in the previously described apparatus.[2] **Ethyl** bromide evolution amounted to 20 g. (theory, 21.8 g.). The product was distilled with a minimum of superheating by the use of a still equipped with a sealed stirrer. The yield of diethyl 2-bromoethanephosphonate, b. p. 86–87° at 2 mm., $n^{25}D$ 1.4555, was 33 g., 67.5%.

Diethyl Vinyl Phosphonate.—Diethyl 2-bromoethanephosphonate (33 g.) was added in the course of thirty minutes to a stirred solution of 7.5 g. of potassium hydroxide in 250 cc. of absolute ethanol with ice cooling. The mixture was warmed to a gentle reflux for fifteen minutes, cooled and filtered. The precipitated potassium bromide was washed with 50 cc. of absolute ethanol and the combined filtrates were distilled to give 21 g. (95%) diethyl vinyl phosphonate as a colorless mobile liquid, b. p. 50° at 1 mm., $n^{25}D$ 1.4260. It decolorized permanganate instantly in the cold and possessed mildly expressed polymerizability.

Diethyl 2-Diethylaminoethanephosphonate.—Diethyl 2-bromoethanephosphonate (24.5 g., 0.1 m.) was added to 25 g. of diethylamine in 50 cc. of water and the mixture was refluxed for two hours. After cooling, 50 cc. of 20% sodium hydroxide was added and the mixture was extracted with 200 cc. of benzene. Distillation of the organic layer gave 17 g. (72%) diethyl 2-diethylaminoethane phosphonate, as a pale yellow oil, b. p. 106–7° at 3 mm., $n^{25}D$ 1.4380, which forms a methiodide, m. p. 104–106°.

Anal. Calcd.: N, 5.9. Found: N, 5.87, 6.01.

Repetition of the above experiment in dry toluene gave only the above described vinyl compound.

Diethyl 2-Di-*n*-butyl-aminoethane Phosphonate.—Diethyl 2-bromoethane phosphonate (24.5 g., 0.1 m.) was refluxed for four hours with 40 g. of di-*n*-butylamine and 50 cc. of water. Isolation, as given above, gave 21 g. (72%) diethyl 2-di-*n*-butyl-aminoethane phosphonate as a pale yellow oil, b. p. 140–142° at 3 mm., $n^{25}D$ 1.4421.

Anal.: Calcd.: C, 57.5; H, 10.9. Found: C, 57.7, 57.64; H, 10.6, 10.9.

(2) Kosolapoff, THIS JOURNAL, **66**, 109 (1944).

CENTRAL RESEARCH DEPARTMENT
MONSANTO CHEMICAL COMPANY
DAYTON 7, OHIO RECEIVED JANUARY 14, 1948

The Preparation of Carboxymethoxylamine Hemihydrochloride

BY MARY HARRIET LOTT

Carboxymethoxylamine has been used frequently as a ketone reagent, for instance in the isolation of α-estradiol from human pregnancy urine.[1] It can be synthesized by the simple procedure of Borek and Clarke[2] whereby acetoxime is condensed with sodium chloroacetate and the resulting acetone carboxymethoxime hydrolyzed with 6 *N* hydrochloric acid. In this Laboratory no difficulty has been encountered in the condensation; however, hydrolysis with 6 *N* hydrochloric acid has not uniformly yielded the desired carboxymethoxylamine hemihydrochloride. Often merely ammonium chloride is obtained. It has furthermore been noted that in the crystallization of the hemihydrochloride from ethanol–ether a fragrant oil often results in the mother liquor. The procedure of Borek and Clarke for hydrolyzing acetone carboxymethoxime has therefore been modified as described below. In this modification the concentration of hydrochloric acid, even after partial evaporation of solvent, is never permitted to become greater than 3.6 normal; isopropyl alcohol is substituted for ethanol under the assumption that esterification with ethanol takes place during crystallization. By the adoption of these modifications it has been possible consistently to obtain carboxymethoxylamine hemihydrochloride in satisfactory yield.

Procedure.—Crude acetone carboxymethoxime is distilled prior to hydrolysis. To a solution of 10.0 g. of acetone carboxymethoxime in 100 cc. of water contained in a 500-ml. wide-mouthed Erlenmeyer flask, 6.0 cc. of concentrated hydrochloric acid is added. The homogeneous solution is then heated on the steam-bath (hood) until the volume of solution is reduced to 20 cc. (approximately three hours time). After having been cooled, this solution is treated with 100 cc. of isopropyl alcohol and 200 cc. of dry, alcohol-free ethyl ether. After a day in the ice-box, the deposited crystals are filtered (Büchner) and washed with cold isopropyl alcohol–ether (1:3). The yield of carboxymethoxylamine hemihydrochloride, after drying, is about 4 g. melting at 150–151° uncor. (with evolution of gas). This material is of sufficient purity for use as a ketone reagent.

Anal.[3] Calcd. for $(C_2H_5O_3N)_2 \cdot HCl$: Cl, 16.22. Found: Cl, 16.08, 16.06.

(1) **Huffman, MacCorquodale, Thayer, Doisy, Smith and Smith,** *J. Biol. Chem.*, **134**, 591 (1940).

(2) Borek and Clarke, THIS JOURNAL, **58**, 2020 (1936).

(3) Analysis by James E. Ashmore.

DEPARTMENT OF BIOCHEMISTRY
SOUTHWESTERN MEDICAL COLLEGE
DALLAS, TEXAS RECEIVED FEBRUARY 17, 1948

The Synthesis of 3,4,9-Trimethoxyphenanthrene

BY S. F. MACDONALD AND A. J. CHECHAK

The significance, in morphine chemistry, of the function of the 9- or 10-hydroxy group in 9-hydroxycodeine and of the structure of Knorr's 9- or 10-acetoxyacetylmethylmorphol, has been indicated by Knorr[1] (in part) and by Holmes.[2] Evidence on these points would definitely locate the position of the nitrogen in morphine, unless the hydroxy group of 9-hydroxycodeine were on 9 and the nitrogen on 10 or 14. The latter publication has led us to report work which we had done to the same purpose, though it is as yet incomplete.

It was pointed out[2] that the 9-hydroxycodeine structure was not consistent with its failure to react as a carbinolamine with malonic acid, etc.; more conclusive evidence to this effect had already been obtained by Knorr,[1] who found that it did not react with hydroxylamine or with semicarbazide, but who failed to interpret the result thus. As codeine N-oxide is known,[3] there would appear to be little justification for the suggestion, made and disposed of by Holmes,[2] that 9-hydroxycodeine is an N-oxide.

The synthesis of 3,4,9-trimethoxyphenanthrene should permit the determination of the structure of Knorr's acetoxyacetylmethylmorphol. Attempts had therefore been made to convert 3,4-

(1) Knorr and Hörlein, *Ber.*, **39**, 3252 (1906); **40**, 2040, 2042 (1907).

(2) Holmes, *et al.*, THIS JOURNAL, **69**, 1996, 1998 (1947).

(3) Freund and Speyer, *Ber.*, **43**, 3310 (1910).