

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

ANIL K. SEN GUPTA and K. AVASTHI

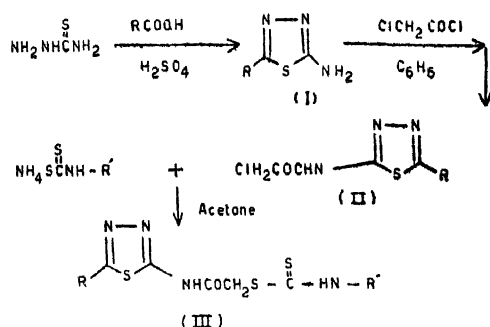
Chemistry Department, Lucknow University, Lucknow

Manuscript received 16 October 1974; revised 3 February 1975; accepted 1 March 1975

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.

In 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 H₂SO₄ was refluxed on a sand bath for 2 hr. Then the reaction mixture was poured into a 40 g. ice H₂O and neutralised with 20 ml. 28% NH₄OH to give the desired compound. The compounds were recrystallised from boiling water or dilute alcohol.

Preparation of 2-chloroacetyl-amino-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 C₆H₆ was refluxed on steam bath for 5-6 hr. Then the C₆H₆ was distilled and compound neutralised with 4% solution of NaHCO₃. 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 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.

Acknowledgement

The authors express their sincere thanks to the Head of the Chemistry Department, Lucknow University for providing laboratory facilities and to Dr. N. Anand of C.D.R.I., Lucknow for providing facilities of elemental analysis. Our deep acknowledgement is to the C.S.I.R., New Delhi, for providing a junior research fellowship to one of us (K.A.) and to the Society of the Sigma XI, U.S.A. for a grant to carry out the work.

References

1. A. K. SEN GUPTA and A. K. RAMRAKHYANI, *Indian J. Pharmacy*, 1974, 36, 9.
2. JAP.P. 70 84,804, 07 Nov. 1970; *Chem. Abs.*, 1971, 74, 87665v.
3. JAP.P. 72 20,612, 12 Jun. 1972; *Chem. Abs.*, 1972, 77, 75012d.
4. JAP.P. 71 11,172, 22 Mar. 1971; *Chem. Abs.*, 1971, 75, 5535m.
5. V. KONECNY, A. SALY, S. PRICHRADNY, S. TRUCHLIK, *Acta. fac. Rerum. Natur. Univ. Comeniane Chim.*, 1971, No. 15, 51.
6. GER. OFFEN. P. 2050,979, 29 Apr. 1971; *Chem. Abs.*, 1971, 75, 4909w.
7. GER. OFFEN. P. 2100,057, 08 Jul. 1971; *Chem. Abs.*, 1971, 75, 76799m.
8. GER. OFFEN. P. 1816,567, 02 Jul. 1970; *Chem. Abs.*, 1970, 73, 45520t.
9. S. AFRICAN. P. 69 04,818, 08 Jul. 1969; *Chem. Abs.*, 1970, 73, 45515v.
10. A. I. VOGEL, "Practical Organic Chemistry", 1957, p. 643.
11. M. TOKUDA, Y. TANAKA, Y. KASE, Y. TAGA, Y. TONINAGA and Y. YAMAMOTO, *Kumamoto Pharm. Bull.*, 1962, 5, 24; *Chem. Abs.*, 1963, 59, 6293e.
12. JAP.P. 20944, 07 Dec. 1966; *Chem. Abs.*, 1967, 66, 46430f.
13. F. GAGIU and AL. MAVRO, *Bull. Soc. Chim. Fr.*, 1967, 3, 1010; *Chem. Abs.*, 67, 82164b.