

Note

Synthesis and insecticidal activity of organophosphorus compounds containing substituted *s*-triazole and fused ring heterocycles

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Some new compounds *O*, *O*-dialkyl-*S*-(4-amino/anilino-3-mercapto-1, 2, 4-triazol-5-ylmethyl)phosphorodithioates (**2** and **3**), *O*, *O*-dialkyl-*S*-(4-amino/anilino-3(2*H*)-oxo-1,2,4-triazol-5-ylmethyl)phosphorodithioates (**4** and **5**), *O*, *O*-dialkyl-*S*-(6-oxo-5*H*, 7*H*-1, 2, 4-triazolo[3, 4-*b*][1, 3, 4]thiadiazin-3-ylmethyl)phosphorodithioates (**6**), *O*, *O*-dialkyl-*S*-(6-phenyl-5*H*, 7*H*-1, 2, 4-triazolo[3, 4-*b*][1, 3, 4]thiadiazin-3-ylmethyl) phosphorodithioates (**7**) and *O*, *O*-dialkyl-*S*-(6-thioxo-5*H*-1, 2, 4-triazolo[3, 4-*b*][1, 2, 4]thiadiazolo-3-ylmethyl)phosphorodithioates (**8**) have been synthesised and tested for their insecticidal activity.

In continuation of our earlier work on the synthesis of organophosphorus pesticides¹, we undertook synthesis of some new 1, 2, 4-triazole derivatives and evaluation of their insecticidal activity.

Treatment of *O*, *O*-dialkyl-dithiophosphoroacetylhydrazides (**1**)² with carbon disulphide and alc. KOH followed by reaction with hydrazine hydrate and phenylhydrazine respectively, gave the corresponding *O*, *O*-dialkyl-*S*-(4-amino/anilino-3-mercapto-1, 2, 4-triazol-5-ylmethyl)phosphorodithioates (**2** and **3**). Similarly, the reaction of **1** with carboxy sulphide in alc. KOH followed by treatment with hydrazine hydrate and phenylhydrazine respectively, yielded *O*, *O*-dialkyl-*S*-[4-amino/anilino-3(2*H*)-oxo-1, 2, 4-triazol-5-ylmethyl]phosphorodithioates (**4** and **5**) (Scheme I).

Cyclocondensation of **2** with ethyl chloroacetate, phenacyl bromide and carbon disulphide in alc. KOH furnished *O*, *O*-dialkyl-*S*-(6-oxo-5*H*, 7*H*-1, 2, 4-triazolo[3, 4-*b*][1, 3, 4]thiadiazin-3-

ylmethyl) phosphorodithioates (**6**), *O*, *O*-dialkyl-*S*-(6-phenyl-5*H*, 7*H*-1, 2, 4-triazolo[3, 4-*b*][1, 3, 4]thiadiazin-3-ylmethyl) phosphorodithioates (**7**) and *O*, *O*-dialkyl-*S*-(6-thioxo-5*H*-1, 2, 4-triazolo[3, 4-*b*-(1,2,4)-thiadiazol-3-ylmethyl)phosphorodithioates (**8**), respectively (Scheme II).

Insecticidal activity

All the compounds synthesised were screened for their insecticidal activities³ against *Odontotermes obessus* (soil termites) at 10 µg/cm² concentration. The results are summarized in Table I.

Compounds **3b**, **4a**, and **4b** showed 60-70% mortality. The remaining compounds showed moderate or less activity against *O. obessus*.

All the compounds were less active in comparison to Abate, an organophosphorus pesticide which was taken as standard.

