

## Preparation of $^{32}\text{P}$ Labelled Compounds from Carrier Free $^{32}\text{P}$ \*

(received on 8 November 1965)

The increasing number of studies on  $^{32}\text{P}$  labelled phosphorothioate insecticides prompted us to study the preparation of  $^{32}\text{P}$  labelled compounds from carrier free  $^{32}\text{P}$ .

$^{32}\text{H}_3\text{PO}_4$  had been already employed, as raw material, in the synthesis of these compounds by chemical <sup>(1)</sup> or exchange <sup>(2, 3)</sup> reactions. We found a new technique <sup>(4)</sup> based on the reaction of carrier free  $^{32}\text{P}$  present in the residue of distillation of neutron irradiated sulphur <sup>(5)</sup>, which is known to contain  $^{32}\text{P}$  formed by  $^{32}\text{S}$  ( $n, p$ ) $^{32}\text{P}$  reaction, with inactive elements.

Exhaustive data, on the chemical form of  $^{32}\text{P}$  present in irradiated sulphur, have not yet been published <sup>(6)</sup>.  $^{32}\text{P}$  is believed to be present at least in part as elementary phosphorus, or as phosphorus sulphides <sup>(7)</sup>.

During the distillation of sulphur, in vacuo, substantial chemical changes must not occur in order for the  $^{32}\text{P}$  containing residue to be able to react, for example, with phosphorus and sulphur to give  $^{32}\text{P}_2\text{S}_5$  or with phosphorus and chlorine to give  $^{32}\text{PCl}_3$ .

The carrier free phosphorus prepared in this way can also exchange with organic or inorganic compounds.

Samples with a  $^{32}\text{P}$  activity of 20-30 mC/g of sulphur were obtained from sulphur cylinders (weight = 30 g) by irradiation in the SORIN's Avogadro reactor.

After distillation in vacuo of the irradiated sulphur, red phosphorus and sulphur in the 2 : 5 ratio were allowed to react in the presence of the residue. The reaction of phosphorus with chlorine was carried on in the same way. After purification we found that the compounds were radioactive. The combination yield was 50-95 % for  $^{32}\text{P}_2\text{S}_5$  and 20-50 % for  $^{32}\text{PCl}_3$ . Yields are remarkably influenced by oxidation reactions, which can affect sulphur during irradiation, particularly if this latter is carried out in air.  $^{32}\text{P}_2\text{S}_5$  is not contaminated by  $^{35}\text{S}$ .

This technique can be useful when applied for the preparation of all  $^{32}\text{P}$  labelled compounds whose syntheses require elementary phosphorus as raw material. Moreover, referring to the same amount of  $^{32}\text{P}$ , irradiated sulphur appears to be the cheapest material among those containing carrier free  $^{32}\text{P}$ .

\* This investigation is a part of a research programme sponsored by Euratom.

$^{32}\text{P}_2\text{S}_5$  and  $^{32}\text{PCl}_3$  prepared by this technique were used in the synthesis of many samples of *O,O*-dimethyl-S-2(2-phenyl-ethylacetate) phosphorodithioate  $^{32}\text{P}$  (trade name : Cidial) and *O,O*-diethyl-*O*-(3-4-tetramethylenumbelliferone)phosphorothionate  $^{32}\text{P}$  (trade name : Dition). The specific activities ranged from 10 to 27 mC/mmoles.

The exchange reaction between  $^{32}\text{P}$  residue of distillation of irradiated sulphur and preformed phosphorus compounds appeared to be less versatile.

The reaction was studied under the conditions reported in Table I.

TABLE I. Exchange reaction between  $^{32}\text{P}$  residue of distillation of irradiated sulphur and phosphorus compounds

Compound	Temperature °C	Time of heating h	Exchange yield %
$\text{P}_2\text{S}_5$ .....	300	3	42
$\text{PCl}_3$ .....	70-80	6	1
$\text{POCl}_3$ .....	105	10	5
$\text{PSCl}_3$ .....	150	41	7.2
$(\text{CH}_3\text{O})_2\text{POH}$ .....	130	10	38.2
$(\text{CH}_3\text{O})_2\text{PS}_2\text{H}$ .....	110	24	3.32

The yield is of practical interest only for  $\text{P}_2\text{S}_5$  and  $(\text{CH}_3\text{O})_2\text{POH}$ .

M. DUBINI

G. P. PERUCCA

G. Donegani Research Institute, Montecatini, Novara, Italy.

#### REFERENCES

1. MURRAY, D. H. and SPINKS, J. W. I. — *Canadian J. Chem.*, **30** : 497 (1952).
2. VIJNE, J. P. and TABAU, R. L. — *Bull. Soc. Pharm. Marseille*, **5** : 321 (1956).
3. CASIDA, J. E. — *Acta Chem. Scand.*, **12** : 1691 (1958).
4. DUBINI, M. (Montecatini Co.). — *Belgian Patent* No. 2,980 (1964).
5. CHARLTON, C. and STEVENSON, J. (UKAEA). — *British Patent* No. 765,489 (1957).
6. HALMANN, M. — *Chemical Reviews*, **64** : 689 (1964).
7. WHITMORE, F. E. — *Nature*, **164** : 240 (1949).