REACTION OF 1,3- AND 1,4-BIS (1,3,4-OXADIAZOLE-5(3H)-THIONE-2-YL) BENZENES WITH ARYL ALDEHYDES

Mahmoud Al-Talib, Sameer Bataineh and Hasan Tashtoush *

Department Of Chemistry, Yarmouk University, Irbid – JORDAN

Abstract: 1,3- and 1,4-bis (1,3,4-oxadiazole-5(4H)-thione-2-yl) benzenes 2m,p, readily react with aryl aldehydes to give 1,3- and 1,4- benzene dicarboxylic acid bis (arylmethylene)dihydrazides 4m(a-e) and 4p(a-e). A mechanism was proposed.

Introduction

A rapidly growing interest in the synthesis of 1,3,4-oxadiazole-5 (4H)-thione derivatives has recently been encountered, this is due to their wide range spectrum of biological activities, and an increasing variety of uses (1-5). The conventional method for the synthesis of 1,3,4-oxadiazole-2 (3H)-thiones consists in the reaction of acid hydrazides with carbon disulfide in ethanolic sodium hydroxide solution (6,7). Only a few reports can be found in the literature describing syntheses and reactions of molecules containing two 1,3,4-oxadiazole-2 (3H)-thione moieties (8). Here we report the reaction of the title heterocycles with aryl aldehydes.

Experimental

Melting points are determined on an electrothermal-digital apparatus and are uncorrected. ^{1}H- and ^{13}C-NMR spectra were recorded on Brucker WP 80-SY, WM- 250 and AC-250 spectrometers in $CDCl_3$ or d^6-DMSO with tetramethylsilane as an internal standard. Infrared spectra were recorded on a Perkin Elmer FT IR SP-2000 spectrometer as KBr pellets. Mass spectra were determined on a double focusing VG 7070E mass spectrometer. Elemental analyses were performed at M.H.W. laboratories, Phoenix, Arizona, USA.

Materials

1,3- and 1,4-Bis (1,3,4-oxadiazol-5 (3H) thione-2-yl) benzene were prepared following literature procedure (9). Chemicals were purchased from Aldrich and Fluka and used without further purification.

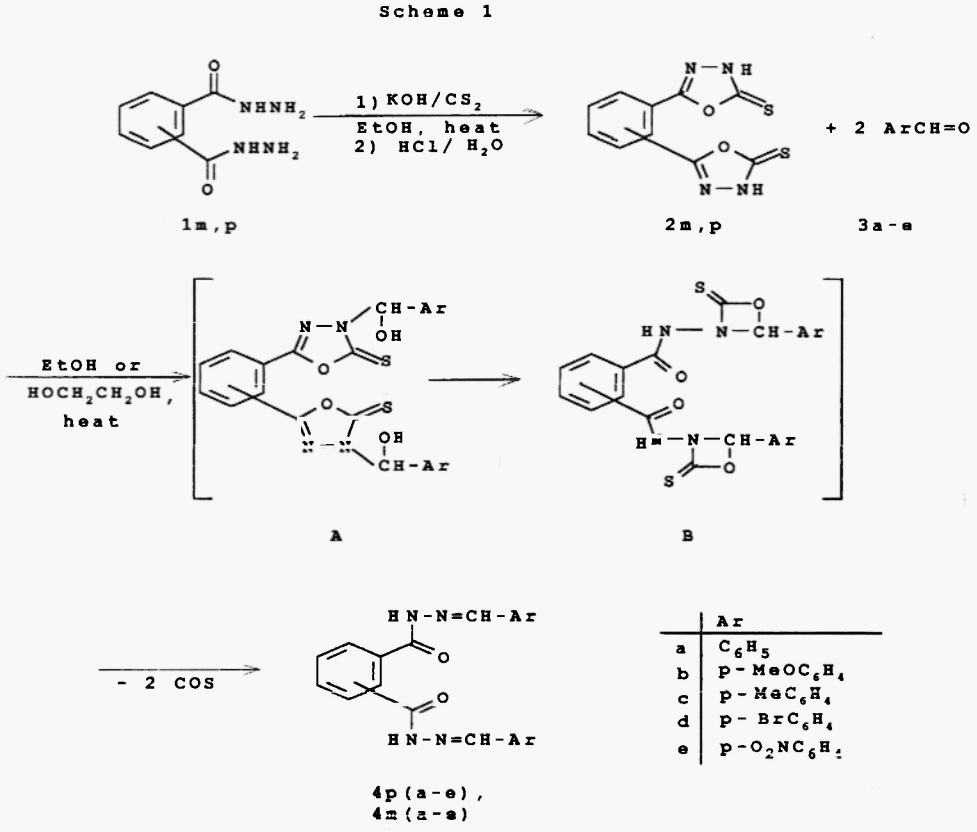
General procedure for the preparation of compounds 4.