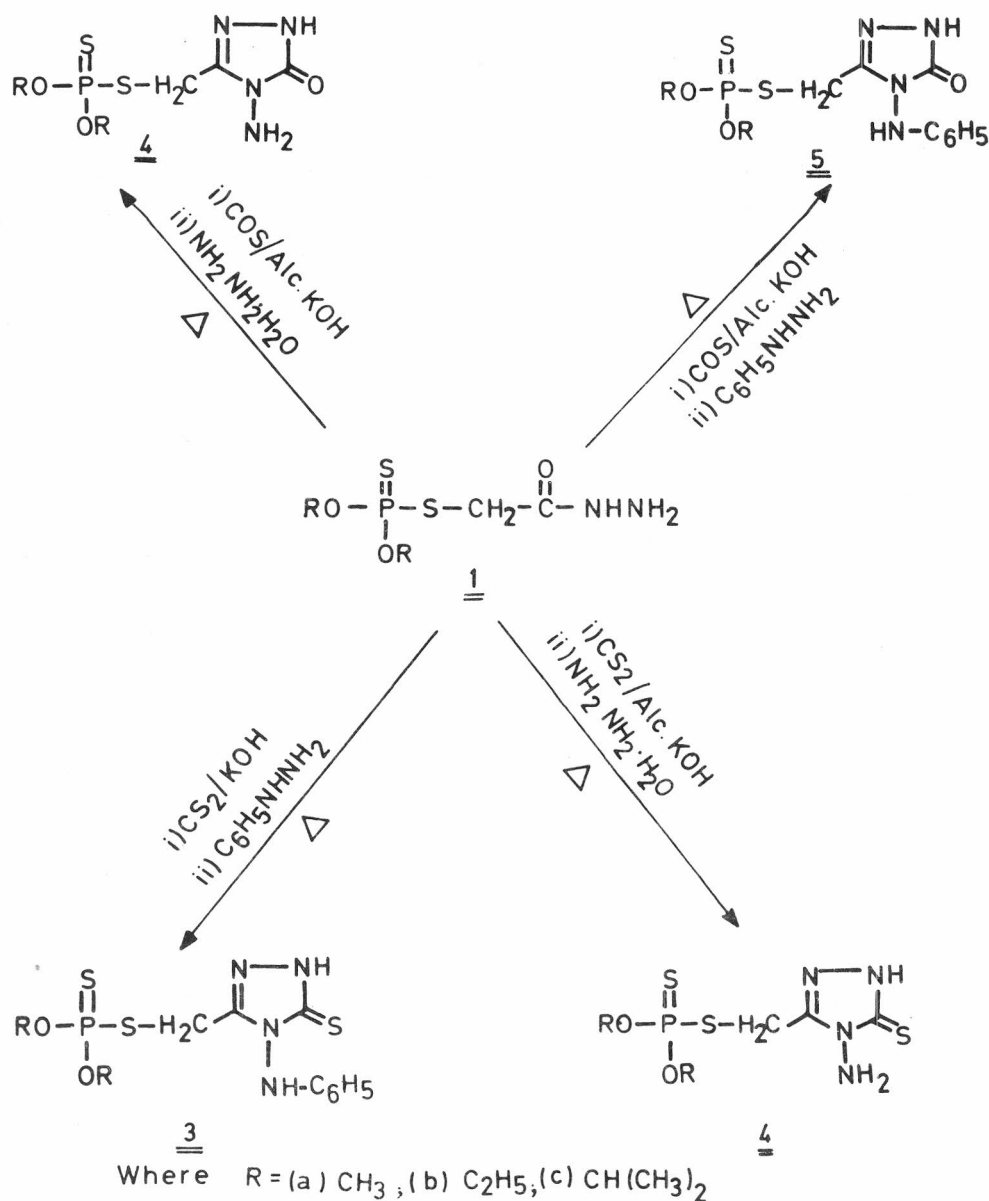
Experimental Section

Melting points were determined in open capillary tubes and are uncorrected. IR spectra were recorded in KBr on a Perkin-Elmer 983 spectrophotometer and ¹H NMR spectra on a Varian VXR = 300s (300 MHz) spectrometer using TMS as internal standard (chemical shifts in δ, ppm).

***O*, *O*-Dialkyl-*S*-(4-amino/anilino-3-mercapto-1, 2, 4-triazol-5-ylmethyl)phosphorodithioates (**2** and **3**): General procedure.** To an ice-cold solution of KOH (0.015 mole) in dry ethanol (50 mL) was added **1** (0.01 mole) followed by CS₂ (0.02 mole) with stirring. The reaction mixture was stirred further at room temperature for 12 hr. The solid thus obtained was filtered, washed with dry ether and used directly without further purification. It was then heated with hydrazine hydrate/phenylhydrazine (0.03 mole) on a water-bath until the evolution of H₂S ceased (about 8 hr). The reaction mixture was then poured into ice-cold water, acidified with gl. acetic acid and crystallised from aq. ethanol to give **2** and **3**. Their physical data are given in Table I.

