(A); the aqueous phase was acidified to *p*H 1 with 1:1 sulfuric acid and then extracted with four 20-ml. portions of chloroform. The chloroform extracts were washed with water, dried and evaporated *in vacuo* to give 3.66 g. of a yellow oil (B). Evaporation of the solvent from A yielded 2 mg. of an oil with a terpene odor.

Separation of B *via* the Calcium Salts.—B was suspended in 30 ml. of water and treated with 1.37 g. of calcium hydroxide. Vigorous shaking and warming caused a solid to separate from the reaction mixture. After the mixture was diluted with an equal volume of ethanol and heated, most of the solid dissolved. The solution was filtered to remove excess calcium hydroxide, concentrated and the first crop of crystals (C, 0.72 g.) collected. The mother liquor was concentrated to dryness and the residue recrystallized from the minimum of hot 90% ethanol to give 2.0 g. of crystals (D). Dilution of the mother liquor with a large volume of acetone precipitated 1.1 g. of white powder (E). The mother liquors from E were discarded.

C was suspended in water, acidified with 1:1 hydrochloric acid and the solution extracted with chloroform. The extracts were washed, dried and the solvent removed *in vacuo*. The partially crystalline residue was recrystallized from petroleum ether to give 95 mg. of tiglic acid. The mother liquor (F) was reserved.

When D was treated as described for A and the acid residue crystallized from light petroleum ether, 359 mg. of large, flat, lustrous plates separated; m.p. 42–43°. Recrystallization furnished pure angelic acid (II) melting at 44–45.2°. The mother liquors (G) were combined and reserved.

Anal. Calcd. for $C_5H_8O_2$: C, 59.99; H, 8.06. Found: C, 60.12; H, 8.00.

***p*-Phenylphenacyl Angelate (III).**—Angelic acid (187 mg. from D) and *p*-phenylphenacyl bromide (515 mg.) were allowed to react according to the usual procedure.[5] The yellow solid which separated (540 mg.) was decolorized with Norite and recrystallized three times from ethanol to give 200 mg. of beautiful, silver-white leaflets of pure *p*-phenylphenacyl angelate, m.p. 89.0–90.5°.

Anal. Calcd. for $C_{19}H_{18}O_3$: C, 77.54; H, 6.16. Found: C, 77.68; H, 6.22.

***p*-Phenylphenacyl Tiglate (IV).**—Tiglic acid (280 mg.) and *p*-phenylphenacyl bromide (770 mg.) were allowed to react according to the procedure described for III. When processed as described, the reaction mixture yielded large, thin, white leaflets of pure *p*-phenylphenacyl tiglate (456 mg., m.p. 105–106°).

Anal. Calcd. for $C_{19}H_{18}O_3$: C, 77.54; H, 6.16. Found: C, 77.79; H, 6.22.

A 50-50 mixture of the *p*-phenylphenacyl esters of angelic and tiglic acids exhibited a large melting point depression, m.p. 75–84°.

When E was dissolved in water and processed as described for C, 25 mg. of tiglic acid resulted. The mother liquor (H) was combined with F and G and the solvent removed *in vacuo*. The liquid residue (1.54 g.) crystallized when cooled to 0°, but remelted at room temperature. It had an odor characteristic of tiglic or angelic acid and consisted presumably of a mixture of unresolved tiglic and angelic acids.

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3-Phenylpyridine[1]

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3-Phenylpyridine has been prepared by a large variety of methods, some of which give only the 3-isomer, but most of which result in a mixture of 2-, 3- and 4-phenylpyridines. In the former group are the procedures involving rearrangement, with ring expansion, of an α- or N-substituted pyrrole.[2-4] The conditions are drastic, the yields are very poor, and the method is of little if any preparative value.[4] Also in this group is the first reported synthesis of 3-phenylpyridine, accomplished from β-naphthoquinoline by oxidation to a dicarboxylic acid and decarboxylation by alkaline fusion,[5] a procedure which is quite lengthy and also gives very poor yields.

The methods which result in mixtures of 2-, 3- and 4-phenylpyridines frequently also give poor yields and suffer from the fact that tedious fractional crystallization of a salt, usually the picrate, is necessary in order to obtain a pure isomer. Variations of the Gomberg (or diazo) reaction in which the decomposition and nitrogen elimination are carried out in pyridine solution have been commonly used. Diazotized *p*-nitroaniline[6] (with subsequent replacement of the nitro group), diazotized aniline,[7] N-nitrosoacetanilide[8] and 3,3-dimethyl-1-phenyltriazene[9] have all been decomposed in pyridine to give the three isomeric phenylpyridines. Similar results are obtained when diphenyliodonium chloride,[10] benzoyl peroxide,[11] or phenylazotriphenylmethane[12] are heated in pyridine.

An obvious alternative which would eliminate the isomer problem would be to use the corresponding aminopyridine derivative and decompose in benzene. This has been tried with 2-aminopyridine but failed due to the difficulty of diazotizing an α-amino group and the inability to nitrosate the N-acetyl derivative,[8] a result which parallels the experience with *o*- and *p*-nitroacetanilide.[13] However, since 3-aminopyridine behaves as an ordinary aromatic amine,[14] there was good reason to believe it could be used for introducing the 3-pyridyl group through some modification of the diazo reaction. 3-Aminoquinoline,[12,15] several 3-aminochloropyridines[12] and 3-amino-2-*n*-butoxypyridine[12] have been successfully converted to the corresponding 3-phenyl compounds, indicating that 3-aminopyridine itself could be used if the operational difficulties could be overcome.

