been expected if a 1,4-butanemercurinium salt had been an intermediate in the reaction. It is unfortunate that 4-methoxycrotylmercuric salt could not be found since its geoisomeric configuration should have been significant.[3] The only contaminant which can be isolated is 1,4-dichloromercuri-2,3-dimethoxybutane (estimated as 0.5% of theoretical yield).

Experimental[4]

4-Chloromercuri-3-methoxy-1-butane. A. Preparation.—To a solution of 31.8 g. (0.1 mole) of mercuric acetate in 300 ml. of methanol at 0° was added 16.3 g. (0.3 mole) of 1,3-butadiene in 50 ml. of methanol. After 5 minutes at this temperature the system gave a negative test for mercuric ion so it was filtered into 100 ml. of 10% aqueous sodium chloride. The precipitated oil was taken up in 100 ml. of chloroform. This extract was twice washed with water and then was evaporated at room temperature leaving 29.1 g. (91%) of product, m.p. 40–44°. This was extracted with 60 ml. of hot methanol leaving 30 mg., m.p. 140–150°. After two hours at room temperature 90 mg., m.p. 146–156°, was precipitated. The two crops (0.14%) of 1,4-dichloromercuri-2,3-dimethoxybutane, combined and crystallized from 24 ml. of methanol, were thus purified to melt at 163–165°. A mixture melting point with an authentic sample was not depressed.

Evaporation of the extract from which the dichloromercurial had been partly removed yielded successive crops of the monochloromercurial, the first and major crop of which melted at 49.2–50° (unchanged by crystallization from methanol, 2 ml. per g.). The less-pure crops, as well as the evaporated mother liquor, could be purified by solution in aqueous alkali followed by acidification with gaseous carbon dioxide after 5 hours; the precipitate ultimately was crystallized from methanol, m.p. 49–50°.

Anal. Calcd. for C_5H_9ClHgO: C, 18.7; H, 2.82. Found: C, 18.9; H, 2.95.

B. **Ozonization.**—A solution of 0.337 g. (0.001 mole) of 4-chloromercuri-3-methoxy-1-butene in 10 ml. of dry chloroform (pre-ozonized, sulfuric acid and water washed) was ozonized for 1 hour at 0°. After vacuum evaporation of the solvent the ozonide was hydrolyzed overnight by 200 mg. of zinc dust in 10 ml. of water. The hydrolysate was distilled and the distillate diluted with an equal volume of ethanol. A drop of piperidine and 0.3 g. of dimedone were added and the system was warmed for 5 minutes on the steam-bath. Water was then added until precipitation occurred and the system cooled to 0° was filtered. The vacuum dried formaldehyde–dimedone derivative, 0.096 g. (31%), melted at 189.5–191.5° and was identified by mixture melting point.

1,4-Dichloromercuri-2,3-dimethoxybutane.—A solution of 0.78 g. (0.0024 mole) of 4-chloromercuri-3-methoxy-1-butene in 5 ml. of methanol was treated with 0.76 g. (0.0024 mole) of mercuric acetate in 10 ml. of methanol. After 2 hours the system was added to 10 ml. of 10% aqueous sodium chloride solution. The precipitate, 0.83 g. (59%), m.p. 132–138°, was twice crystallized from ethanol (200 ml. per g.), m.p. 165–166°.

Anal. Calcd. for $C_6H_{12}Cl_2Hg_2O_2$: C, 12.2; H, 2.05. Found: C, 12.2; H, 2.31.

This compound was also accessible from 1,3-butadiene by utilization of 2 equivalents of mercuric acetate in the procedure outlined for the monomercurial.

1,4-Diacetoxymercuri-2,3-dimethoxybutane.—To a solution of 2.67 g. (0.005 mole) of 1,4-dichloromercuri-2,3-dimethoxybutane in 125 ml. of methanol was added 1.67 g. (0.01 mole) of silver acetate. After 30 minutes shaking the silver chloride was filtered off, 1.33 g. (92%). The filtrate, partially vacuum evaporated, yielded 2.35 g. (74%), m.p. 150–153°. Crystallization from ethanol (10 ml. per g.) gave a product, m.p. 153–154°, which was identical according to mixture melting point with that previously prepared.[2]

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(3) K. Mislow and H. M. Hellman, THIS JOURNAL, **73**, 244 (1951).

