

NEW SYNTHESIS OF CARBAMATE, THIOCARBAMATE AND UREA TYPE  
HERBICIDES: PREPARATION OF  $^{14}\text{C}$ -LABELLED DIURON AND E P T C.

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#### SUMMARY

N,N-dialkyl-carbamic acid-trimethylsilyl-esters were synthesized starting with  $^{14}\text{CO}_2$ . The new synthesis route is simple and provides good radiochemical yield. Silyl-carbamates directly or thorough carbamoyl-halogenides may be used for preparation of labelled herbicides: carbamates, thiocarbamates and ureas.

Key words: N-alkyl-trimethylsilyl-carbaminates, EPTC- $^{14}\text{C}$ ,  
diuron- $^{14}\text{C}$ .

#### INTRODUCTION

Carbamate, thiocarbamate and urea herbicides are widely

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used in modern agricultural practice.<sup>1,2</sup> The detailed knowledge of their metabolism, mode of action and environmental fate is of considerable importance. In order to facilitate related studies of representatives of these herbicides we needed the compounds labelled with radionuclides in various positions of the molecule. EPTC (S-ethyl-N,N-di-n-propyl-thiocarbamate; IV b) and diuron (N-3,4-dichlorophenyl-N,N'-dimethyl-urea; IV a) have been labelled with <sup>14</sup>C in the carbonyl moiety by new synthetic method.

Strongly basic primary and secondary amines absorb CO<sub>2</sub> producing stoichiometric amounts of N-mono- or di-substituted amine salts of carbamic acid. "Carbaminates" may be silylated by using trimethylchlorosilane. N-alkyl-carbamic acid-trimethylsilyl-esters<sup>3</sup> are produced almost 100 % yield, therefore starting from carrier free <sup>14</sup>CO<sub>2</sub> it is possible to prepare high specific activity labelled compounds. When chemically pure trimethylsilyl compounds are produced certain loss in yield may be observed. This loss is caused by not sufficiently dry vessels and atmosphere and because of the volatility of the products. Labelled N,N-dimethyl-carbamic acid-trimethylsilyl-ester (II a) was condensed with 3,4-dichloro-N-silyl-aniline producing diuron-carbonyl-<sup>14</sup>C (IV a) with 78 % yield. The by-product was hexamethyldisiloxane. Carbamoyl-chlorides may be produced with good yield by the reaction of substituted carbamic acid-silyl-esters and PCl<sub>5</sub>.<sup>4</sup>

3,4-Dichloroaniline may be acylated by N,N-dimethyl-carbamoyl-chloride, but the separation of aniline and diuron is difficult. When thiocarbamate type EPTC are produced it is

advisable to use lead mercaptide instead of alkali mercaptide for exchanging chlorine to sulphur in N,N-di-n-propyl-carbamoyl-chloride-carbonyl-<sup>14</sup>C (III b). The crude product was purified by molecular distillation.

#### EXPERIMENTAL

Melting and boiling points are uncorrected. Radioactivity measurements were carried out by liquid scintillation counting in a Packard TRI-CARB system. Radiochemical purity was determined with thin layer chromatography on Kieselgel 60/Kieselgur F<sub>254</sub> DC Alufolien Merck. The developed radiochromatograms were determined by Berthold thin layer scanner.

Chemical purity of EPTC was checked by gas liquid chromatography on a Packard 9800 GC instrument with 2 m long glass column packed with 5 % SE-30 on Chromosorb W, at 160 °C column temperature. The purity of diuron was checked on Packard 8000 liquidchromatograph with Whatman Partisil PXL 10/25 ODS column using methanol:water=80:20 solvent and UV detector.

The chemical and radiochemical purity of the labelled compounds is better than 99.8 %.

#### N,N-dimethyl-carbamic acid-trimethylsilyl-ester-carbonyl-<sup>14</sup>C (IIa)

In a solution of 540 mg 12 mmol dimethylamine<sup>+</sup> in 4 ml abs. dichloromethane 2 mmol <sup>14</sup>CO<sub>2</sub><sup>5</sup> thereafter 5 mmol unlabelled CO<sub>2</sub> was absorbed at -80 °C. The temperature of mixture was

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+ Dimethylamine was passed thorough a drying column packed with KOH. After condensation it was dried over KOH pellets for 24 hours, then distilled.

allowed to increase to  $-40^{\circ}\text{C}$  and under dry argon atmosphere 652 mg (6 mmol, 0.81 ml) trimethylchlorosilane in 1 ml dichloromethane was added dropwise over a period of 30 minutes with continuous stirring. White crystals precipitated. The reaction mixture was stirred for one hour and the solvent was removed by reduced pressure distillation. 10-15 ml petroleum ether was added and the amine.HCl was filtered off and washed with few ml of petroleum ether. The solvent was evaporated at atmospheric pressure at  $120-130^{\circ}\text{C}$  temperature. The almost colourless residue was distilled in vacuo into a trap kept at  $-80^{\circ}\text{C}$ . Yield 680 mg (4.2 mmol, 70 %) b.p.:  $56-57^{\circ}\text{C}$  (12-13 torr).