A solution of precursor 2p (3.6 mmol) and the appropriate aryl aldehyde 3a-e (7.2 mmol) in absolute ethanol (50 ml) was heated under reflux for 12 hours. The solid was filtered and recrystallized from dimethylsulfoxide / water (1/4). The reactions of 2m with 3a-e were carried out in ethylene glycol under reflux. Products were recrystallized from tetrahydrofuran. Tables 1 and 2 include the physical and spectroscopic properties of these compounds.

Results and Discussion

Compounds 2m,p react with two equivalents of aryl aldehydes 3a-e to give the dihydrazides 4m(a-e) and 4p(a-e), (Scheme 1). The reactions of 2m were carried in boiling ethylene glycol. The formation of products 4 involves the extrusion of COS from each oxadiazole ring. Such thermal fragmentation is not unusual in heterocylic chemistry (8). The reaction is believed to proceed as shown in scheme 1. Condensation of compounds 2 with aryl aldehydes gives the condensation intermediate A. Nucleophilic attack of the hydroxyl group on the thiocarbonyl group results in ring transformation to intermediates B, which eliminate two COS units to give the final products 4.

Scheme 1



The structures of compounds 4m(a-e) and 4p(a-e) were confirmed spectroscopically and by elemental analyses (Tables 1 and 2). The infrared spectra show broad absorption in the range of 3252 – 3204 cm^{-1}, which are assigned to the N-H stretching vibration. The strong absorptions at 1643 – 1646 cm^{-1} are assigned to the C=O groups and absorption bands at 1580 – 1605 cm^{-1} to the C=N groups. In ^{13}C-NMR spectra the signal located at δ 163.1-164.1 ppm is assigned to the carbonyl groups.

The mass spectra show peaks for the molecular ion $[M]^+$. The main fragmentation proceeds through McLaffarty's rearrangement with the loss of two units of aryl nitrils (m/z = 164), other fragmentation's are shown in Table 2.

It is worth mentioning that the reaction of 1,3,4-oxadiazole-2 (3H)-thione derivatives with formaldehyde in the presence of arylamines or alkylamine has recently been reported to give exclusively the corresponding Mannich bases (10, 11). The 1,3,4-oxadiazole moiety remains intact under these conditions.

Table 1: Melting points, Yields, IR and ^{1}H-NMR spectral data of compounds 4.

Compound No.[a]	M.P (C°)	Yield (%)	IR(cm^{-1}) KBr disc	^{1}H-NMR d^6-DMSO/TMS δ(ppm). J(Hz)
4ma	b	53	3233. 1646. 1600	11.57(bs. 2H. NH); 8.40(s. 2H. CH); 8.02(s. 4H. Ar): 7.72-7.69(m. 6H. Ar); 7.46-7.42(m. 6H. Ar)
4mb	b	65	3252. 1643 1600	11.58(bs. 2H. NH); 8.42(s. 2H. CH); 8.00(s. 4H. Ar); 7.66(d. J=8.7. 4H. Ar); 7.01(d. J=8.7. 4H. Ar)
4mc	b	61	3252. 1646 1605	11.17(bs. 2H. NH); 8.44(s. 2H. CH); 7.97(s. 4H. Ar); 7.57(d. J=8.1. 4H. Ar); 7.23(d. J=7.9. 4H. Ar); 2.33(s. 6H. CH_3)
4md	b	61	3214. 1646 1600	11.44(bs. 2H. NH); 8.46(s. 2H. CH); 7.98(s. 4H. Ar); 7.61(s, 8H, Ar)
4me	b	69	3204. 1646 1580	12.11(bs, 2H, NH); 8.57(s, 2H. CH); 8.05(s, 4H, Ar); 8.30(d, J=8.7, 4H, Ar);7.97(d, J=8.7, 4H, Ar)
4pa	258-9	55	3194, 1652 1587	12.02(bs, 2H, NH); 8.51(s, 2H, CH); 8.50-7.44(m 14H, Ar)
4pb	254-5	65	3194, 1642 1603	11.89(bs, 2H, NH); 8.44(s, 2H, CH); 8.53-7.66(m. 4H, Ar); 7.72(d, J=8.6, 4H. Ar); 7.04(d, J=8.6, 4H, Ar); 3.83(s, 6H, CH_3)
4pc	288-9	57	3184, 1647 1605	11.96(bs, 2H, NH); 8.47(s, 2H, CH); 8.47-7.61(m, 4H, Ar); 7.66(d, J=7.7, 4H. Ar); 7.29(d, J=7.8, 4H, Ar); 2.36(s, 6H, CH_3)
4pd	296-7	60	3194, 1647 1605	12.10(bs, 2H, NH); 8.47(s, 2H, CH); 8.47-7.70(m, 4H, Ar); 7.70(s, 8H, Ar)
4pe	185-7	73	3194, 1657 1611	12.33(bs, 2H, NH); 8.58(s, 2H, CH); 8.50-7.71(m, 12H. Ar)

