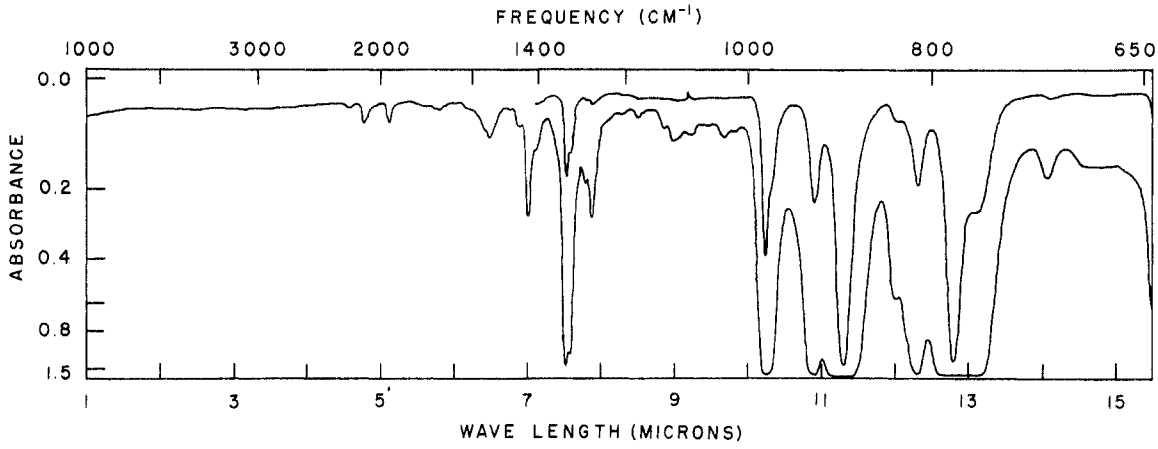

FIG. 1. INFRARED SPECTRA OF TETRACHLOROETHYLENE OXIDE; Determined on the pure liquid in a 0.0273 mm. cell; and a 2.5% carbon disulfide solution in a 0.109 mm. cell (10–14 microns).

to hexachloroethane by addition of chlorine and exposure to sunlight. This solution was distilled through an 18-in., modified center-rod column at 40° (65 mm.). A trace of trichloroacetyl chloride was removed with a caustic-water wash and the material was dried with calcium chloride. One hundred ml. of purified tetrachloroethylene oxide was recovered, n_D^{25} 1.4588, d_4^{25} 1.63, b.p. *ca.* 110° (1 atm.), f.p. −58° to −59° (corr.). Molecular weight, by freezing point depression of benzene, was 189 (theoretical 182). Boiling point data are in Table I.

Anal. Calcd. for C_2Cl_4O: Cl, 78.0%. Found 77.5%.

TABLE I

BOILING POINT DATA OF TETRACHLOROETHYLENE OXIDE

Pressure, Mm.	Temperature, ° C.
50	35.2
100	50.8
150	60.3
200	68.5
250	74.5
760 (Extrapolated)	109

Oxidation of tetrachloroethylene at various temperatures. Chlorine and oxygen were continuously passed through 35–40 ml. tetrachloroethylene in a 50–60 ml. glass bulb with the solution exposed to sunlight. Temperature was controlled externally. The results are given in Table II.

TABLE II

OXIDATION OF TETRACHLOROETHYLENE AT VARIOUS TEMPERATURES

Temperature, ° C.	Reaction Time (Min.)	$(CCl_2)_2O$, Vol. %	CCl_3COCl, Vol. %
−3–0	30	Trace	7
60–75	30	5	16
80	25	6[a]	20[a]

(a) Results are analyses of filtrate after the solution was cooled and filtered to remove excess hexachloroethane. Filtrate contained 21% C_2Cl_6.

Thermal rearrangement. Tubes containing the epoxide were immersed in boiling baths of methanol (65°), benzene (80°), and water (100°). The solutions were analyzed by infrared at 1-hr. intervals.

Reactions. A. Tetrachloroethylene oxide (9×10^{-4} mole) was stirred with 1*N* sodium hydroxide solution. A gas slowly evolved (5×10^{-4} mole) which was identified by infrared analysis to be carbon monoxide. The solution was extracted with carbon disulfide and tests for chloride and trichloroacetate on the extract were positive.[11]

B. Tetrachloroethylene oxide (9×10^{-3} mole) was stirred with 12*N* sulfuric acid, evolving a gas (3.5×10^{-3} mole) whose infrared analysis showed it to contain carbon monoxide and carbon dioxide. The acid solution contained 1.45×10^{-2} equivalent of chloride.

C. Tetrachloroethylene oxide, stirred with 96% H_2SO_4, reacted rapidly (exothermic) without evolution of gas. Infrared analysis of the acid-insoluble layer showed it to be trichloroacetyl chloride.

D. Tetrachloroethylene oxide (2.2×10^{-3} mole) was dissolved in 1*N* potassium hydroxide-methanol solution. The solution was acidified with hydrochloric acid, then boiled to remove the methanol and excess hydrogen chloride. Saturated barium chloride solution was added and a precipitate (0.37 g.) was collected. This product was undoubtedly barium oxalate, and corresponded to 1.65×10^{-3} mole of the latter.

