $3J_{HH}$ = 7.3, $OCH_2\underline{CH_3}$); 4.35 (q.2H, $3J_{HH}$ = 7.3, OCH_2); 7.2–8.2 (m, 5H, Ph)	181.6(dt, $2J_{PNC}$=21.2, $3J_{CCCH}$ = 4.4, C–2); 167.7 (d, $1J^{PC}$ = 75.8, C–5); 139.0 (dtt, 3 J_{PNCC} = 7.5, $3J_{CCCH}$ = 7.1, $2J_{CH}$ = 2.1, C–i); 127.6 (ddddd, $1J_{CH}$ = 161.1, $3J_{CCCH}$ = 5.9, $4J_{PNCCC}$ = 1.2.2J_{CCH} < 1.0.C–o); 129.0 (dddd, $1J_{CH}$ = 161.9, $3J_{CCCH}$ = 5.4, $2J_{CCH}$ = 1.3, $2J_{CCH}$ = 7.4, $2J_{CCH}$ = 1.3. C–m); 131.5 (dtt. $1J_{CH}$ = 161.7, $3J_{CCCH}$ = 7.4, $2J_{CCH}$<1.0, C–p); 162.9 (dt, $2J_{PCC}$ = 21.2, $3J_{COCH}$ = 3.2, $\underline{C}OOC_2H_5$); 61.8 (tq.$1J_{CH}$ = 148.1, $2J_{CCH}$ = 4.4, $COO\underline{C}H_2CH_3$); 14.1 (qt, $1J_{CH}$ = 127.2, $2J_{CCH}$ = 2.6, $COOCH_2\underline{C}H_3$).
4e	CN	311.9	7.4–8.3 (m, 5H, Ph)	—

(2 + 4) Cycloaddition reaction of 5–methoxycarbonyl–2–phenyl–1,3,4–thiazaphosphole (4a) with 2,3–dimethyl–1,3–butadiene :

PM3–calculations of differently substituted 1,3,4–thiazaphospholes and 2,3–dimethyl–1,3–butadiene have been carried out and the energies of their frontier molecular orbitals are given in Table 3.

Table 3. Energies of Frontier Molecular Orbital of 1,3,4–Thiazaphospholes (4) and 2,3–Dimethyl–1,3–butadiene

Compd.	4a	4b	4c	2,3–Dimethyl–1,3–butadiene
HOMO (eV.)	–9.31	–9.34	–9.26	–9.21
LUMO (eV)	–1.97	–1.86	–2.03	0.34

It may be noted that the energy difference between the HOMO of 2,3–dimethyl–1, 3–butadiene and LUMO of 5–methoxycarbonyl–2–phenyl–1,3,4–thiazaphosphole (**4a**) is 7.24 eV, which is much below the limit of 8 eV and hence, a possibility of a successful (2 + 4) cycloaddition between them could be predicted. It is shown diagrammatically in Figure 1.

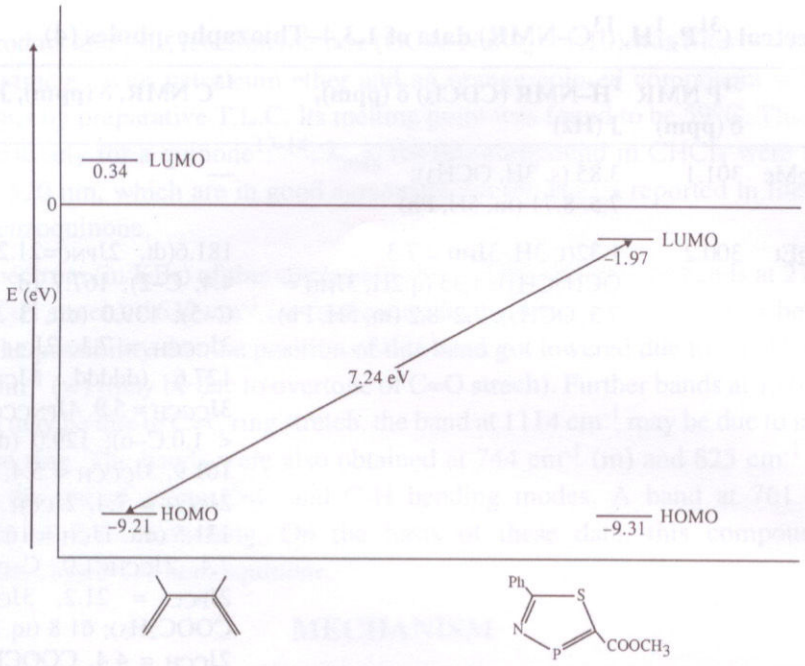
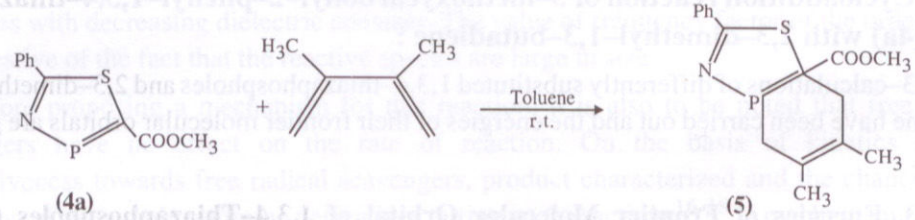


