

PREPARATION OF CARBON-14 LABELLED MECARBAM (O,O-DI-[1-¹⁴C]-ETHYL
S-[N-ETHOXYCARBONYL-N-METHYLCARBAMOYLMETHYL] PHOSPHOROTHIOLOTHIONATE)

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SUMMARY

O,O-Di-[1-¹⁴C]-ethyl S-[N-ethoxycarbonyl-N-methylcarbamoylethyl] phosphorothiolothionate has been prepared with a specific activity of 1.97 mCi mmol⁻¹. The procedure involved the interaction of [1-¹⁴C]-ethanol with phosphorus pentasulphide in benzene, followed by conversion of the so-formed diethyl dithiophosphoric acid to its potassium salt and reaction of this with ethyl N-chloroacetyl-N-methylcarbamate in acetone. G.l.c. analysis of the final product in benzene solution showed the purity to be not less than 97 %.

INTRODUCTION

Mecarbam is an example of an organophosphorus carbamate having insecticidal and acaricidal properties.^(1,2) It is used for the protection of olives, citrus fruits, and rice, and for the control of a number of root larvae. The compound was required with carbon-14 labelling of the phosphorus-bonded ethoxy groups, for use in a programme of metabolic studies. Its preparation from [1-¹⁴C]-ethanol is described below.

EXPERIMENTAL

$[1-^{14}\text{C}]$ -Ethanol was supplied by The Radiochemical Centre, Amersham, U.K., and ethyl N-chloroacetyl-N-methylcarbamate⁽⁶⁾ by Cheminova AS, Lemvig, Denmark. Anala[®] solvents were used, benzene and ether being dried over sodium. Phosphorus pentasulphide was BDH Laboratory Reagent grade (not less than 98 %).

Preparation of O,O-di- $[1-^{14}\text{C}]$ -ethyl dithiophosphoric acid. - The ampoule of $[1-^{14}\text{C}]$ -ethanol (2.5 mCi, 577 $\mu\text{Ci mg}^{-1}$) was opened at -78°C and absolute ethanol was added to give a total of 109.5 mg (2.38 mmol). The labelled alcohol was transferred with benzene (2.5 cm^3) to a 5 cm^3 round-bottomed flask fitted with a reflux condenser, and phosphorus pentasulphide (132 mg, 0.595 mmol) was added. With gentle agitation, the mixture was heated in an oil bath (3 h at 85°C followed by 5 h at $88 - 90^\circ\text{C}$) until evolution of H_2S ceased and a clear solution remained.

Preparation of an acetone solution of the potassium salt. - Powdered 85 % potassium hydroxide (823 mg, 1.25 mmol) was thoroughly mixed with the benzene solution of labelled diethyl dithiophosphoric acid. The white solid which was formed was filtered off, washed with benzene, and ether, and dried. It was then extracted with acetone (10 cm^3) to leave a small insoluble residue (24.6 mg) and to give a solution containing the required potassium salt (229 mg).

Formation of $[^{14}\text{C}]$ -labelled mecarbam. - Recrystallized ethyl N-chloroacetyl-N-methylcarbamate⁽⁶⁾ (183.5 mg, 1.02 mmol) was added to the acetone solution of potassium di- $[1-^{14}\text{C}]$ -ethyl dithiophosphate (229 mg, 1.02 mmol) and the mixture was heated under gentle reflux (2 h).⁽³⁾ Potassium chloride was removed by filtration and the solution was evaporated under reduced pressure to leave an almost colourless oily residue of mecarbam (340 mg, 1.03 mmol). The product was taken up in benzene (50 cm^3) to give a solution which was shown by g.l.c.⁽⁵⁾ to contain 0.64 % w/v of mecarbam (320 mg, overall yield 81.7 %) (purity $\leq 97\%$). The specific activity was $1.97 \text{ mCi mmol}^{-1}$ (Calc. $2.10 \text{ mCi mmol}^{-1}$ based on the activity of the ethanol used).

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REFERENCES

1. Pianka, M. , Chem. and Ind., 324 (1961).
2. Pianka, M. and Polton, D.J. (Murphy Chemical Co. Ltd.), British Patent 867, 780 (1961).
3. Pianka, M., J. Sci. Fd. Agric., 18, 63 (1967).
4. Kosolapoff, G.M., "Organophosphorus Compounds", p.236, Wiley, New York (1950).
5. Lynch, V.P., Analytical Methods for Pesticides and Plant Growth Regulators, Vol. III, p.135, Academic Press, London (1976).
6. Pianka, M., and Polton, D.J., J. Chem. Soc., 983 (1960).