

TABLE I
COMPARISON OF THE PROPERTIES OF SUBSTITUTED ACRIDINES

Substituent	1-Amino-	3-Amino-
Fluorescence in alc. soln.	None	Intense green
M. p., °C.	{ 178 (uncorr.) 182.3 (corr.) ^a	{ 218 (uncorr.) ^b 223.5 (corr.)
Hydrochloride {	Cryst. color	Blue-black
	Aq. soln.	Violet-red color with no fluores.
	M. p., °C. (uncorr.)	285 (dec.) ^c
		Orange-red
		Orange-yellow color with green fluores.
		328-329 (dec.)

^a Albert and Linnell [*J. Chem. Soc.*, 22 (1938)] give m. p. 181° (corr.), and Lehmsstedt [*Ber.*, 71, 808 (1938)] gives m. p. 165-170°. ^b Albert and Linnell [*J. Chem. Soc.*, 1618 (1936)] give m. p. 219° (corr.) and Scherlin [*Ann.*, 516, 218 (1935)] m. p. 221-222° for their products, respectively. ^c Lehmsstedt (*loc. cit.*) gives m. p. 286° (dec.) for his product.

the basis of further investigations as follows. The aminoacridine (IV) which was obtained from the aminoacridone in question (III), on admixture with synthesized 3-aminoacridine, showed a great depression of the melting point, while with synthetic 1-aminoacridine it showed no depression; moreover, its other properties were in good agreement with those of 1-aminoacridine shown in Table I.

The nitroacridone-carboxylic acid must, therefore, be 1-nitroacridone-4-carboxylic acid.

Experimental

1-Aminoacridine.—Four-tenths gram of the aminoacridone in question (m. p. 289-290°) and 5 g. of sodium amalgam (5%) in 30 cc. of dilute alcohol (33%) were heated on a water-bath for three hours with frequent shaking. The solution was decanted from mercury, acidified with hydrochloric acid and oxidized with 2 g. of ferric chloride. The base (yield, 0.25 g.) which was set free from the hydrochloride, crystallized from alcohol (33%) into gold-yellow prismatic needles, melting at 178° alone or on admixture with a sample of 1-aminoacridine (m. p. 178°), whereas a mixture (7:3) of this compound with an authentic specimen of 3-aminoacridine (m. p. 218°) melted at 135-140°.

Anal. Calcd. for C₁₃H₁₀N₂: C, 80.41; H, 5.15. Found: C, 80.22; H, 5.28.

The hydrochloride gives blue-black prismatic needles from dilute hydrochloric acid (5%), m. p. 285° (dec.). The aqueous solution assumes a violet-red color, while an alcoholic solution has a violet-blue color, both showing no fluorescence in any dilution.

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Synthesis of Aldehydes by Stephen's Method¹

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The application of Stephen's² procedure to the preparation of several aldehydes has led to the conclusion that the method is not as general as

(1) Presented before the Division of Organic Chemistry at the Baltimore meeting of the American Chemical Society, April, 1939.

(2) Stephen, *J. Chem. Soc.*, 127, 1874 (1925).

claimed. Stephen states, "the method is applicable to aliphatic and aromatic nitriles, and the yields are usually almost quantitative." Exceptions are made by Stephen only in the cases of *o*-tolualdehyde and α -naphthaldehyde, where "steric hindrance" is offered as an explanation for poor yields.

The method has been tried in this Laboratory with good results in the preparation of benzaldehyde, *p*-tolualdehyde and β -naphthaldehyde, and with only fair results in the preparation of phenylacetaldehyde and isocaproaldehyde. Stephen's poor yields with α -naphthaldehyde and *o*-tolualdehyde have been verified, and the method has been found completely unsatisfactory for the preparation of β -hydroxypropionaldehyde.

Experimental

Preparation of Phenylacetaldehyde.—Eleven runs were made, each different, and the following was found to give the highest yield.

A mixture of anhydrous stannous chloride (57 g., 0.3 mole, prepared by heating the hydrated salt for one hour in a 200° bath, cooling and pulverizing the resulting solid mass) and dry ether (400 ml., twice distilled from sodium) was placed in a 2-liter three-necked round-bottomed flask, provided with a mechanical stirrer and a reflux condenser fitted with a calcium chloride drying tube. The mixture was saturated with dry hydrogen chloride,³ using slow stirring to agitate the stannous chloride. Within two hours all of the solid stannous chloride had dissolved, forming a separate lower viscous layer.

The source of hydrogen chloride was then disconnected and phenylacetonitrile (16 g., 0.136 mole, freshly distilled) was added rapidly by means of a dropping funnel. The mixture was stirred vigorously for one hour and then allowed to stand for eighteen hours. The aldimine hydrochloride-stannic chloride complex began to separate after five hours.

The ethereal hydrogen chloride was removed by decantation and the residue washed twice with 100-ml. portions of dry ether to remove hydrogen chloride. To the residue were added 800 ml. of water and sufficient solid sodium bicarbonate to render the solution neutral to congo red.

(3) "Organic Syntheses," Coll. Vol. I, p. 287 (1932).

The mixture was then brought to boiling and live steam passed through it until the total volume of distillate was 250 ml.

