

stainless steel planchets as uniformly thin films (<2 mg. per sq. cm.).

$P_2^{32}S_5$ was assayed following hydrolysis with dilute NH_4OH which served to distribute the sample more uniformly.

The dithioic acid, which showed a significant vapor pressure and per se leads to contamination of the counter window, was assayed as the sodium salt, which is nonvolatile.

Ethion- P_2^{32} was assayed by counting a suitable aliquot of an ethyl alcohol solution.

Paper chromatograms were prepared with ethion- P_2^{32} by means of several solvent systems. When the chromatograms were autoradiographed, it was not possible to resolve clearly any impurities with the exception of a qualitative indication of a small amount of dithioic acid.

A silicic acid column chromatographic procedure (7) was employed to obtain additional information. Radiometrical assay of the ethion fraction indicated that the original sample had a purity of 90% which was in excellent agreement with the chemical assay of this fraction. The rest of the radioactivity was contained in five components present to the extent of 0.3 to 2.8%. These could not be further identified.

VAPOR PRESSURE OF ETHION. For the vapor pressure studies, the radioactive ethion was initially purified by means of a silicic acid column. Following the evaporation of the solvent, the residue which consisted of pure ethion-

P_2^{32} was brought to constant weight by heating in vacuo at 40° C.; the liquid was next transferred to a 1-ml. beaker which was then placed in a brass vessel. The latter was closed by a thin (1 ml.) plate equipped with a cylindrical orifice of known dimensions through which the vapor could effuse into a highly evacuated space (<0.1 micron) and condense upon the center of a chilled stainless steel coupon or disk. The latter was secured to the cold finger of a sublimation apparatus by means of high-vacuum grease. The technique is essentially similar to that of Carson *et al.* (2), except that the use of the demountable coupon lends itself, it is believed, to a more reproducible and accurate means of counting the distillate. Initially, the specific activity was determined by counting minute quantities of the purified radioactive ethion which had been weighed out on similar coupons with a microbalance.

The first half hour's reading was subtracted from that of a subsequent 1 hour's run. This automatically corrected for any uncertainty about just when the good vacuum took effect during the first few minutes of the run (5). The apparatus was calibrated using National Bureau of Standards benzoic- C^{14} acid. Runs were made at three constant temperatures—namely, 43°, 56°, and 67° C.—and the weight of the ethion was determined from the activity deposited on the coupon. A plot of log vapor pressure vs. $1/T$ gave a

straight line which fits the equation

$$\log_{10} P \text{ (mm.)} = 12.39 - \frac{5440}{T}$$

This equation gives 1.5×10^{-6} mm. for the vapor pressure of ethion at 25° C.

Acknowledgment

The authors are grateful for the help from John E. Zarembo and the analytical section who analyzed the ethion- P_2^{32} . The infrared spectrum of the product was determined and interpreted by Herman Adelman.

Literature Cited

- (1) Bowman, J. S., Casida, J. E., *J. Agr. Food Chem.* **5**, 192-7 (1957).
- (2) Carson, A. S., Stranks, D. R., Wilmshurst, B. R., *Proc. Roy. Soc. (London) Ser. A* **244**, 72 (1958).
- (3) Casida, J. E., *Acta Chem. Scand.* **12**, 10-11 (1958).
- (4) Kinsman, S., *et al.*, eds., "Radiological Health Handbook," p. 176, Bureau of State Services, Cincinnati, Ohio, 1956.
- (5) Mack, E., Jr., Francc, W. G., "Laboratory Manual of Elementary Physical Chemistry," 2nd ed., pp. 71-3, Van Nostrand, New York, 1946.
- (6) Siwinski, G. W., Food Machinery and Chemical Corp., Niagara Chemical Division, unpublished data.
- (7) Zarembo, J. E., Gilbert, B. L., Food Machinery and Chemical Corp., Chemical Research Center, unpublished data.

Received for review July 5, 1960. Accepted October 14, 1960.

ISOTOPE-LABELED INSECTICIDES

Preparation of Labeled 2-Ethylthioethanol, a Demeton Intermediate

KERMIT GROVES and ROGER HAGUWITZ

Department of Agricultural Chemistry, Washington State University, Pullman, Wash.

A small scale synthesis of 2-ethylthioethanol by the catalytic condensation of ethylene oxide and ethyl mercaptan is described. A S^{35} or C^{14} label may be incorporated in the alcohol, which is an intermediate in the preparation of demeton.

THE SYSTEMIC insecticide demeton, *O,O*-diethyl *O*-ethylmercaptoethyl phosphorothioate, is prepared conventionally by the reaction of diethylchlorothionophosphate with the sodium salt of 2-ethylthioethanol, or with the alcohol in the presence of copper and potassium carbonate (8). The first step in the

enzymatic-, acid-, or base-catalyzed hydrolysis of demeton results in formation of 2-ethylthioethanol (4). Labeling of sulfur or carbon in this alcohol is of interest in investigations of the reactions of the insecticide in biological systems.

2-Ethylthioethanol has been prepared by the reaction of ethylene chlorohydrin

with the sodium salt of ethyl mercaptan (3, 6, 9, 10), diethyl sulfate with the sodium salt of β -thioethanol (7), and ethylene oxide with ethyl mercaptan (2, 7). These procedures were examined to determine their practicality for labeling syntheses. In small scale preparations of labeled material, it is desirable

to use a method that gives good yields of pure product with a minimum of transfers in order to avoid mechanical losses.