a) All compounds gave correct CHN-elemental analyses.
b) Decomposition above 300 °C.

Table 2: ^{13}C-NMR and Mass spectral data for compounds 4.

Compd No.	^{13}C-NMR ($CDCl_3$/TMS), δ(ppm)	MS(rel. int. %)
4ma	163.7, 148.1, 163.6, 130.0 128.7, 127.8, 124.1	370(12.5), 251(100), 164(53.8) 148(76.0), 104(55.5)
4mb	*	430(52), 281(56), 164(5), 148(52), 133(100), 104(51)
4mc	163.1, 147.5, 139.0, 135.5 131.2, 128.4, 126.9, 126.2, 19.9	398(7.6), 265(69), 164(64), 148(100), 117(54), 104(49), 91(36)
4md	164.1, 147.0, 136.6, 134.1 131.9, 129.0, 127.9, 123.4	366(69), 211(97), 209(100), 182(19), 157(21), 155(24), 103(55)

4me	*	296(12), 164(15), 148(34), 104(12)
4pa	162.6, 148.2, 134.2, 133.7, 130.8 130.2, 128.9, 127.2, 126.9	370(3), 251(100), 164(33), 148(71), 104(47)
4pb	162.4, 160.9, 148.1, 133.9, 130.6, 128.8, 126.8, 114.4, 55.3	430(9), 281(47), 164(10), 148(30), 133(100), 104(18)
4pc	162.5, 148.2, 140.0, 133.8, 131.5 130.7, 129.4, 128.8, 127.1, 126.9	398(5), 265(88), 164(24), 148(100), 117(18), 104(44)
4pd	162.6, 147.0, 133.7, 133.6, 131.9, 130.9, 129.1, 128.9, 127.0, 123.5	530(1), 528(2), 331(97), 329(100), 164(31), 148(76), 104(32)
4pe	162.8, 147.9, 145.7, 140.5, 133.8, 131.1, 129.0, 128.1, 127.2, 124.1	296(100), 164(20), 148(99), 104(82)

* ^{13}C-NMR was not determined due to solubility problems.

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Synthesis of α-Thiocarbamoyl Phosphoranes and Their Utility for Formation of Some Pyrazole and Thiophene Derivatives.

Nadia Ragab Mohamed,

National Research Centre, Department of Photochemistry, Dokki, Giza, EGYPT.

Abstract:- Synthesis of phosphoranes **3a-d** by the reaction of some stable wittig reagents with phenylisothiocyanate have been achived. The study of their behaviour towards hydrazonoyl halides and phenacylchloride is reported.

Introduction:- Phosphonium ylides[1-5] have been proven to be valuable synthons for the synthesis of wide variety of biological active systems[6-8]. As an extention of our efforts[9,10] directed towards the development of convenient synthetic approaches for the construction of such active compounds[9-11], the synthetic scope of the α-thiocarbamoyl phosphoranes **3a-d** for the formation of some new polyfunctionally substituted systems was performed. The products formed are known as systems with expected broad spectrum of bioresponses.