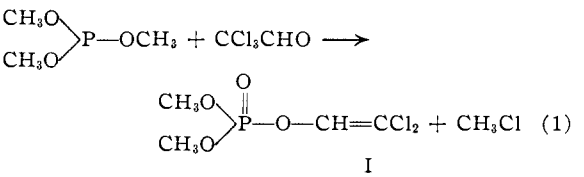
(4) Melting points have been corrected against reliable standards.

The New Insecticide O,O-Dimethyl 2,2,2-Trichloro-1-hydroxyethylphosphonate

BY W. LORENZ, A. HENGLEIN AND G. SCHRADER

RECEIVED NOVEMBER 18, 1954

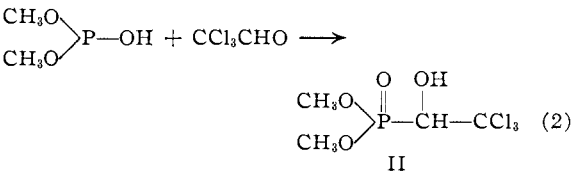
The condensation of chloral and trialkyl phosphite[1] yields O,O-dialkyl O-(2,2-dichloroethenyl)-phosphate in an interesting reaction with the elimination of alkyl chloride



I

This new group of phosphoric esters shows high insecticidal activity associated with a high degree of toxicity toward mammals.[2]

The condensation of chloral and dimethyl phosphite proceeds quite differently to yield O,O-dimethyl 2,2,2-trichloro-1-hydroxyethylphosphonate (II)[3,4]



II

The ester II is a solid readily soluble in water. The determination of its molecular weight revealed that it is present in the bimolecular state.[6] It is relatively non-toxic to mammals. The following LD-50 values were found: rat oral 450 mg./kg., rat (male) intraperitoneal[7] 225 mg./kg., mouse subcutaneous 400 mg./kg., mouse intraperitoneal 500 mg./kg.[7] 100% mortality of houseflies was obtained in 11 minutes at a concentration of 0.01%, in 24 minutes at 0.001%, and in 280 minutes at 0.0001%.

The ester II is relatively stable at room temperature in aqueous solution. In an alkaline medium, however, a very interesting rearrangement takes place.

TABLE I

Time, hr.	Alkaline dec. at room temperature: Ml. of 0.1 *N* NaOH[a] used/g.	Dec., %	Dec by boiling in water at 100°; determination of acid liberated: Ml. of 0.1 *N* NaOH used/g.	Dec., %
1	152.5	78	22.3	11.5
2	174.5	90	45.5	23.3
3	178.5	91	63.8	33.0
4	183.2	94	88.5	45.6
8	192.0	99	92.0	47.5

[a] 1 equivalent = 19.4 ml. of 0.1 *N* NaOH.

(1) W. Perkow, *et al.*, *Chem. Ber.*, **87**, 755 (1954).

(2) W. Perkow, K. Ullerich and F. R. Meyer, *Naturwissenschaften*, **39**, 353 (1952).

(3) W. Lorenz, U. S. Patent 2,701,225.

(4) This compound has been made available as an insecticide in 1952 under the code number Bayer L 13/59. It has been later described by Barthel, Giang and Hall.[5] It is currently being marketed under the trade name Dipterex.

(5) W. F. Barthel, P. A. Giang and S. A. Hall, THIS JOURNAL, **76**, 4186 (1954).

(6) V. S. Abramow, *Doklady Acad. Nauk.* (*U.S.S.R.*), **73**, 487 (1950); *J. Gen. Chem.* (*U.S.S.R.*), **22**, 547 (1952).

(7) K. P. DuBois and G. J. Cotter, A.M.A. Archives of Industrial Hygiene and Occupational Medicine, in press.