Nenitzescu and Scarlatesca obtained 2-ethylthioethanol by passing ethylene oxide through a packed tower containing ethyl mercaptan, and by reacting the compounds in a closed vessel with activated carbon (7). We found that both procedures gave poor yields in small scale preparations. The condensation of ethylene oxide with ethyl mercaptan was investigated further, by reacting equal molar quantities of the reagents in sealed tubes in the presence of catalytic amounts of one of the following: metallic sodium, aluminum oxide, silica, sulfuric acid, and aluminum chloride. Anhydrous aluminum chloride gave promising results, but the other catalytic materials either were not effective, or carried the condensation too far, forming highly viscous products. Condensation in the presence of aluminum chloride could be controlled, and optimum concentration, temperature, and time of reaction were determined. It was found that the reaction could be carried out in a tightly stoppered flask, thus avoiding transfer from a sealed tube. S^{35} -labeled ethyl mercaptan was used in the synthesis, but C^{14} -labeling could be effected by use of the appropriately labeled reagents.

Larger scale preparations can be made by this procedure, if a rise in

temperature during the reaction is prevented by constant stirring and cooling in a water bath.

Experimental Procedure

One-tenth gram of anhydrous aluminum chloride was placed in a 15-ml. conical flask fitted with a 15/35 standard taper stopper that could be clamped in position. The ampoules of ethylene oxide and labeled ethyl mercaptan, two 10-ml. graduated cylinders, and the flask were chilled in a dry ice-acetone bath. After cooling, 4.0 ml. (54 mmoles) of ethyl mercaptan and 2.5 ml. (53 mmoles) of ethylene oxide were added to the flask, the contents mixed, and the stopper was clamped in place. The flask was removed from the bath and allowed to stand at room temperature (25° C.) for 24 hours. A longer period of standing produced no apparent change in yield. A small distilling head and condenser were attached to the flask and the product was distilled at 60° to 62° C. at 5 mm. of Hg pressure, yielding 4.2 grams of product (75% based on the mercaptan), n_D^{25} 1.4828, and d_4^{25} 1.013. The theoretical amount of bromine was absorbed when the product was titrated with standard bromate-bromide solution (5). The sample was analyzed at 120° C., by gas-liquid chromatography, on a 1/4-inch silicone column, 5 feet long with helium as carrier gas. No

impurities were observed and the retention time was the same as that of a pure, authentic sample of ethylthioethanol. Infrared absorption curves for the two samples were identical for the range 2.8 to 15 μ .

Literature Cited

- (1) Bergmann, E. D., *J. Am. Chem. Soc.* **74**, 828 (1952).
- (2) Culvenor, C. C. J., Davies, W., Heath, N. S., *J. Chem. Soc.* **1949**, 278.
- (3) Dumuth, Robert, Meyer, Victor, *Ann.* **240**, 307 (1887).
- (4) Gardner, K., Heath, D. F., *Anal. Chem.* **25**, 1849 (1953).
- (5) Groves, Kermit, *J. Agr. Food Chem.* **6**, 30 (1958).
- (6) Kirner, W. R., *J. Am. Chem. Soc.* **50**, 2446 (1928).
- (7) Nenitzescu, D. D., Scarlatesca, N., *Ber.* **68B**, 587 (1935).
- (8) Schrader, G. (Farbenfabriken Bayer, Leverkusen, Germany), U. S. Patent **2,571,989** (Oct. 16, 1951).
- (9) Steinkopf, W., Herold, J., Stohr, J., *Ber.* **53B**, 1007 (1920).
- (10) Windus, W., Marvel, C. S., *J. Am. Chem. Soc.* **52**, 2576 (1930).

Received for review November 28, 1960.
Accepted February 7, 1961. Investigation supported in part by funds provided for biological and medical research by the State of Washington, Initiative Measure No. 171. Scientific Paper No. 2038, Washington Agricultural Experiment Stations. Work conducted under Project No. 1229.

Chromatographic Separation of Heptachlor, Gamma Chlordan, and Heptachlor Epoxide from High-Heptachlor Residues

HAROLD W. RUSK and
J. E. FAHEY

Entomology Research Division,
Agricultural Research Service,
U. S. Department of Agriculture,
Vincennes, Ind.

ANALYTICAL methods recently developed for the determination of heptachlor and heptachlor epoxide in forage crops use chromatographic columns to separate heptachlor from its epoxide (1, 2). The column recommended is activated Florex (a specially selected form of hydrated fuller's earth) and the solvents used are pentane (colorimetric grade) for heptachlor, followed by 2% ethyl ether in pentane for heptachlor epoxide. In the application of this technique to the determination of heptachlor residues on several crops, an apparent spilling over of heptachlor into the ether-pentane fraction which contained the heptachlor epoxide was observed. With low residues the quantity of apparent heptachlor found in the epoxide residues was very small and

usually negligible. When high heptachlor residues were determined, there was an increase in the quantity of apparent heptachlor spilling over into the heptachlor epoxide fraction with resultant interference in analysis of heptachlor epoxide. Processing the residues twice on the Florex column did not decrease the contamination, indicating that it was not a simple spilling of excessive heptachlor into the epoxide.

Following a suggestion (3) that the contaminating material was gamma chlordan, a minor constituent of technical heptachlor, the authors directed their efforts toward separating gamma chlordan from heptachlor epoxide by column chromatography. Since Florisil (a synthetic magnesia-silica gel) has been observed to have a slower elution

rate than Florex, it was thought that Florisil could be used for this purpose.

Experimental

Procedure. With 50-ml. Mohr burets as chromatographic tubes, columns were prepared, using 10 grams of activated Florex (washed with pentane, dried, and heated at 135° C. for 24 hours) and 15 grams of activated Florisil (washed with hexane, dried, and heated at 130° C. for 24 hours). Solutions from corn plants that contained about 300 μ g. of heptachlor, 30 μ g. of gamma chlordan (evaluated as heptachlor), and 100 μ g. of heptachlor epoxide were processed on these columns. The columns were wet with pentane and the solutions were added to the columns and eluted with