Carbethoxymethylenetriphenylphosphorane **1a** and phenylisothiocyanate **2** were found to react readily in a one pot reaction to give an excellent yield of an addition product having the molecular formula $C_{29}H_{26}NO_2PS$. The structure of the produced ylide α-ethoxy-carbonyl-α-(phenylthio-carbamoyl)methylenetriphenylphosphorane **(3a)** was established by the study of its spectroscopic data. The IR spectrum revealed the presence of bands at 3420 cm^{-1} (NH) and 1720 cm^{-1} (C=O). The ^{1}H-NMR showed besides the aromatic signals, a singlet signal at δ = 12.30 ppm for (NH) group. This signal disappeared upon the addition of D_2O to the NMR sample. The ^{13}C-NMR showed besides the aromatic signals, down field signals at δ = 188.17, 188.42 for the thiocarbamoyl group and the carbonyl ester respectively. The MS and the microanalytical data supported the proposed structure. To

generalize the synthetic methodology, **3b-d** were obtained through the reaction of the ylides **1b-d** with phenylisothiocyanate **2**, respectively. (Scheme 1).

To explore the synthetic utility of the phosphoranes **3a-d**, they were allowed to react with some hydrazonoyl halides. Thus, the reaction of **3a** with hydrazonoyl halides **4a-c** in dry benzene containing anhydrous potassium carbonate afforded 1,3 cycloaddition products **7a-c**. (Scheme 2).

Structure elucidation for compound **7a**, for example, was accomplished with the following evidence:

(a) The IR spectrum, in (KBr) , revealed the presence of bands at 3200 cm^{-1} (NH) and 1680 cm^{-1} (C=O).

(b) ^{1}H-NMR showed the aromatic signals and a signal at δ = 11.05 ppm for the NH, this signal disappeared upon the addition of D_2O to the NMR sample.

(c) MS and microanalalytical data were in accordance with the suggested fully substituted pyrazole structure. (c.f. experimental section)

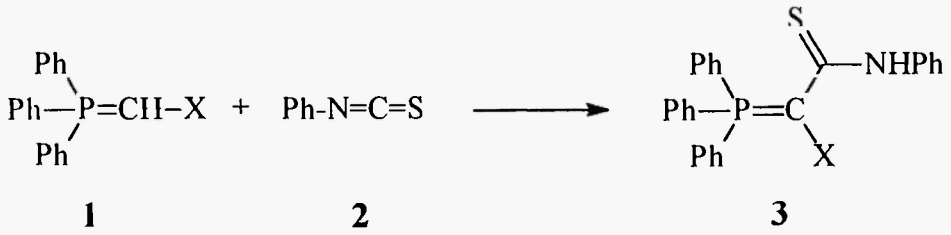
(d) Triphenylphosphine oxide was isolated from the reaction medium (mp and mixed mp)[12].

Similarly compounds **7a,b** were obtained and their structures were established by the study of the spectroscopic and microanalytical data (c.f experimental section).

The reaction apparently involves the formation of dipolar cycloadduct intermediate **5** which cyclized by nucleophilic attack of the nitrogen to the carbethoxy group to yield the cyclic intermediate **6** which aromatized by loss of triphenylphosphine oxide to give the isolable pyrazoles **7a-c** (Scheme 2).

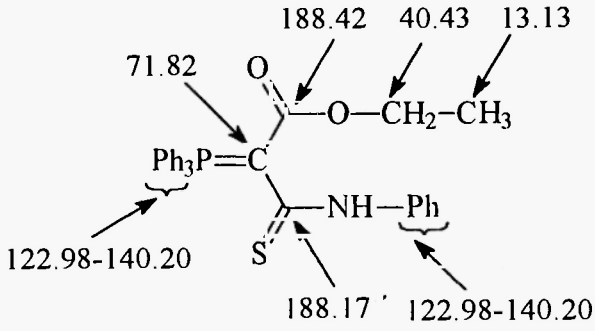
Similarly, The treatment of **3a** with **4a** afforded the 5-methyl pyrazole derivative **8**. The structure of **8** was also confirmed by studying its analytical and spectroscopic data.