The steam distillate was extracted with two 75-ml. portions of ether and the ethereal extract dried over sodium sulfate. The ether was removed on the steam-bath and the residue vacuum-distilled: yield of phenylacetaldehyde, b. p. 87–88° (18 mm.), 5.4 g., 0.045 mole, 33%.

The other aldehydes studied were prepared by much the same procedure. The results are summarized in the table.

Aldehyde prepared	Time allowed for pptn. of addn. complex	Yield, %
Benzaldehyde ⁴	5 hours	97
β -Naphthaldehyde ⁵	12 hours	91
<i>p</i> -Tolualdehyde ⁴	12 hours	77
Phenylacetaldehyde ⁴	18 hours	33
Isocaproaldehyde	7 days	31
<i>o</i> -Tolualdehyde ^{7,8}	8 days	9
α -Naphthaldehyde ⁷	7 days	7
β -Hydroxypropionaldehyde ⁶	7 days	0

(4) Reported by Stephen² in almost quantitative yields.

(5) One liter of hot water was added to the residue and live steam passed through the mixture as long as any solid came over in the steam distillate. The solid was recrystallized from 50% aqueous alcohol. Fulton and Robinson, *J. Chem. Soc.*, **152**, 200 (1939), reported the preparation of β -naphthaldehyde by the Stephen technique in 75% yield. Their work was published after the preparation had been completed at the University of Maryland.

(6) Removal of the aldehyde by steam distillation was not attempted; 500 ml. of water was added to the addition complex, the mixture warmed on the steam-bath for one hour, allowed to cool and extracted with ether. The product was a thick, tarry liquid which gave negative tests with Schiff and Tollens reagents.

(7) Reported by Stephen² in poor yield.

(8) There was no precipitate after seven days so one-half of the ether was removed and the reaction mixture allowed to stand another twenty-four hours.

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Crystalline Lead Orthophosphate

BY EDWARD J. ROEHL

In the preparation of crystalline metathetical reaction products where the solubility of the reaction product is very low, it is often difficult to obtain crystals large enough for microscopic examination, and a number of methods have been employed for maintaining the necessary slight supersaturation. The writer has successfully employed a cellophane membrane for a number of such cases.

By treating a solution of lead acetate with sodium hydrophosphate, Aiders and Stähler¹ succeeded in preparing lead orthophosphate, but without any signs of microscopically recognizable crystals. In fact, it appears from the literature that the only method of preparing this salt is the rather cumbersome one of Zambonini,² who fused

(1) Aiders and Stähler, *Ber.*, **42**, 2263 (1909).

(2) Zambonini, *Z. Kryst.*, **58**, 226 (1923).

and slowly cooled the white powder. In our experiments, a cellophane membrane was tied over the mouth of a test-tube (an open tube could of course be used) containing a 1% solution of Na₂HPO₄ and the tube inverted in a slightly acidified 0.2% solution of Pb(C₂H₃O₂)·3H₂O. At once an almost amorphous precipitate of lead orthophosphate appeared on the under side of the membrane and in about a minute crystals of the white salt started to fall.

The crystals (some of which were 2 mm. in length) were uniaxial hexagonal prisms exhibiting strong birefringence and showing an optically negative character. The values of $\omega = 1.970$ and $\epsilon = 1.936$ check the data in the literature for the refractive indices of lead orthophosphate. Analysis of the crystals gave a value of 17.4% as compared with the calculated value of 17.5% for Pb₃(PO₄)₂.

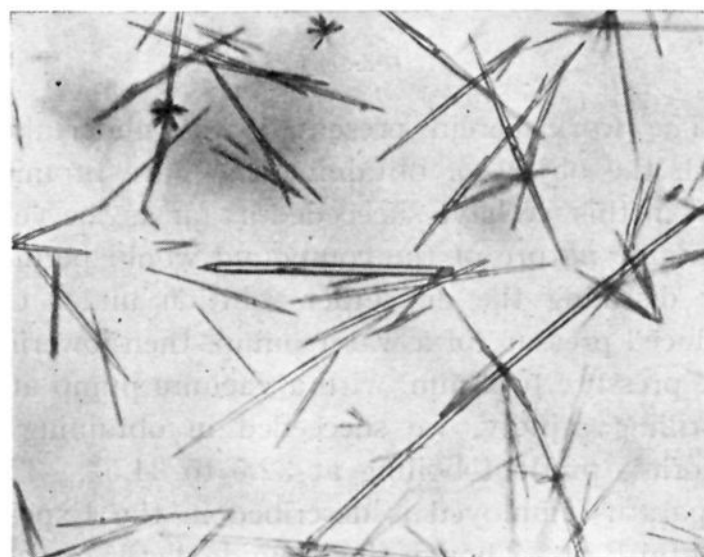


Fig. 1.

The accompanying photomicrograph at (50 X) shows some of the crystals obtained.

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α -Furfuryl Bromide (2-Bromomethylfuran)

BY J. E. ZANETTI AND J. T. BASHOUR

In 1927 one of us¹ prepared an ether solution of α -furfuryl bromide by acting on furfuryl alcohol with phosphorus tribromide. The solution proved satisfactory in the synthesis of various furfuryl ethers but the pure bromide was not separated as its decomposition was rapid once the solvent was evaporated. Von Braun and Kohler² had

(1) Zanetti, *THIS JOURNAL*, **49**, 1065 (1927).

(2) Von Braun and Kohler, *Ber.*, **51B**, 86 (1918).