O,O-diethyl S-(*p*-bromophenyl)-phosphate, b.p. 115–117° (40 μ), $n^{25}\text{D}$ 1.5445 (calcd. for $C_{10}H_{14}O_3PSBr$: 36.93; H, 4.34; S, 9.62; Br, 24.39); 96% of triethyl phosphate, b.p. 33° (0.15 mm.), $n^{25}\text{D}$ 1.4036; and 81% of ethyl chloride.

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RECEIVED OCTOBER 24, 1956

THE DESULFURIZATION OF MERCAPTANS WITH TRIALKYL PHOSPHITES

Sir:

The attempted extension of the transesterification of triethyl phosphite with aliphatic alcohols[1] to mercaptans resulted in the formation of triethyl thionophosphate with simultaneous conversion of the alkanethiol to the corresponding alkane according to the equation $(C_2H_5O)_3P + RSH \rightarrow (C_2H_5O)_3PS + RH$. This unusual desulfurization reaction proceeds practically to completion at reflux temperature during several hours, or at a slower rate at room temperature, and is effectively catalyzed by ultraviolet irradiation.

Thus, a mixture of 83 g. (0.5 mole) of triethyl phosphite (previously distilled from sodium) and 73 g. (0.5 mole) of *n*-octyl mercaptan in a Pyrex flask fitted with a 24-in. fractionating column was irradiated with a General Electric 100-watt S-4 bulb at a distance of 5 inches from the flask. After 6.25 hours of irradiation, the mixture was distilled to give 50.3 g. (88%) of octane, b.p. 122.0–124.5°, $n^{25}\text{D}$ 1.3951–1.3959 (reported,[2] b.p. 125.59°, $n^{25}\text{D}$ 1.3953) and 90.9 g. (0.459 mole) of triethyl thionophosphate, b.p. 45° (0.50 mm.), $n^{20}\text{D}$ 1.4461 (reported,[3] b.p. 105–106° (20 mm.), $n^{20}\text{D}$ 1.4480, calcd. $n^{25}\text{D}$ 1.4460).

Likewise, 83 g. (0.5 mole) of triethyl phosphite and 62 g. (0.5 mole) of benzyl mercaptan were treated in an identical manner to give 43.1 g. (93.6%) of crude toluene, b.p. 90–110°, $n^{25}\text{D}$ 1.4945 (reported[4] 110.56°, $n^{20}\text{D}$ 1.4963, calcd. $n^{25}\text{D}$ 1.4942) and 94 g. (95%) of crude triethyl thionophosphate, b.p. 55° (0.9 mm.), $n^{25}\text{D}$ 1.4461–1.4500, contaminated with some benzyl mercaptan, b.p. 194°, $n^{25}\text{D}$ 1.5715.

Preliminary results show that a wide variety of thiols undergoes the reported desulfurization reaction with triethyl and other trialkyl phosphites. The results of a current investigation of the scope and mechanism of the reaction will be reported later.

[1] F. W. Hoffmann, R. P. Usinger, Jr., and R. J. Ess, THIS JOURNAL, **78**, 5817 (1956).

[2] A. F. Shepard, A. L. Henne and T. Midgley, Jr., *ibid.*, **53**, 1948 (1931).

[3] G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 258.

[4] W. T. Richard and J. H. Wallace, Jr., THIS JOURNAL, **54**, 2705 (1932).

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RECEIVED NOVEMBER 12, 1956

LABELING OF BENZENE WITH A CARBON-14 ION BEAM[1]

Sir:

A recent communication[2] described the production of labeled organic material with accelerated tritium ions, and the suggestion was made that C^{14} ions might be used for the same purpose. The labeling of organic compounds by C^{14} atoms derived from the $N^{14}(n,p)C^{14}$ reaction has been reported by several workers.[3] However, organic compounds thus labeled (using a nuclear reactor) are subjected to high neutron and gamma ray fluxes, and, in addition, the energy of the C^{14} atom (about 45,000 e.v.) is fixed. Both of these factors cause radiation decomposition to become a serious problem. During the past several months we have been observing the effects produced on irradiating solid benzene with a C^{14} ion beam in a mass spectrometer. Work in this direction has already been reported by Croatto and Giacomello.[4] Since there is great theoretical and practical interest in this type of experiment, we wish to present the results we have obtained in determining the efficiency of a C^{14} ion beam in labeling solid benzene. Benzene was chosen for this work because it is resistant to radiation decomposition and because its purification may be carried out with high efficiency by means of vapor-phase chromatography.

The carbon-14 ion beam was obtained using a 60°-sector, 15-cm. radius mass spectrometer. Labeled carbon dioxide (23% C^{14}) was introduced into the ion source and the singly charged, mass-14 beam thus produced (energy = 2 kv.) amounted to between 10^{-9} and 10^{-10} amp. During the irradiations, benzene vapor was directed slowly and continuously onto the surface of a cold trap at the target end of the spectrometer. This trap was maintained at $-155 \pm 5°$; a lower temperature would have led to condensation of carbon dioxide from the ion source.

The irradiated benzene (about 500 mg.) was purified by repeated passages through vapor-phase chromatographic columns[5] (elution-partition type); two different substrate liquids, silicone and Carbowax, were used.[6] Since labeled toluene is also a possible product in these irradiations,[7] toluene was added to the benzene after an irradiation and the toluene fraction was purified on the chromatographic columns along with the benzene. The specific radioactivity of the benzene and toluene fractions was determined by liquid-scintillation counting.

Two passages through Carbowax columns are

[1] The work described in this paper was sponsored by the U. S. Atomic Energy Commission.

[2] R. Wolfgang, T. Pratt and F. S. Rowland, THIS JOURNAL, **78**, 5132 (1956).

[3] *E.g.*, P. E. Yankwich, *et al.*, *J. Chem. Phys.*, **14**, 131 (1946); G. Giacomello, *Ricerca sci.*, **21**, 1211 (1951); A. P. Wolf and R. C. Anderson, THIS JOURNAL, **77**, 1608 (1955); A. G. Schrodt and W. F. Libby, *ibid.*, **78**, 1267 (1956).

[4] Abstracts of the Naples, 1954, Meeting of the Italian Society for Scientific Progress (S.I.P.S.). See also *Ricerca sci.*, **26**, 529 (1956).

[5] We wish to thank Drs. K. P. Dimick and J. Corse, Department of Agriculture, Western Utilization Research Branch, Albany, California, for the use of their vapor-phase chromatography apparatus.

[6] K. P. Dimick and J. Corse, *J. Food Tech.*, **10**, 360 (1956).

[7] A. G. Schrodt and W. F. Libby, THIS JOURNAL, **78**, 1267 (1956).