brown solid was obtained which had a strong phenolic odor, and from which no 5,7-dichlorocoumaran-3-one could be isolated by steam distillation. The residue was triturated with a small amount of cold methanol, and the solid was recrystallized from Skelly C, m. p. 111.5–112.5° (yield 8.0 g.) A mixed m. p. with an authentic sample of 2,4-dichlorophenyl-2',4'-dichlorophenoxyacetate showed no depression.

Anal. Calcd. for $C_{14}H_8Cl_4O_3$: C, 45.9; H, 2.18; Cl, 38.8. Found: C, 46.0; H, 2.18; Cl, 40.1.

A shorter reaction time of ten minutes afforded a lower yield of ester, and none of the 5,7-dichlorocoumaran-3-one.

Preparation of the Phenyl Esters of the Phenoxyacetic Acids.—The ester 2,4-dichlorophenyl 2',4'-dichlorophenoxyacetate was prepared by heating equivalent amounts of 2,4-dichlorophenol and 2,4-dichlorophenoxyacetyl chloride at 130–140° for three hours. The reaction product was recrystallized from Skelly C, m. p. 112–113°.

Anal. Calcd. for $C_{14}H_8Cl_4O_3$: Cl, 38.8. Found: Cl, 38.0.

In a similar manner, 4-chlorophenyl 4'-chlorophenoxyacetate was prepared, m. p. 118–119°.

Anal. Calcd. for $C_{14}H_{10}Cl_2O_3$: Cl, 23.9. Found: Cl, 24.0.

Phenyl phenoxyacetate was prepared in a similar manner, m. p. 54–57° (reported[6] m.p. 58°).

Herbicidal Activity Tests

The various phenoxyacetic acids, cyclized derivatives, and phenyl esters were tested for plant growth regulating activity. Snap beans, grown under field conditions, were used as the test plant. Approximately 40 mg. of a solution of 1% of the compound in lanolin was applied to the pulvinus of the primary leaves when the first trifoliate leaves were expanding. Each of the compounds was applied to two plants, and the treated plants were observed over a period of eight weeks.

Phenoxyacetic acid, coumaran-3-one, and phenyl phenoxyacetate were without action.

The 4-chlorophenoxyacetic acid was very active, as was the 4-chlorophenyl ester. A slight effect was noted within two days after application, and within ten days the stems were badly swollen and the trifoliate leaves were dwarfed. After eight weeks the plants were alive but were very stunted. When 4-chlorophenoxyacetic acid was cyclized to 5-chlorocoumaran-3-one all herbicidal activity was lost.

As was expected, 2,4-dichlorophenoxyacetic acid was very active. The 2,4-dichlorophenyl ester possessed the same order of activity, but seemed to act somewhat more slowly.

(6) Morel, *Bull. soc. chim.*, [3] **21**, 967 (1899).

CHICAGO 29, ILLINOIS RECEIVED DECEMBER 31, 1947

Difluoroboron-acetoacetanilide

BY JOSEPH R. KILLELEA

A recent application of the Knorr reaction in this laboratory[1] prompted a study of the use of boron fluoride as the acid catalyst for the cyclization. Small quantities of the expected 4-methylcarbostyril (I) were obtained in some cases. In every case the principal product was difluoroboron-acetoacetanilide (II).[2]

Experimental

Difluoroboron-acetoacetanilide.—To 20 ml. of a 40% solution of boron fluoride in absolute ethanol[3] is added 5.0 g. of acetoacetanilide. The solution is allowed to stand for fifteen minutes and then poured cautiously into an excess of dilute sodium carbonate. The filtered solid is stirred with normal hydrochloric acid to remove inorganic matter and dried over sodium hydroxide. It is dissolved in the minimum volume of dry dioxane, the solution filtered, and the product precipitated by the addition of petroleum ether. The product (5.0 g., 79%) forms fine needles and melts at 154–155°.

Anal. Calcd. for $C_{10}H_{10}O_2NBF_2$: B, 4.8; F, 16.9; N, 6.23. Found: B, 5.2; F, 16.7; N, 6.22.

Properties.—(a) **Hydrolysis.**—One gram of (II) is stirred with 50 ml. of a very dilute ferric chloride solution at room temperature. No color is observed until considerable time (one-half to one hour) has elapsed. The color gradually deepens as hydrolysis proceeds and reaches its maximum after six to eight hours. The solution gives positive qualitative tests for boric acid and fluorides. Nearly the theoretical quantity of acetoacetanilide may be recovered by extraction.

(b) **Cyclization.**—One gram of (II) is stirred with 3 ml. of concentrated sulfuric acid and the solution warmed to 80–90°. Reaction sets in with the evolution of acidic gases (wet litmus) containing boron (green flame). Nearly the theoretical quantity of (I) may be isolated by the usual method.[1]

(2) Similar compounds from β-diketones have been reported by Morgan, *J. Chem. Soc.*, **125**, 1963 (1924).

(3) The Knorr cyclization was attempted in other solvents and under various conditions. These directions represent a convenient method of preparation of (II).

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Isomerization of Alkyl Phosphites. VII. Some Derivatives of 2-Bromoethane Phosphonic Acid

BY GENNADY M. KOSOLAPOFF

The reaction of triethyl phosphite with ethylene bromide readily leads to a very reactive diethyl 2-bromoethane phosphonate. It was felt to be of interest to prepare a number of derivatives of this substance through the reactive halogen atom.

The action of alcoholic potassium hydroxide on this ester was found to give good yields of diethyl vinyl phosphonate, which had been earlier reported by Kabachnik,[1] who used a rather involved reaction sequence for his synthesis.

Dialkylamines react with the bromo compound in aqueous solution to give good yields of the corresponding diethyl 2-dialkylaminoethane phosphonates. As might be expected, the use of a nonpolar solvent leads to dehydrohalogenation and the formation of the above-mentioned vinyl derivative.

Experimental Part

Triethyl phosphite (33.2 g., 0.2 m.) and ethylene bromide (150 g., 0.8 m.) were heated for three hours to 160°

(1) Searles and Lindwall, THIS JOURNAL, **68**, 988 (1946).

(1) Kabachnik, *Izvest. Akad. Nauk. S. S. S. R.*, No. 2, 233 (1947).

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
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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 icebox, 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.

(3) Analysis by James E. Ashmore.

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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) Huffman, MacCorquodale, Thayer, Doisy, Smith and Smith, *J. Biol. Chem.*, **134**, 591 (1940).
(2) Borek and Clarke, THIS JOURNAL, **58**, 2020 (1936).

(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).