S-Alkylation of **3a,b** with equimolecular amount of phenacyl chloride in ethanol containing anhydrous potassium carbonate produced the corresponding thiophene derivatives **10a,b** (scheme 4). It is beleived that the thiophene derivative **10** was obtained via S-alkylation of **3a** to give the acyclic intermediate **9** which cyclized under the reaction conditions by loss of triphenylphosphine oxide (mp and mixed mp)[12]. The structure of the final isolable products was confirmed by the analytical and spectroscopic data. IR spectrum of **10a,b** showed the presence of a broad band



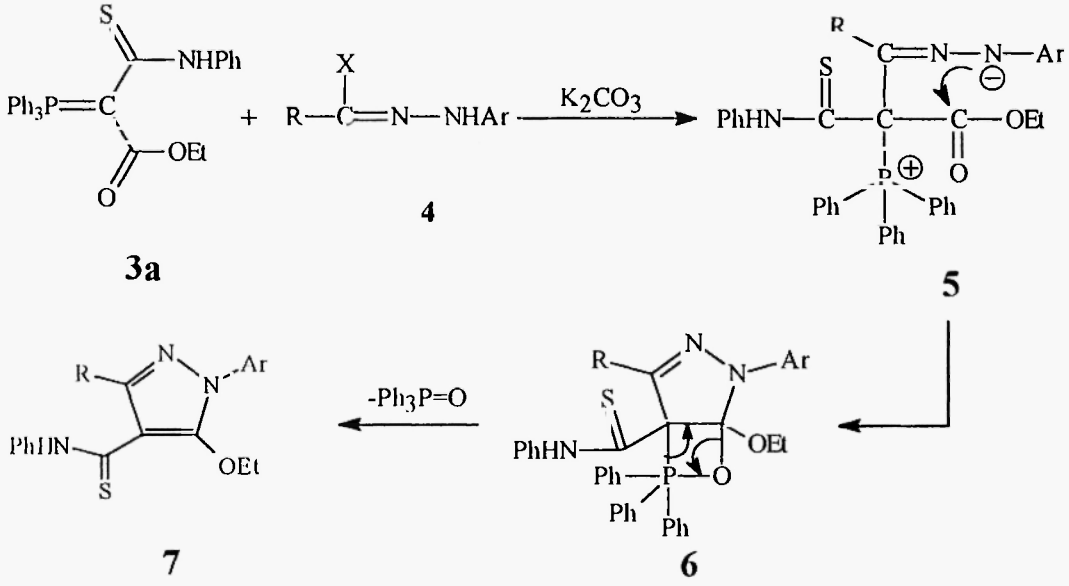
1 **2** **3**

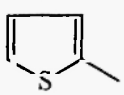
1,3, a, X = CO_2Et; b, X = $COCH_3$
c, X = CN; d, X = COPh



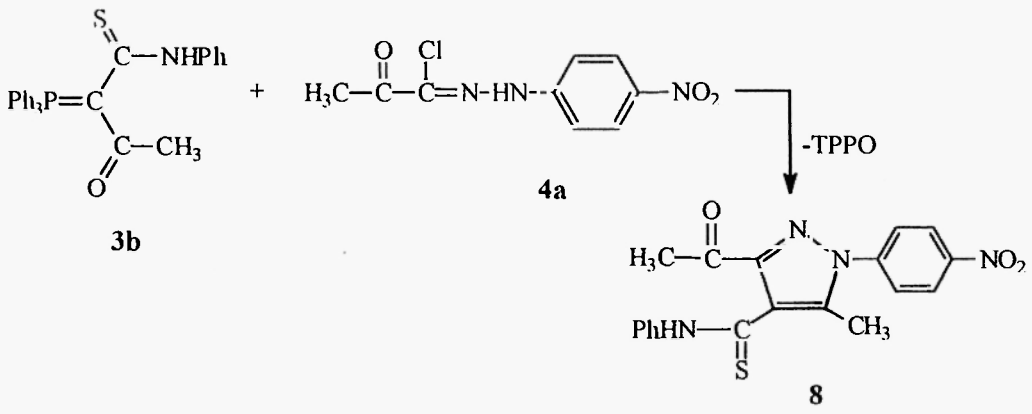
3a

(Scheme 1)