E. With methanol containing a small amount of mercuric chloride, tetrachloroethylene oxide undergoes a rapid exothermic reaction after an induction period of a few minutes. The infrared spectrum of the reaction product is almost identical to that of methyl trichloroacetate.

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(11) $AgNO_3$ was used for chloride test; cuprous chloride and ammonia for trichloroacetate test.

A Crystalline Monoprocaine Salt of Pyridoxal Phosphate

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Pyridoxal phosphate is a coenzyme involved in transamination processes, in amino acid decar-

boxylation, in thioether cleavage, and in other enzymatic reactions. Crystalline sodium[1,2] and acridine[3] salts have been reported. We should like to describe here the preparation of a crystalline monoprocaine salt of the coenzyme.

Pyridoxamine dihydrochloride was phosphorylated with a mixture of phosphoric acid and phosphorus pentoxide,[4] and the product was isolated in crystalline form[5] by means of ion-exchange chromatography on Amberlite resin IRC-50. The pyridoxamine phosphate was oxidized to pyridoxal phosphate by manganese dioxide in aqueous solution at *p*H 6. The coenzyme was separated from inorganic compounds and was obtained as a bright yellow solid[2] by drying its aqueous solution in the frozen state.

The procaine salt was prepared by dissolving pyridoxal phosphate in water and adding to the solution an ethanolic solution of one equivalent of procaine. The procaine salt of pyridoxal phosphate crystallized in the form of orange needles.

Bioassay of the crystalline monoprocaine salt of pyridoxal phosphate by Dr. W. W. Umbreit of the Merck Institute for Therapeutic Research using a tyrosine-decarboxylase system indicated that the theoretical amount of coenzyme was present.

The procaine salt of pyridoxal phosphate is more stable than the calcium salt. The calcium salt, kept in a desiccator in the dark for $4^1/_2$ years, lost 60% of its codecarboxylase activity; the procaine salt, stored under similar conditions for $1^1/_2$ years, retained full codecarboxylase activity.

EXPERIMENTAL

Pyridoxal phosphate. One g. of pyridoxamine phosphate was dissolved in 84 ml. of 0.1*N* sulfuric acid. Manganese dioxide (0.4 g.) was added, and the mixture was stirred and heated at 65–75° for 1 hr. The reaction mixture was cooled and filtered. The filtrate was passed through a column of Amberlite resin IR-120 (H^+ cycle), and the column was washed with water. The eluate was treated with enough barium hydroxide to neutralize the sulfuric acid, and the precipitate of barium sulfate was removed. The filtrate was concentrated to about 100 ml. at reduced pressure and at a temperature below 40°. The concentrate was filtered through Super-Cel and was dried in the frozen state, giving 0.75 g. of pyridoxal phosphate.

Pyridoxal phosphate procaine salt. One hundred mg. of pyridoxal phosphate was dissolved in 3 ml. of water. To this solution was added 96 mg. (1 equivalent) of procaine, dissolved in 3 ml. of ethanol. The reaction mixture was chilled for several days in the refrigerator, and 120 mg. (60%) of the procaine salt of pyridoxal phosphate separated. Two recrystallizations from 50% water-ethanol (85% recovery) provided a sample of m.p. 150° (dec.), $\lambda_{max}^{0.1N\ NaOH}$ 275 mμ (ε16,000) and 390 mμ (ε6800). The sample was dried at 25°/0.1 mm. for analysis.

Anal. Calcd. for $C_{21}H_{30}N_3O_8P$: C, 52.17; H, 6.26, N, 8.69; P, 6.41. Found: C, 51.72; H, 6.32; N, 8.81; P, 6.24.

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Direct Preparation of Aryllithium Compounds from Aryl Fluorides

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The investigation of Wittig and coworkers, which was concerned with the preparation of organolithium derivatives from aryl fluorides, was confined to the metalation of fluoroaromatics with phenyllithium.[1–4] More recently, some success in the preparation of fluoroaryllithium derivatives from the halogen-metal interconversion reaction has been reported from this laboratory.[5] The attempts, however, to prepare the aryllithium compound directly from an aryl fluoride and lithium met with some success. By refluxing lithium ribbon and fluorobenzene in diethyl ether for 24 hours, 0.7% of benzoic acid was obtained on carbonation.[6] Benzoic acid was obtained in 0.5% yield when fluorobenzene and lithium dispersion were refluxed in diethyl ether for 5 hours and then carbonated.[6]

The first attempt to prepare aryllithium compounds from aryl fluorides and lithium in tetrahydrofuran under reflux conditions was unsuccessful.[6] Recently, it was reported that benzoic acid was obtained in a yield of 54% from chlorobenzene and lithium in tetrahydrofuran on carbonation.[7] The preparation of α-naphthyllithium from α-fluoronaphthalene and lithium wire in tetrahydrofuran illustrated the importance of solvent and temperature control in these reactions. On carbonation of α-naphthyllithium, 23% of crude α-naphthoic acid was obtained. Although the initiation of this reaction did not require a catalyst, the reaction which involved fluorobenzene and *p*-fluorotoluene would not commence until their respective bromo analogs were added. The yields of phenyl- and *p*-tolyllith-

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