Compound **2b**; IR (KBr) : 3305, 3273, 3206, 2924, 1143 cm⁻¹ (C=S); ¹H NMR (DMSO-*d*₆) : δ1.22 (t, 6H, *J*=7 Hz, 2×CH₃), 3.14 (q, 4H, *J*=7 Hz, 2×CH₂), 3.76 (s, 2H, -SCH₂), 7.28 (s,

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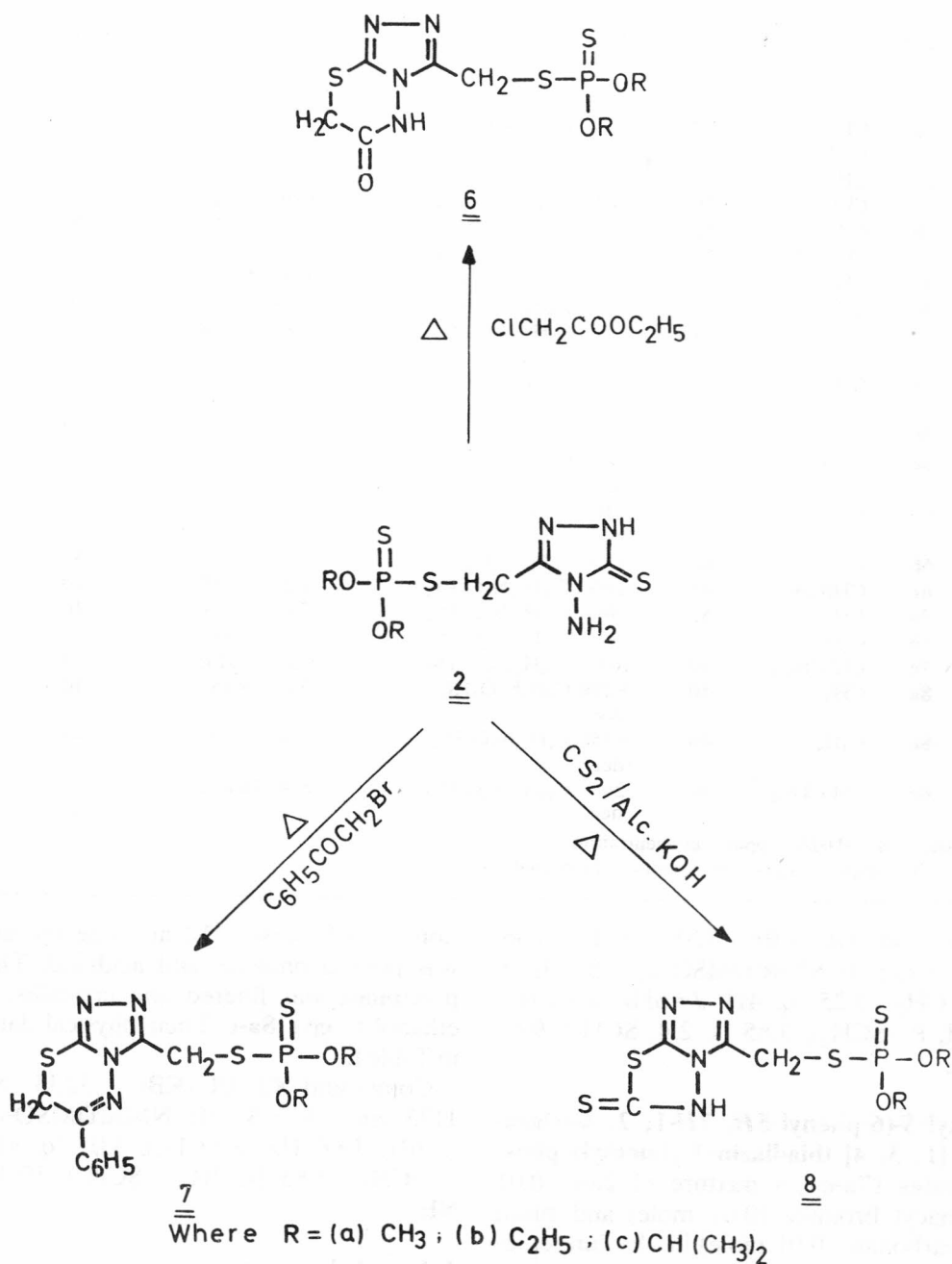
Scheme I

2H, NH₂), 11.44 (s, 1H, -NH, D₂O exchangeable).