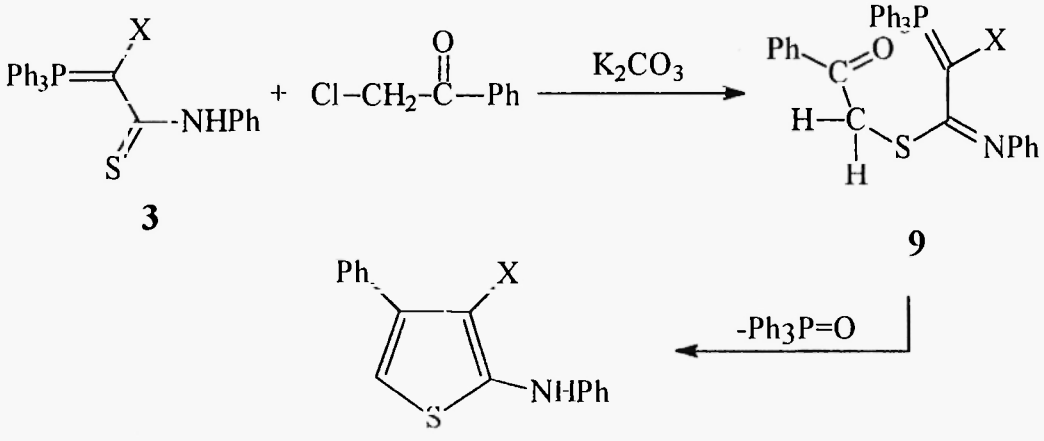


4,5,6,7a,	R = CH_3CO-,	Ar = C_6H_4-NO_2p,	X = Cl
b,	R = 	Ar = C_6H_4-NO_2p,	X = Cl
c,	R = Ph-CO-,	Ar = C_6H_5,	X = Br

(Scheme 2)



(Scheme 3)



3,9,10, a, X = CO_2Et
b, X = $COCH_3$

(Scheme 4)

for the NH group in both products at 3200 cm^{-1} and 3240 cm^{-1}, respectively. MS and microanalytical data were in accordance with the suggested substituted thiophene structure (cf. experimental section).

EXPERIMENTAL

All melting points are uncorrected. The IR spectra were obtained (KBr disc) on a Pye Unicam sp 1100 spectrophotometer, ^{1}H-NMR spectra were measured on a Varian EM-390 MHz spectrometer for solutions in $(CD_3)_2SO$ and $CDCl_3$ using TMS as internal standard. Mass spectra were recorded with MS 30 (AEI) spectrometer at 70 ev. Analytical data were obtained from Microanalytical Center at Cairo University, Giza, EGYPT.

α-Ethoxycarbonyl-α-(phenylthiocarbamoyl)methylene triphenylphosphorane 3a: Ethoxycarbonylmethylenetriphenylphosphorane (0.01 mol) in dry chloroform (30 ml) was treated with phenylisothiocyanate (0.01 mol) and the solution set aside at room temperature overnight. Solvent and excess of isothiocyanate were then removed in vacuo. The remaining residue was crystallized from benzene-petrolum ether (40-60°C) mixture. **3a:** mp 147°C; white crystals, 80% yield: ν_{max}/cm^{-1} (KBr) 3420 (NH), 1720 (C=O); δ H ($CDCl_3$) 0.45 (t, 3H, CH3), 3.45 (q, 2H, CH_2), 7.42-7.45 (m, 2H, aromatic protons), 7.55-7.80 (m, 15H, aromatic protons), 7.90-7.95 (m, 3H, aromatic protons), 12.30 (s, 1H, NH); ^{13}C-NMR: 13.13 (CH_3), 40.43 (CH_2), 71.82 [(q) C=P], 122.98, 124.10, 127.17, 128.23, 128.59, 128.78, 131.34-140.20 (aromatic protons), 188.17 (thiocarbamoyl carbon), 188.42 (ester carbonyl carbon). m/z 483; (Found: C, 72.00; H, 5.36; N, 2.85; S, 6.58; P, 6.39. $C_{29}H_{26}NO_2PS$ requires C, 72.04; H, 5.38; N, 2.89; S, 6.62; P, 6.41.

