Studies on Potential Pesticides: Part IV. Synthesis of Several New Dithiocarbamates

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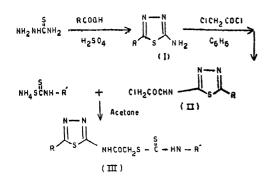
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Twentyfour substituted dithiocarbamates have been synthesised as possible insecticidal agents by the condensation of 2-acylamino-5-alkyl 1,3,4-thiadiazoles, with sodium or ammonium salts of various dithiocarbamic acids.

I N continuation of our work¹ in Part III we have now prepared a large number of thiadiazolyl dithiocarbamates. Carbamate insecticides are biologically active because of their structural complementarity to the active site of acetyl cholinesterase and their consequent action as substrates with very low turnover numbers.

A group of Japanese workers have manufactured a number of dithiocarbamates effective as agricultural bactericides, fungicides and insecticides²⁻⁵. Moreover the importance of dithiocarbamate derivatives as pesticides have been emphasised by many workers and random screening of a very large number of 1,3,4-thiadiazole derivatives enlightened the importance of above compounds as insecticides and herbicides⁶⁻⁹. In all twenty four substituted thiadiazolyl dithiocarbamate have been prepared according to the scheme given below :---



Experimental

Preparation of 2-amino-5-alkyl-1,3,4-thiadiazole¹² (I)

A mixture of 0.2 mole of appropriate acid, 0.075 mole of thiosemicarbazide and 10 g. of H_2SO_4 was refluxed an a sand bath for 2 hr. Then the reaction mixture was poured into a 40 g. ice H_2O and neutralised with 20 ml. 28% NH₅OH to give the desired compound. The compounds were recrystallised from boiling water or dilute alcohol.

Preparation of 2-chloroacetylamino-5-alkyl-1,3,4-thiadiazole¹³ (II)

A mixture of 0.1 mole of appropriate amino thiadiazole and 0.1 mole of chloroacetyl chloride in 100 ml. dry C_6H_6 was refluxed on steam bath for 5-6 hr. Then the C_6H_6 was distilled and compound neutralised with 4% solution of NaHCO₈. The compounds were crystallised from absolute alcohol.

Synthesis of S-(2-acylamino-5-alkyl)1,3,4-thiadiazolyl, N-aryl/alkyl dithiocarbamates (III)

To a 0.01 mole of ammonium or sodium salt of N-substituted dithiocarbamic $\operatorname{acid}^{10,11}$ in 15 ml. dry acetone was added a suspension of 0.01 mole of appropriate chloroacetyl-2-amino-5-alkyl-1,3,4-thiadiazole^{12,13}, in 25 ml. dry acetone. The mixture was stirred at room temperature for 30 min. and then heated on steam bath for further 1 hr. The reaction mixture was then poured into 200 ml. of ice-cold water. The white crystalline product thus obtained was washed several times with cold water and the compound recrystallised from appropriate solvent such as ethanol. The melting points and analytical data are given in the Table 1.

The insecticidal activity of these compounds will be communicated later on as it is under investigation.

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	TABLE 1				
$\mathbf{R} \xrightarrow{\mathbf{N}} \mathbf{N} \mathbf{H} \mathbf{COCH}_{2} \mathbf{S} \xrightarrow{\mathbf{U}} \mathbf{R}'$					
S N% Analysis					
Sl. R No.	R'	Molecular Formula	M.P.* - °C	Found	Caled.
1. H	$-NH-C_{6}H_{5}$	$C_{11}H_{10}N_4OS_3$	227	18.31	18.07
2. H	-NH-C ₈ H ₄ CH ₃ (0)	$C_{12}H_{12}N_4OS_3$	250	17.10	17.28
3. H	-NH-C ₆ H ₄ CH ₃ (m)	$C_{12}H_{12}N_4OS_3$	146	17.43	17.28
4. H	$-\mathrm{NH}-\mathrm{C}_{6}\mathrm{H}_{4}\mathrm{CH}_{3}(p)$	$C_{12}H_{12}N_4OS_3$	213	17.20	17.28
5. H	$-\mathrm{NH}-\mathrm{C}_{6}\mathrm{H}_{4}\mathrm{Cl}(p)$	$C_{11}H_9ClN_4OS_3$	170	16.50	16.26
6. H	$-N-(C_2H_5)_2$	C ₉ H ₁₄ N ₄ OS ₃	220	19,11	19.31
7. H	-NO	$\mathrm{C_9H_{12}N_4O_2S_3}$	218	18.23	18.42
8. H	-м	$\mathrm{C_{10}H_{14}N_4OS_3}$	215	18.41	18.54
9. C ₂ H ₅	-NH-C ₆ H ₅	$\mathbf{C_{13}H_{14}N_4OS_3}$	219	16.32	16.60
10. C ₂ H ₅	$-\mathbf{NH}\mathbf{-}\mathbf{C_6H_4CH_3}(o)$	$\mathbf{C_{14}H_{16}N_4OS_3}$	224	15.78	15.91
11. C ₂ H ₅	$-\mathrm{NH-C_6H_4CH_3}(m)$	$\mathrm{C_{14}H_{16}N_4OS_3}$	185	15.69	15.91
12. C ₂ H ₅	$-\mathrm{NH}-\mathrm{C_6H_4CH_3}(p)$	$\mathrm{C_{14}H_{16}N_4OS_3}$	245	15.80	15.91
13. C ₂ H ₅	$-\mathrm{NH-C_6H_4Cl}(p)$	$\mathrm{C_{13}H_{13}N_4OS_3Cl}$	216	15.31	15.03
14. C ₂ H ₅	, -N-(C ₂ H ₅) ₂	$\mathbf{C_{11}H_{18}N_4OS_3}$	190	17.40	17.61
15. C ₂ H,	5 ·NO	$C_{11}H_{16}N_4O_2S_3$	228	16.49	16.87
16. C ₂ H	5 -N	$\mathrm{C_{12}H_{18}N_4OS_3}$	217	16.73	16.97
17. C ₃ H	7 -NH-C ₆ H ₅	$\mathrm{C_{14}H_{16}N_4OS_3}$	225	15.78	15,91
18. C ₃ H	7 -NH-C6H4CH3(0)	$\mathrm{C_{15}H_{18}N_4OS_3}$	229	15.13	15.30
19. C ₃ H	-NH-C ₆ H ₄ CH ₃ (m)	$\mathrm{C_{15}H_{18}N_4OS_3}$	150	15.20	15.30
20. C ₃ H	$C_7 - NH - C_8 H_4 CH_3(p)$	$\mathbf{C_{15}H_{18}H_4OS_3}$	204	15.41	15.30
21. C ₃ H	-NH-C ₆ H ₄ Cl(p)	C14H15ClN4OS3	224	14.81	14.49
_	$I_7 - N - (C_2 H_5)_2$	$C_{12}H_{20}N_4OS_3$	140	16.69	16.87
23. C ₃ H	I ₇ -NO	$C_{12}H_{18}N_4O_2S_3$	235	16.01	16.18
24. C ₃ H	$I_7 - N $	$C_{13}H_{20}N_4OS_3$	205	16.15	16.28

* ill the m.p.s are uncorrected.

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