N,N-di-n.propyl-carbamic acid-trimethylsilyl-ester-carbonyl- $^{14}\text{C}$  (IIb).

This compound was prepared according to the method described formerly using 1210 mg (12 mmol, 1.62 ml) di-n.propylamine Yield 851 mg (3.9 mmol, 66 %) b.p.:  $91-92^{\circ}\text{C}$  (13 torr).

Diuron-carbonyl- $^{14}\text{C}$  (IVa).

A mixture of 680 mg (4.2 mmol) labelled N,N-dimethyl-carbamic acid-trimethylsilyl-ester and 950 mg (4.1 mmol) 3,4-dichloro-N-trimethylsilyl aniline<sup>+</sup> was kept in pressure bomb at  $180^{\circ}\text{C}$  for 16 hours. Over fawn-coloured solid product colourless liquid of hexamethyldisiloxane was accumulated. The dry product was filtered and washed with 5 ml of petroleum ether. 760 mg crude product was collected. After recrystallization

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+ To a solution of 3,4-dichloroaniline in  $\text{CH}_2\text{Cl}_2$  equivalent amount of trimethylchlorosilane was added dropwise while dry  $\text{NH}_3$  is flushing thorough the reaction mixture. After filtration and evaporation of solvent the 3,4-dichloro-trimethylsilylaniline was distilled in vacuo b.p.:  $143-144^{\circ}\text{C}$ , (12 torr).

from 4 ml ethanol the yield was 516 mg (2.2 mmol) m.p.: 156-157°C  
Radiochemical yield approximately : 566 MBq, 1.106 GBq/g, 38 % .

#### Diuron.

1130 mg (7 mmol) 3,4-dichloroaniline in 3 ml dichloro-  
methane was placed into the reaction flask. 365 mg (3.3 mmol)  
N,N-dimethyl-carbamoyl-chloride dissolved in 1 ml dichloro-  
methane was added dropwise thorough 30 minutes while the tem-  
perature was kept at 0 °C. Next day the solvent was removed by  
distillation and the solid residue was macerated with saturated  
solution of Na<sub>2</sub>CO<sub>3</sub> (pH: 10) and 3 X 15-20 ml petroleum ether  
then filtered; 800 mg fawn-coloured amorphous product was col-  
lected. Recrystallization from ethanol gave 440 mg, m. p.: 153-  
156 °C. TLC : R<sub>f</sub> 0.5, in solvent hexane:acetone = 1:1

#### N,N-dimethyl-carbamoyl-chloride (IIIa).

644 mg (4 mmol) N,N-dimethyl-carbamic acid-trimethylsilyl-  
ester in 1 ml chloroform was added to a slurry of 840 mg  
(4 mmol) PCl<sub>5</sub> in 1 ml abs. chloroform at 0 °C. The reaction  
mixture was stirred under dry argon for 30 minutes. After 1  
hour standing at room temperature reaction mixture turned to a  
clear solution. The solvent and the by-product POCl<sub>3</sub> were  
evaporated at atmospheric pressure (max. temperature 130 °C).  
The faint yellow coloured residue was distilled **in vacuo**.  
Yield 360 mg (3.3 mmol) colourless oil, b.p.: 54-56 °C  
(13 torr).

#### N,N-di-n.propyl-carbamoyl-chloride-carbonyl-<sup>14</sup>C (IIIb).

The labelled compound was prepared according to the above  
described method, using 851 mg (3.9 mmol) labelled N,N-di-  
n.propyl-carbamic acid-trimethylsilyl-ester. Yield 435 mg  
(2.6 mmol, 66 %), b.p.: 95-97 °C (12-13 torr).

EPTC-carbonyl-<sup>14</sup>C (IVb).

500 mg (1.5 mmol)  $\text{Pb}(\text{SC}_2\text{H}_5)_2$  was added to a solution of 435 mg (2.6 mmol) labelled di-n.propyl carbamoyl-chloride in 2 ml chlorobenzene and under argon atmosphere, at 140-150 °C was stirred for 3 hours; the initially yellow mercaptide faded. After cooling the reaction mixture was filtered, washed with petroleum ether, then the solvent was evaporated. The pale yellow residue was distilled in vacuo. Yield 367 mg (1.9 mmol) b.p.: 53-56 °C (1 torr). Radiochemical yield approximately : 388.5 MBq, 1.0/ GBq/g, 26 %. TLC:  $R_f$  0.15 in hexane:benzene = 30:2,  $R_f$  0.8 in hexane:ethanol = 30:2.

## REFERENCES

1. Herbicide Handbook of the Weed Society of America, Humphrey Press Inc, Geneva, New York, ed. 2, 1967.
2. Martin H.,-Pesticid Manual, British Crop Protection Concil, 1968.
3. Knausz D., Csákvári B., Meszticzky A. and Ujszászi K.- 5.th. Int. Symp. Organosilyl Chem. Karlsruhe, 1978.
4. Birkofer L. and Krebs K.- Tetrahedron Letters, 7 : 885 1968.
5. "Organic Syntheses with Isotopes", Murray A. and Williams D.L., Interscience Publishers Inc., New York, 1958.

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