α-Substituted-α-(thiocarbamoyl)methylenetriphenylphosphorane 3b-d: General procedure: To a solution of **1b-d** (0.01 mol) in dry chloroform (40 ml), phenylisothio-cyanate (0.01 mol) was added. The reaction mixture was heated under reflux for 3 hours, then evaporated in vacuo. The remaining residue was treated with hot petroleum ether (40-60°C) and the isolated solid product was crystallized from the suitable solvent. **3b:** mp 162°C; Yellow crystals from (benzene), 90% yield; ν_{max}/cm^{-1} (KBr) 3400 (NH), 1680 (C=O); δ H ($CDCl_3$) 1.75 (s, 3H, CH_3), 7.32-7.35 (m, 2H, aromatic protons), 7.45-7.75 (m, 15H, aromatic protons), 7.87-7.90 (m,

3H, aromatic protons), 12.30 (s, 1H,NH); m/z 453; (Found: C, 74.15; H, 5.24; N, 3.04; S, 7.03; P, 6.80. $C_{28}H_{24}NOPS$ requires C, 74.17; H, 5.29; N, 3.09; S, 7.06; P, 6.84%). **3c:** mp 204°C; Yellow crystals from (benzene), 70% yield; ν_{max}/cm^{-1} (KBr) 3380 (NH), 2218 (CN), 1580 (C=C); δ H ($CDCl_3$) 7.05-7.35 (m, 3H, aromatic protons), 7.40-7.45 (m, 2H, aromatic protons), 7.55-7.90 (m, 15H, aromatic protons), 9.80 (s, 1H, NH); m/z 436 (Found: C, 74.30; H, 4.78, N, 6.40; S, 7.31; P, 7.10- $C_{27}H_{21}N_2PS$ requires C, 74.31; H, 4.81; N, 6.42; S, 7.33; P, 7.11%). **3d:** mp 167°C; Yellow crystals from (petroleum ether 60-80°C), 75% yield; ν_{max}/cm^{-1} (KBr) 3400(NH), 1660(C=O), 1580 (C=C); m/z 515; (Found: C, 76.85; H, 5.00; N, 2.70; S, 6.19; P, 6.00- $C_{33}H_{26}NOPS$ requires C, 76.89; H, 5.04; N, 2.71; S, 6.21; P, 6.01%).

5-Ethoxy-1,3-substituted-4-thiocarbamoyl-pyrazoles 7a-c: General procedure: To a stirred solution of 4a-c (0.01 mol) in dioxane (40 ml), the phosphorane 3a (0.01 mol) and anhydrous potassium carbonate (0.02 mol) were added. The reaction mixture was stirred for two days, then filtered and evaporated in vacuo. The remaining oil was triturated with hot petroleum ether (60-80°C). The final solid product was crystallized from the suitable solvent. **7a:** mp 178°C; orange crystals from ethanol; 65% yield; ν_{max}/cm^{-1} (KBr) 3200 (NH), 2900 (CH_3), 1680 (C=O), 1580 (C=C); δ H ($CDCl_3$) 1.40 (t, 3H, CH_3), 2.80 (s, 3H, CH_3), 4.35 (q, 2H, CH_2), 7.00-7.20 (m, 2H, aromatic protons), 7.30-7.45 (m, 3H, aromatic protons), 7.72-7.75 (m, 2H, aromatic protons), 8.20 (d, 2H, aromatic protons), 11.05 (s, 1H, NH); m/z 410; (Found: C, 58.50; H, 4.36; N, 13.64; S, 7.80. $C_{20}H_{18}N_4O_4S$ requires C, 58.53; H, 4.39; N, 13.65; S, 7.80%). **7b:** mp 118°C; orange crystals from ethanol; 60% yield; ν_{max}/cm^{-1} (KBr) 3410 (NH), 2950-2930 (CH_3, CH_2), 1580 (C=C); δ H [$(CD_3)_2SO$] 1.55 (t, 3H, CH_3); 4.30 (q, 2H, CH_2), 7.05-7.10 (m, 1H, thiophene proton); 7.20-7.40 (m, 2H, thiophene protons); 7.45-7.75 (m, 4H, aromatic protons), 7.80-8.05 (m, 5H, aromatic protons); 12.30 (s, 1H, NH); m/z 450; (Found: C, 58.65; H, 4.00, N, 12.42; S, 14.20. $C_{22}H_{18}N_4O_3S_2$ requires C, 58.66; H, 4.00; N, 12.44; S, 14.22%). **7c:** mp 130°C; Yellow crystals from (benzene); 62% yield; ν_{max}/cm^{-1} (KBr) 3420 (NH), 2950-2920 (CH_3, CH_2), 1660 (C=O), 1580 (C=C); δ H [$(CD_3)_2SO$] 1.55 (t, 3H, CH_3), 4.25 (q, 2H, CH_2), 7.05-7.15 (m, 3H, aromatic protons), 7.20-7.35 (m, 2H, aromatic protons), 7.45-7.75 (m, 5H, aromatic protons),