Fig. 1 Interaction of frontier molecular orbitals of 2,3–dimethyl–1, 3–butadiene and 5–methoxycarbonyl–2–phenyl–1,3,4–thiazaphosphole (4a)

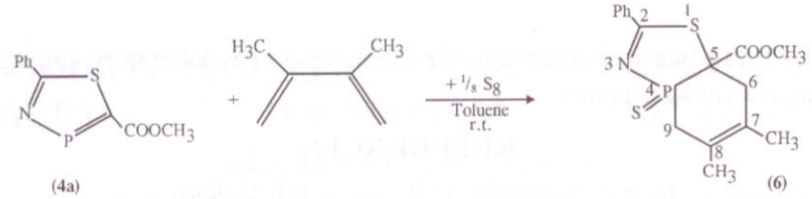
5–Methoxycarbonyl–2–phenyl–1,3,4–thiazaphosphole (**4a**) reacts with 2,3–dimethyl–1,3–butadiene (1 equiv.) in toluene at room temperature to give (2 + 4) cycloadduct (**5**).



Scheme 4

The progress of the reaction is monitored by ^{31}P NMR spectroscopy. After about two hours stirring, three ^{31}P signals are observed at δ 137.9, 96.38 and 68.25. On further stirring, it is found that the reaction is not clean. In view of this, the reaction of **4a** with 2,3–dimethyl–1, 3–butadiene was carried out in the presence of sulfur.

On stirring 5–methoxycarbonyl–2–phenyl–1, 3, 4–thizaphosphole (**4a**) with 2,3–dimethyl–1,3–butadiene (1 equiv.) and sulfur (1 equiv.) in toluene at r.t., a stable white product (**6**) is obtained. The structure of cycloadduct (**6**) has been elucidated on the basis of ^{31}P and ^{1}H NMR spectroscopy.



Scheme 5

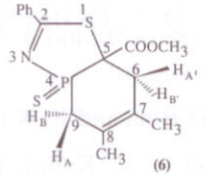
^{31}P NMR : In ^{31}P NMR spectrum, of **(6)** a signal at δ 132.2 is observed, which is characteristic of the four coordinate phosphorus[18].

^{1}H NMR : In ^{1}H NMR spectrum of **(6)**, the methylene protons at C–6 and C–9 constitute an ABX system (X being phosphorus).

Protons of 9–CH_2 group give two sets of doublet centered at δ 2.65 and δ 3.01. The protons H_A can be assigned the double doublet at δ 2.65 ($2J_{HCH}$ = 15.5 (J_{AB}) and $2J_{PCH}$ = 2.5 (J_{AX}), while the other double doublet at δ 3.01 is due to H_B ($2J_{HCH}$ = 15.5 (J_{AB}) and $2J_{PCH}$ = 28.0 (J_{AX}).

Similarly, 6–CH_2 constituting an ABX system gives two sets of double doublets centered at δ 3.07 and δ 3.21. The proton H_A is assigned the double doublet at δ 3.07 and the H_B give another double doublet at δ 3.21. The 7– and 8–CH_3 groups give signals at δ 1.89 and δ 1.75, respectively. Aromatic protons absorb in the expected region of δ 7.1–8.0. The chemical shifts of different protons and their assignments are given in the Table 4.

