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).

dimethoxy-9-phenanthrylamine into 3,4-dimethoxy-9-phenanthrol.[1,2] This conversion was carried out quantitatively by a modification of the Bucherer reaction wherein sulfur dioxide replaced the usual bisulfite,[4] and the presence of much aqueous dioxane prevented the formation of the diphenanthrylamine derivative. Analogous deaminations have been carried out by other methods in low or in unstated yields.[5] 3,4-Dimethoxy-9-phenanthrol gave the required 3,4,9-trimethoxyphenanthrene on methylation.

Experimental

α-Phenyl-2-nitro-3,4-dimethoxycinnamic Acid.—This was obtained in 75% yield by Pschorr's method[6] or in 90% yield by the following modification. 2-Nitroveratraldehyde, 2.1 g., phenylacetic acid, 1.4 g., triethylamine, 1.0 g., and acetic anhydride, 5 ml., were heated together at 60° for two days. Isolation and purification according to Pschorr gave the product, 3.0 g., m. p. 222.5–223.5° (uncor.).

3,4-Dimethoxy-9-aminophenanthrene.—Prepared according to Knorr,[1] the base was obtained from its hydrochloride with alcoholic potassium hydroxide.

3,4-Dimethoxy-9-phenanthrol.—3,4-Dimethoxy-9-aminophenanthrene, 4.7 g., was dissolved in 50 ml. of dioxane, 50 ml. of water added, the mixture saturated with SO_2 at 0°, and heated in a sealed tube at 100° for one day. Removal of the solvent *in vacuo*, grinding the residue with water, filtering and drying, gave 3,4-dimethoxy-9-phenanthrol, 4.7 g., m. p. 147–152°. The crude product was distilled (1×10^{-4} mm., bath temp. 130°) and crystallized from toluene, giving pale yellow prisms, m. p. 156°.

Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55; OCH_3, 24.4. Found: C, 75.53; H, 5.43; OCH_3, 21.9, 22.4.

3,4,9-Trimethoxyphenanthrene.—3,4-Dimethoxy-9-phenanthrol, 390 mg., was refluxed under nitrogen with water, 10 ml., and *N* sodium hydroxide, 2 ml. Methyl sulfate, 0.5 ml. then 0.4 ml., and *N* sodium hydroxide, 5 ml. then 4 ml., were added alternately. The cooled mixture was extracted with chloroform, the chloroform washed with dilute hydrochloric acid, with dilute sodium hydroxide with water, and dried with sodium sulfate. 3,4,9-Trimethoxyphenanthrene, 330 mg., m. p. 85–95°, was obtained by distilling (1×10^{-4} mm., bath temp. 110°) the residue left on evaporating the chloroform. It was purified by crystallizing from petrol ether (b. p. 60–80°, 20 parts) giving colorless prisms, m. p. 96.5–97.5° after drying.

Anal. Calcd. for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01; OCH_3, 34.70. Found: C, 76.21; H, 6.32; OCH_3, 31.76.

(4) Franzen and Kempf, *Ber.*, **50**, 101 (1917).

(5) Pschorr and Schröter, *Ber.*, **35**, 2726 (1902); Schmidt and Strobel, *Ber.*, **36**, 2508 (1903).

(6) Pschorr and Sumuleanu, *Ber.*, **33**, 1810 (1900).

BANTING & BEST DEPARTMENT OF MEDICAL RESEARCH
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X-Ray Diffraction in Aqueous Systems of Dodecyl Sulfonic Acid

BY SULLIVAN S. MARSDEN, JR., AND JAMES W. MCBAIN

Aqueous systems of lauryl sulfonic acid are especially interesting because their X-ray diffraction shows different kinds of patterns for ordinary isotropic solution, concentrated anisotropic liquid crystalline region, and the highly concentrated anisotropic liquid crystalline, and the pure crystalline acid.

1. The ordinary isotropic liquid solution existing at room temperature exhibits only a very diffuse indication of a long spacing even near the highest concentration (23%) at which it can exist. The phase diagram giving the boundaries of this[1] and the two anisotropic phases was published by M. J. Vold. X-Ray diffraction therefore indicates the absence of any strongly repeating structure such as that found in solutions of potassium laurate, except high angle scattering due to neighboring molecules in the colloidal particles of the sulfonic acid.

However, when 3.6% of benzene is added to 19.0% solution of the dodecyl sulfonic acid the solution is still isotropic but gives a diffraction line corresponding to a single order of Bragg spacing of 63.4 Å. But when the amount of benzene is increased to 6.9% the system becomes anisotropic and gives two long Bragg spacings of 67.0 Å. and 48.4 Å. It is assumed that this structure is lamellar in analogy with the system Triton X-100: water: benzene.[2]

2. Most interesting is the aqueous liquid-crystalline phase existing between 23 and 70% of lauryl sulfonic acid. The colloidal particles apparently consist of *fibers* or long rods or elongated ellipsoids. These lie parallel at a distance from each other in hexagonal arrangement. Such a structure was found for certain aqueous systems of tobacco mosaic virus by Bernal and Fankuchen.[3]

The evidence for this interpretation of the X-ray diffraction patterns follows from: (a) The ratios of the successive Bragg spacings to each other are in the proportions $1:1/\sqrt{3}:1/\sqrt{4}:1/\sqrt{7}$. These correspond to hexagonal indices $10\bar{1}0$, $11\bar{2}0$, $20\bar{2}0$, $21\bar{3}0$, respectively.

(b) Most important, the relative intensities of the various diffractions, which in the order given above are: very strong, strong, weak and very weak, respectively; in a few cases the second and third lines are strong and strong, respectively.

(c) The variation of the inter-particle distance with concentration, which is approximately as the reciprocal of the square root of the concentration.

The thickness or diameter of the fibers seems to be in the neighborhood of the double length of the soap molecule. The short spacings consist of halos at 7–8 Å. and 4.5–4.6 Å., which indicates a liquid arrangement of neighboring molecules within the fibers.

It should be mentioned that this structure is quite different from that of the anisotropic phases of aqueous potassium laurate as is shown by studies in this laboratory by Oscar A. Hoffman being reported elsewhere. He shows that the potassium laurate systems contain a repeating *lamellar* structure such as was first suggested by Hess and his collaborators.

(1) Vold, THIS JOURNAL, **63**, 1427 (1941).

(2) Marsden and McBain, *J. Phys. & Coll. Chem.*, **52**, 110 (1948).

(3) Bernal and Fankuchen, *J. Gen. Physiol.*, **25**, 111 (1941).