Compound **3c**; IR(KBr): 3192 (NH), 1157 cm⁻¹ (C=S); ¹H NMR (DMSO-*d*₆): δ 1.35 (d, 12H, *J*=6.12Hz, 2×CH₃), 3.65 (s, 2H, -SCH₂) 4.84 (septet, *J*=6.12Hz, 2H, 2×CH of isopropyl), 7.50 (m, 5H, Ar-H), 8.94 (s, 1H, NH), 8.97 (s, 1H, NHC₆H₅, D₂O exchangeable).

O, O-Dialkyl-S-[4-amino/anilino-3(2H)-oxo-1, 2, 4-triazol-5-ylmethyl]phosphorodithioates (4 and 5): General procedure. To an ice-cold solution of KOH (0.075 mole) in dry ethanol (50 mL), 1

(0.05 mole) was added. A stream of dry COS₂ was passed through the solution (about 4 hr). The potassium salt of thiocarbazine acid thus formed was filtered, washed with dry ether and used directly. A mixture of the potassium salt (0.05 mole) and hydrazine hydrate/phenylhydrazine (0.05 mole) was heated on a water-bath for 8 hr till the evolution of H₂S gas ceased. The reaction mixture was then cooled, poured into ice-cold water and acidified. The solid thus obtained was filtered, washed with cold water and crystallised from aq. ethanol to give **4** and **5**. Their physical data are given in Table I.



Scheme II

Compound **4b**; IR(KBr) : 3427, 3242, 1706 cm^{-1} ; ^1H NMR (DMSO- d_6): δ 1.15 (t, 6H, $J=6\text{Hz}$, $2 \times \text{CH}_3$), 3.09(q, 2H, $J=6\text{Hz}$, $-\text{OCH}_2$), 3.30(q, 2H, $J=6\text{Hz}$, OCH_2), 3.77(s, 2H, SCH_2), 7.62(s, 2H, NH_2), 10.40(s, 1H, NH).

Compound **5a**; IR (KBr) : 3195, 3005, 1700 cm^{-1} ; ^1H NMR (DMSO- d_6): δ 3.50 (s, 6H, $2 \times \text{CH}_3$), 4.40 (s, 2H, $-\text{SCH}_2$), 7.30-7.50 (m, 5H, Ar-H), 9.75(s, 1H, NH), 9.90(s, 1H, NHC_6H_5).

O, O-Dialkyl-*S*-(6-oxo-5*H*, 7*H*-1, 2, 4-triazolo [3, 4'-*b*] [1, 3, 4] thiadiazin-3-ylmethyl)phosphorodithioates (**6a-c**). A mixture of **2a-c** (0.01 mole), ethyl chloroacetate (0.01 mole) and sodium ethoxide (0.01 mole) in absolute ethanol (25 mL) was refluxed on a water-bath for 12 hr. The solid thus separated was filtered, washed with cold water and crystallised from absolute ethanol to give **6a-c**. Their physical data are given in Table I.