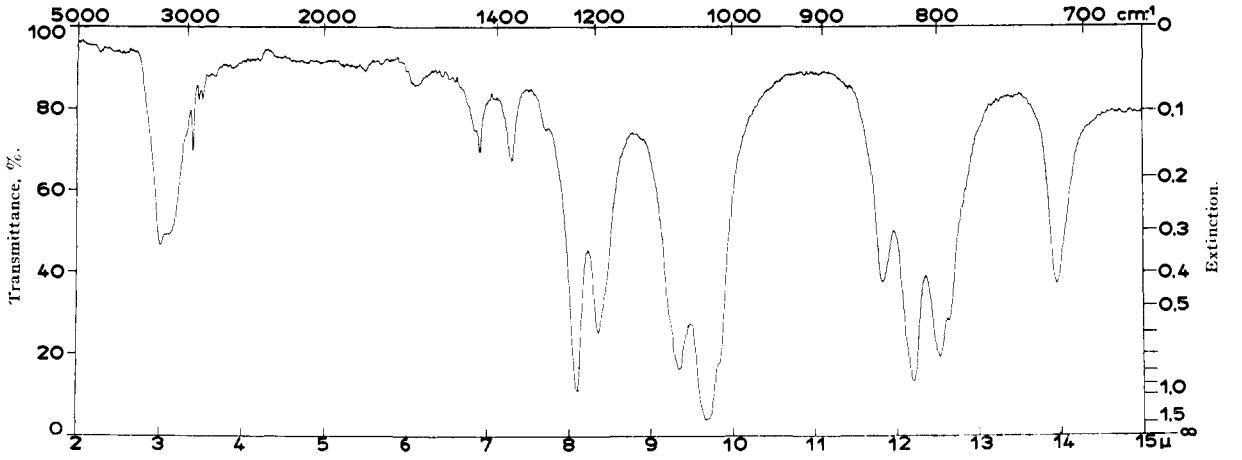


Fig. 1.—Infrared spectrum of ester II (1 mg. of ester II and 300 mg. KBr pressed).

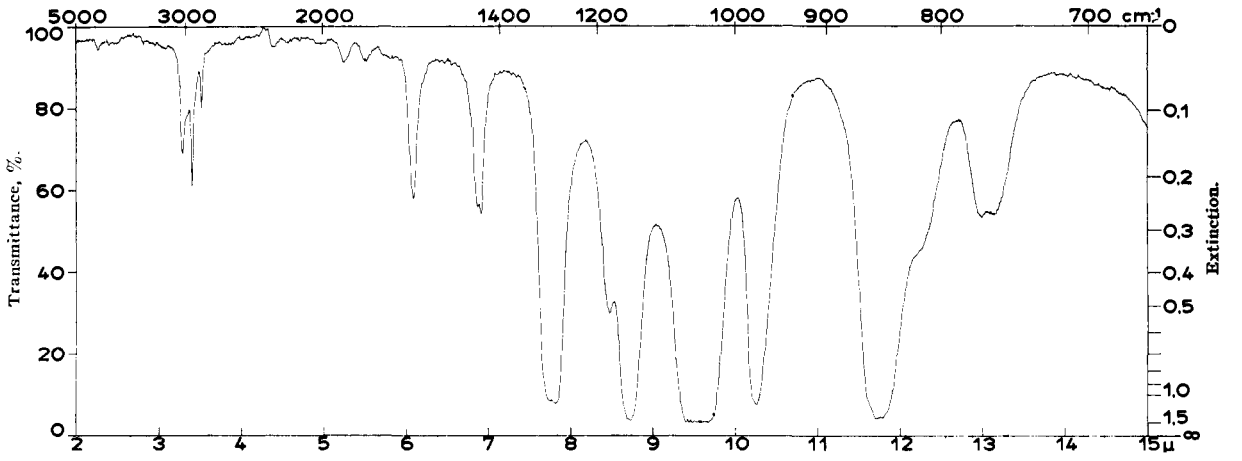
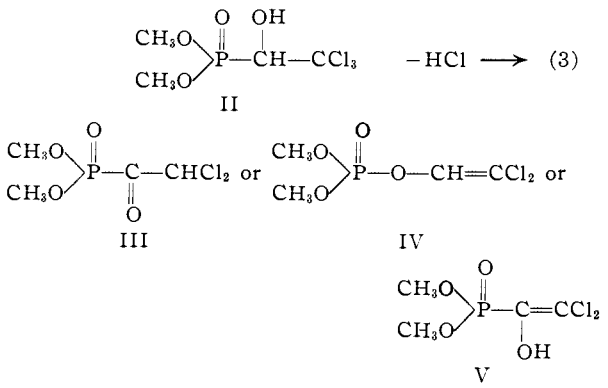


Fig. 2.—Infrared spectrum of the product obtained by alkaline treatment of ester II.