Table 4. Physical and Spectral (^{31}P and ^{1}H NMR) data of the Cycloadduct (6)



Compd.	Yield (%)	m.p. (°C)	^{31}P NMR δ (ppm)	^{1}H NMR ($CDCl_3$) δ (ppm), J(Hz)
6	45	80–82	132.2	1.75 (s,3H,8–CH_3), 1.89(s, 3H, 7–CH_3), 2.65 (dd, 1H, $2J_{HCH}$ = 15.5 (J_{AB}), $2J_{PCH}$ = 2.5 (J_{AX}), 9–H_A), 3.01 (dd, 1H, $2J_{HCH}$ = 15.5 (J_{AB}), $2J_{PCH}$ = 28.0 (J_{BX}), 9–H_B), 3.07 (dd, 1H, $2J_{HCH}$ = 13.9 ($J_{A'B'}$), $3J_{PCCH}$ = 13.9 ($J_{B'X}$), 6–$H_{B'}$), 3.21 (dd, 1H, $2J_{HCH}$ = 13.9 ($J_{A'B'}$), $3J_{PCCH}$ = 4.9 ($J_{A'X}$), 6–$H_{A'}$), 4.43 (s, 3H, OCH_3), 7.1–8.0 (m, 5H, Ar–H).

ACKNOWLEDGEMENT

The author is heartily thankful to Prof. R.K. Bansal, Professor, Department of Chemistry, University of Rajasthan, Jaipur (Raj.); for guidance and motivation during the course of this

research work. This paper is dedicated to the memories of my laboratory colleague Late Dr. Anushka Surana, a young scientist.

REFERENCES

1. A. Schimidpeter : In A.R. Katritzky, C.W. Rees, E.F.V. Seriven (Eds.), *Comprehensive Heterocyclic Chemistry II* Chaps. 3.15, 3.16 and 4.22, Pergamon Press, Oxford (1996).
2. A. Schmidpeter and K. Karaghiosoff : in M. Regitz and O.J. Scherer (Eds), *Multiple Bonds and Low Coordination in Phosphorus Chemistry* : Thieme, Stuttgart, (1990) p.258.
3. A. Schmidpeter and K. Karaghiosoff : In H.W. Roesky (Ed.), Rings, *Clusters and Polymers of Main Group and Transition Elements*, Elsevier, Amsterdam, (1989) p.307.
4. A. Schmidpeter and K. Karaghiosoff, *Nachr. Chem. Tech. Lab.*, **33**,793 (1985).
5. R. K. Bansal, K. Karaghiosoff and A. Schmidpeter, *Tetrahedron*, **50**, 7675 (1994).
6. R. K. Bansal, K. Karaghiosoff, N. Gupta, A. Schmidpeter and C. Spindler, *Chem. Ber.* **124**, 475 (1991).
7. R. K. Bansal, N. Gupta, V. Kabra, C. Spindler, K. Karaghiosoff and A. Schmidpeter, *Hetroatom Chem.*, **3**, 259 (1992).
8. N. Gupta, C. B. Jain, J. Heinicke, N. Bhartiya, R. K. Bansal and P. G. Jones, *Heteroatom Chem.*, **9**, 333 (1998).
9. K. Karaghiosoff, R. K. Bansal and N. Gupta, *Z. Naturforsch*, **47B**, 373 (1982).
10. R. K. Bansal, N. Gandhi, K. Karaghiosoff and A. Schmidpeter, Z. Naturforsch, **50b**, 558 (1995).
11. R. K. Bansal, R. Mahnot, D. C. Sharma and K. Karaghiosoff, *Synthesis*, 267 (1992).
12. R. K. Bansal, C. B. Jain, N. Gupta, V. Kabra, K. Karaghiosoff and A. Schmidpeter, *Phosphorus, Sulfur, Silicon and Relat. Elem.*, **86**, 139 (1994).
13. J.V. Metzger (Ed), Heterocyclic Compounds, Vol. **34**, Part 1, Thiazoles and its Derivatives, John Wiley (1979).
14. A. Schmidpeter, R. K. Bansal, K. Karaghiosoff, F. Steinmuller and C. Spindler, *Phosphorus, Sulfur and Silicon*, **49/50**, 349 (1990).
15. M. Robba and R. C. Moreau, *Ann. Pharm. Franc.* **22**, 14 (1964).
16. A. Schmidpeter, K. Karaghiosoff, C. Cleve and D. Schomburg, *Angew. Chem. Int. Ed. Engl.*, **24**, 123, (1985).
17. K. Karaghiosoff, C. Cleve and A. Schmidpeter; *Phosphorus Sulfur*, **28**, 289 (1986)
18. H. R. Hudson, K. B. Dillon and B. J. Walkar in *Handbook of Phosphorus*–31, *Nuclear Magnetic Resonance Data*, J.C. Tebby (Ed.) CRC Press, (1999) p. 181

Accepted : 4.8.2003