Table I—Physical data and insecticidal activity of compounds 2-8

Compd	R	Yield (%)	m.p. °C	Mol. formula	P (%) [†]		Mortality (%) <i>O. obessus</i>
					Found	(Calcd.)	
2a	CH ₃	72	235	C ₅ H ₁₁ N ₄ O ₂ PS ₃	10.39	(10.839)	10
2b	C ₂ H ₅	60	113	C ₇ H ₁₅ N ₄ O ₂ PS ₃	9.43	(9.872)	100
2c	CH(CH ₃) ₂	55	110	C ₉ H ₁₉ N ₄ O ₂ PS ₃	8.86	(9.064)	100
3a	CH ₃	70	241	C ₁₁ H ₁₅ N ₄ O ₂ PS ₃	8.06	(8.563)	10
3b	C ₂ H ₅	62	237	C ₁₃ H ₁₉ N ₄ O ₂ PS ₃	7.64	(7.948)	70
3c	CH(CH ₃) ₂	50	200	C ₁₅ H ₂₃ N ₄ O ₂ PS ₃	7.19	(7.416)	20
4a	CH ₃	68	160	C ₅ H ₁₁ N ₄ O ₃ PS ₂	11.04	(11.481)	60
4b	C ₂ H ₅	62	182	C ₇ H ₁₅ N ₄ O ₃ PS ₂	10.09	(10.402)	60
4c	CH(CH ₃) ₂	51	220	C ₉ H ₁₉ N ₄ O ₃ PS ₂	9.19	(9.509)	20
5a	CH ₃	52	(dec) 210	C ₁₁ H ₁₅ N ₄ O ₃ PS ₂	8.49	(8.959)	10
5b	C ₂ H ₅	50	(dec) 233	C ₁₃ H ₁₉ N ₄ O ₃ PS ₂	7.91	(8.288)	20
5c	CH(CH ₃) ₂	46	(dec) > 275	C ₁₅ H ₂₃ N ₄ O ₃ PS ₂	7.92	(7.711)	0
6a	CH ₃	50	(dec) 210	C ₇ H ₁₁ N ₄ O ₃ PS ₃	9.10	(9.509)	0
6b	C ₂ H ₅	60	(dec) 190	C ₉ H ₁₅ N ₄ O ₃ PS ₃	8.35	(8.757)	30
6c	CH(CH ₃) ₂	40	(dec) 200	C ₁₁ H ₁₉ N ₄ O ₃ PS ₃	8.25	(8.115)	20
7a	CH ₃	52	(dec) 50	C ₁₃ H ₁₅ N ₄ O ₂ PS ₃	7.91	(8.031)	10
7b	C ₂ H ₅	60	(dec) 61	C ₁₅ H ₁₉ N ₄ O ₂ PS ₃	7.37	(7.487)	0
7c	CH(CH ₃) ₂	50	(dec) 103	C ₁₉ H ₂₃ N ₄ O ₂ PS ₃	7.23	(7.0135)	0
8a	CH ₃	50	(dec) > 250	C ₆ H ₉ N ₄ O ₂ PS ₄	9.61	(9.451)	10
8b	C ₂ H ₅	40	(dec) > 250	C ₈ H ₁₃ N ₄ O ₂ PS ₄	8.96	(8.707)	40
8c	CH(CH ₃) ₂	40	(dec) 266	C ₁₀ H ₁₇ N ₄ O ₂ PS ₄	8.49	(8.072)	0

Abate at 0.025 ppm concentration

[†] All the compounds gave satisfactory C, H, N analysis.

Compound **6b**; IR (KBr): 3200 (NH), 2966, 1675 cm⁻¹ (CO); ¹H NMR(DMSO-*d*₆): δ 1.38 (t, 6H, *J*=2 × CH₃), 3.25 (q, 4H, *J*=6Hz, 2 × CH₂), 3.64 (s, 2H, P-SCH₂), 3.85 (s, 2H, SCH₂), 9.60 (s, 1H, NH).

O, O-Dialkyl-*S*-(6-phenyl-5*H*, 7*H*-1, 2, 4-triazolo [3, 4-*b*] [1, 3, 4] thiadiazin-3-ylmethyl) phosphorodithioates (**7a-c**). A mixture of **2a-c** (0.01 mole); phenacyl bromide (0.01 mole) and fused potassium carbonate (0.01 mole) in absolute ethanol (30 mL) was refluxed for 8 hr. The product obtained on cooling was filtered, washed with water, dried and crystallized from ethanol to give **7a-c** (cf. Table I).

Compound **7b**; IR (KBr): 2850, 1465 cm⁻¹; ¹H NMR (DMSO-*d*₆): δ 1.453 (t, 6H, *J*=6 Hz, 2 × CH₃), 3.278 (q, 4H, *J*=6Hz, 2 × CH₂), 4.959 (s, 4H, 2 × SCH₂), 7.50-7.62 (m, 5H, Ar-H).

O, O-Dialkyl-*S*-(6-thioxo-5*H*-1, 2, 4-triazolo[3, 4-*b*] [1, 2, 4]thiadiazol-3-ylmethyl) phosphorodithioates (**8a-c**). A mixture of **2a-c** (0.01 mole), carbon disulphide (0.015 mole) and KOH (0.84 g) in ethanol (50 mL) was refluxed until the evolu-

tion of H₂S ceased (12 hr). The reaction mixture was poured onto ice and acidified. The resulting precipitate was filtered and crystallised from aq. ethanol to give **8a-c**. Their physical data are given in Table I.

Compound **8b**; IR (KBr) : 3233 (NH), 2964, 1173 cm⁻¹ (C=S); ¹H NMR(DMSO-*d*₆): δ 1.155 (t, 6H, *J*=6 Hz, 2 × CH₃), 3.05 (q, 4H, *J*=6Hz, -OCH₂), 3.83 (s, 2H, -SCH₂), 10.388 (s, 1H, NH).

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