Upon treatment with mild alkali in aqueous solution, the ester II releases one mole of HCl, and a new, slightly water soluble compound results for which the structural formula III has been suggested.[8]



However, it is conceivable that this compound has either structure IV or V.

The products of reactions (1) and (3) have been prepared, and their physical characteristics such as boiling point, index of refraction and density are identical. A comparison of the infrared spectra for O,O-dimethyl 2,2,2-trichloro-1-hydroxyethylphosphonate (II, Fig. 1), and the product of reaction (3) establishes structure IV as the correct one for the dehydrochlorination product, from the following evidence.

In accordance with its structural formula, the spectrum of II shows a broadened band at 3.15 μ due to the –O–H valency vibration. This band is missing in the spectrum of the product obtained by elimination of HCl. Thus, formula V may be disregarded as being the structure of this compound.

The spectrum of the product of reaction (3) shows a band at 6.07 μ, having approximately the intensity of the band of the C–H deformation vibration at 6.9 μ. The intensity and wave length of this band indicate that it results from the valency vibration of a polarized (terminal) $\rangle C{=}C$ bond. The band should possess a greater intensity when caused by a $\rangle C{=}O$ valency vibration according to formula III. In general, the absorption of a $\rangle C{=}O$ vibration is of the same order as the absorption of a $\rangle P{=}O$ vibration; the latter, however, produces a much more intense band at 7.8 μ than the 6.7 μ band in the spectrum of Fig. 2. Furthermore, the absorption of the $\rangle C{=}O$ vibration is expected at a shorter wave length. Although it cannot be excluded that the $\rangle C{=}O$ bond may obtain the character of a

(8) A. M. Mattson, J. T. Spillane and G. W. Pearce, paper presented at the A.C.S. meeting in New York on September 17, 1954.

single bond due to the adjacent >P=O bond in the formula III (as it is the case with carboxylic acid amides), it appears improbable that such a decrease in intensity of the >C=O band occurs. Thus, this region of the spectrum suggests formula IV as the reaction product.

In the range of the H valency vibrations the reaction product has several absorption maxima. The sharp maxima at 3.51 μ and at 3.40 μ with a weak shoulder at 3.33 μ are caused by the methyl groups. However, the band at 3.28 μ can no longer be assigned to a methyl group. Because of its longer wave length and sharpness this band cannot be an O–H band. Therefore, it corresponds to the C–H valency vibration of the >C=CH group.[9,10] Thus, an additional proof is given for formula IV.

In the spectra of isomeric O,O-dialkyl phosphates and O,O-dialkyl phosphonates,[11] the maxima of the >P=O band are 7.8 and 8.1 μ, respectively. The >P=O band of the phosphonates dissolved in CS is split into a doublet, whereas in the phosphates the band is slightly displaced toward a shorter wave length while its form is preserved. The >P=O band of the reaction product is at 7.8 μ, and after dissolving this substance in CS_2 it is split into a doublet at 7.67 and 7.81 μ. Therefore, this region of the spectrum is additional evidence for structural formula IV.

This rearrangement of O,O-dimethyl 2,2,2-trichloro-1-hydroxyethylphosphonate is of considerable theoretical interest as it represents the first reported instance of such transformation of a phosphonate to a phosphate.

The phosphoric acid ester IV is considerably more toxic to rats, mice and houseflies than the phosphonate II. Thus, the LD-50 values for IV are: rat oral 25 mg./kg., mouse subcutaneous 25 mg./kg.; and the LD-100 values to the housefly were: contact 0.01 γ and oral 0.005 γ, as opposed to 0.1 γ and 0.03 γ, respectively, for II.

Experimental Part

O,O-Dimethyl 2,2,2-Trichloro-1-hydroxyethylphosphonate (II) was prepared following the procedures described by Lorenz.[3] These differ from the method later described by Barthel, *et al.*,[4] only in that a reaction temperature of 120–130° was used, and that the product was recrystallized from water.