7.80-7.95 (m, 5H, aromatic protons), 12.30 (s, 1H, NH); m/z 427; (Found: C, 70.20; H, 4.90; N, 9.83; S, 7.48. $C_{25}H_{21}N_3O_2S$ requires C, 70.25; H, 4.91; N, 9.83; S, 7.49%).

3-Acetyl-5-methyl-1-(p-nitro)phenyl-4-thiocarbamoyl-pyrazole 8: To a stirred solution of **4a** (0.01 mol) in benzene (30 ml), the phosphorane 3b (0.01 mol) and anhydrous potassium carbonate (0.02 mol) were added. The reaction mixture was stirred for 24 hours, then filtered and evaporated in vacuo. The remaining oil was triturated with hot petroleum ether (60-80°C) to produce the final product **8**: mp 208°C; orange crystals from ethanol; 60% yield; ν_{max}/cm^{-1} (KBr) 3400 (NH), 2945-2920 ($2CH_3$), 1720 (C=O), 1580 (C=C), δ H ($CDCl_3$) 2.60 (s, 3H, CH_3), 2.85 (s, 3H, $COCH_3$), 7.25-7.55 (m, 5H, aromatic protons), 7.75 (d, 2H, aromatic protons), 8.20 (d, 2H, aromatic protons); ^{13}C-NMR: 12.80, 25.50 ($2CH_3$), 113.33, 114.64, 119.84, 125.74, 129.54, 140.51 (aromatic carbons), 141.65, 148.42, 149.33 (pyrazole carbons), 160.63 (thiocarbamoyl carbon), 192.09 (carbonyl carbon). m/z 380; (Found: C, 60.02; H, 4.20; N, 14.70; S, 8.41. $C_{19}H_{16}N_4O_3S$ requires C, 60.00; H, 4.21; N, 14.73; S, 8.42%).

4-Iminophenyl-3-phenyl-4-substituted-thiophene 10: A mixture of the phosphorane **3a,b** (0.01 mol) and phenacyl chloride (0.01 mol) in dioxane (40 ml) contain potassium carbonate (0.02 mol) was heated under reflux for 5 hours, The solution of the reaction was filtered, then evaporated in vacuo and triturated with ethanol to produce the final product. **10a:** mp 80°C; Yellow crystals from ethanol; 70% yield; ν_{max}/cm^{-1} (KBr) 3200 (NH), 1710 (C=O), 1580 (C=C); δ H [$(CD_3)_2SO$] 1.45 (t, 3H, CH_3), 4.25 (q, 2H, CH_2), 6.80 (s, 1H, thiophene protons), 7.25-7.45 (m, 5H, aromatic protons), 7.55-7.75 (m, 5H, aromatic protons), 10.20 (s, 1H, NH); m/z 323; (Found: C, 70.55; H, 5.25; N, 4.32; S, 9.90. $C_{19}H_{17}NO_2S$ requires C, 70.58; H, 5.26; N, 4.33; S, 9.90%). **10b:** mp 75°C; Yellow crystals from ethanol; 73% yield; ν_{max}/cm^{-1} (KBr) 3240 (NH), 1690 (C=O), 1580 (C=C); δ H [$(CD_3)_2SO$] 2.25 (s, 3H, CH_3), 6.60 (s, 1H, thiophene protons), 7.00-7.15 (m, 2H, aromatic protons), 7.20-7.40 (m, 3H, aromatic protons), 7.45-7.80 (m, 5H, aromatic protons); m/z 293; (Found: C, 73.70; H, 5.12; N, 4.76; S, 10.90. $C_{18}H_{15}NOS$ requires C, 73.72; H, 5.11; N, 4.77; S, 10.92%).

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