O,O-Dimethyl O-(2,2-Dichloroethenyl) Phosphate (IV) from Ester II by Alkaline Treatment.—One hundred and twenty-nine grams (0.5 mole) of O,O-dimethyl 2,2,2-trichloro-1-hydroxyethylphosphonate is dissolved in 500 ml. of water and warmed to 30°. A solution of 20 g. (0.5 mole) of sodium hydroxide in 50 ml. of water is added dropwise with stirring. The temperature rises and O,O-dimethyl O-(2,2-dichloroethenyl) phosphate (IV) separates as a colorless oil. The oil is dissolved in benzene, washed twice with ice-water and then dried with sodium sulfate (sicc.). On fractionating the benzene solution 54 g. of IV having the boiling point 86–87° at 3 mm. are obtained; yield 58% of the theoretical; $n^{20}D$ 1.4541; d^{20}_4 1.423.

Anal. Calcd. for $C_4H_7O_4Cl_2P$: Cl, 32.09; OCH_3, 28.08. Found: Cl, 31.34; OCH_3, 28.36.

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(9) V. Z. Williams, *Rev. Sci. Instr.*, **19**, 143 (1948).

(10) W. Brügel, "Einführung in die Ultrarotspektroskopie," Verlag von Dr. Dietrich Steinkopff, Darmstadt, 1954, p. 209.

(11) A detailed report will appear in *Zeitschrift für Naturforschung*.

The Complete Degradation of Carbon-14 Labeled Succinic Acid and Succinic Anhydride by the Schmidt Reaction[1]

BY E. F. PHARES AND MARY V. LONG

RECEIVED NOVEMBER 11, 1954

Succinic acid labeled with isotopic carbon previously has been degraded completely by the use of various combinations of enzymatic and chemical steps[2] and by the Curtius reaction.[3] These methods are laborious, and the last procedure gave less than 30% yield of the methylene carbons.

A partial degradation employing the Schmidt reaction as applied to fatty acid degradation[4] has been used by Strassman and Weinhouse,[5] and at this Laboratory. A 70% yield of carbon dioxide from the carboxyl carbons is obtained by this method, but the recovery of ethylenediamine, derived from the methylene carbons, is only 10% when steam distillation is used for isolation. The same yield was reported when precipitation of the picrate derivative was employed.[6] With these low recoveries, carbon-14 specific activity values for the methylene carbons usually must be calculated by difference.[5]

The present paper presents: (a) a procedure which increases the recovery of ethylenediamine from the Schmidt reaction by vacuum distillation, and (b) an additional step involving conversion of the succinic acid to the anhydride prior to degradation, which considerably increases the yield of both products.

When vacuum distillation was used for separation of the ethylenediamine, 45% yields of products having satisfactory specific activities were obtained (Table I). Excellent agreement of melting points of dibenzenesulfonamide and dibenzamide derivatives of this product with the literature val-

TABLE I

CARBON RECOVERIES AND SPECIFIC ACTIVITIES

Starting compd.	Yield,[a] % CO_2	Ethylenediamine[e]	Relative C^{14} Specific activities[b] Carboxyl	Methylene
Sodium succinate-2-C^{14}	75	45	0.28	101.0 ± 1.6[c]
Sodium succinate-1-C^{14}	63	42	99.0	0.56
Succinic anhydride-2-C^{14}	84[d]	73	0.10	97.0
Succinic anhydride-1-C^{14}	85[d]	64	97.9	0.05
Succinic anhydride	95	71		
	91	71		
	82	78		

[a] Assayed as barium carbonate. [b] Total molecule × 2 = 100. [c] Standard deviation of six degradations. [d] Over-all yields from succinic acid. [e] Isolation by vacuum distillation.

(1) Work performed at the Oak Ridge National Laboratory under Contract Number W-7405-Eng-26 for the Atomic Energy Commission.

(2) (a) M. Calvin, C. Heidelberger, J. C. Reid, B. M. Tolbert and P. F. Yankwich, "Isotopic Carbon," John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 253–255; (b) S. F. Carson, J. W. Foster, W. E. Jefferson, E. F. Phares and D. S. Anthony, *Arch. Biochem. Biophys.*, **33**, 448 (1951).

(3) A. A. Benson and J. A. Bassham, THIS JOURNAL, **70**, 3939 (1948).

(4) E. F. Phares, *Arch. Biochem. Biophys.*, **33**, 173 (1951).

(5) M. Strassman and S. Weinhouse, THIS JOURNAL, **74**, 3457 (1952); *ibid.*, **75**, 1680 (1953).

(6) M. Oesterlin, *Z. angew. Chem.*, **45**, 336 (1932).