Although N-(3-pyridyl)-acetamide was easily nitrosated, the high water solubility of the product made it difficult to extract and hence unsuitable. 3,3-Dimethyl-1-(3′-pyridyl)-triazene was readily prepared and in good yield, but it proved to be much too stable, being recovered unchanged from refluxing benzene in the presence of glacial acetic acid or dry hydrogen chloride. An alternative was

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then sought in a higher molecular weight acyl derivative of 3-aminopyridine which could be nitrosated and then extracted from the aqueous nitrosating mixture. The isobutyryl derivative was chosen since it should be less water-soluble than the acetyl compound, and especially since, among various N-nitrosoacylanilides, the isobutyryl derivative was found to be the most reactive.[16]

Isobutyric anhydride and 3-aminopyridine gave a good yield of N-(3-pyridyl)-isobutyramide which was nitrosated with nitrosyl chloride, and the product was easily extracted from the diluted solution with ether or benzene. On warming in benzene, decomposition occurred and a 39% yield of 3-phenylpyridine was isolated. Its properties agreed well with those reported for material isolated, by picrate fractionation, from reactions giving the three isomeric phenylpyridines. Gillam, Hey and Lambert[17] have measured the absorption spectrum of a sample of 3-phenylpyridine which they state may have been (but most probably was not) a mixture. Their spectrum agrees quite well with what we find for isomer-free 3-phenylpyridine (Fig. 1). There is a maximum at 246 mμ (log ε 4.1) and a shoulder in the region of 276 mμ (log ε 3.8) (reported[17] 246 mμ, log ε 4.2; 275 mμ, log ε 4.0). In addition, we find a minimum at 224 mμ (log ε 3.8).

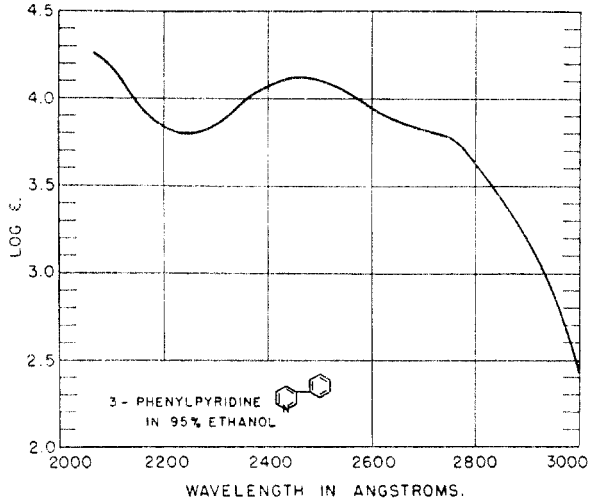

Fig. 1.—Ultraviolet absorption spectrum of 3-phenylpyridine (5.7×10^{-5} *M*) in 95% ethanol at 25°; cell length, 1 cm.

Experimental[18]

3,3-Dimethyl-1-(3′-pyridyl)-triazene.—A solution of 7.0 g. (0.10 mole) of sodium nitrite in 40 ml. of water was added during 15 minutes to a stirred solution of 9.4 g. (0.10 mole) of 3-aminopyridine[19] and 28 ml. of 36 *N* sulfuric acid in 100 ml. of water maintained at 0 to 2°. After an additional 15 minutes at this temperature, the cold diazonium sulfate solution was added to a cooled (0 to 5°), stirred solution of dimethylamine (22.1 ml. of 5.2 *N* aqueous solution, 0.11 mole) in 267 ml. of 2.2 *N* potassium carbonate. Stirring and cooling were continued for 30 minutes, followed by extraction with four 250-ml. portions of ether. Drying the combined ether extracts over sodium hydroxide and distilling gave 10.9 g. (73%) of triazene, b.p. 126–129° (9–10 mm.), $n^{25}D$ 1.6093.

Anal. Calcd. for $C_7H_{10}N_4$: C, 56.0; H, 6.7; N, 37.3. Found: C, 56.3; H, 6.5; N, 36.9.

The picrate was prepared with ethanolic picric acid and was recrystallized from ethanol, m.p. 141–142°.

Anal. Calcd. for $C_{13}H_{13}O_7N_7$: C, 41.2; H, 3.5; N, 25.9. Found: C, 41.3; H, 3.4; N, 25.6.

N-(3-Pyridyl)-isobutyramide.—To 10.0 g. (0.11 mole) of 3-aminopyridine was added, slowly and with cooling, 25.2 g. (0.16 mole) of isobutyric anhydride.[20] The mixture, protected from atmospheric moisture, was allowed to stand at room temperature for one hour and then heated on the steam-bath for one-half hour, after which butyric acid and excess anhydride were removed at the water-pump (bath temperature up to 100°). The residue, dissolved in 200 ml. of chloroform, was washed with saturated sodium bicarbonate until the washings were basic to litmus, followed by four 50-ml. portions of water, and then distilled after drying over sodium sulfate. The product boiled at 159–162° (1.5 mm.) and solidified in the receiver. Recrystallization of the 14.7 g. (85%) of distillate from benzene–methylcyclohexane (4 ml. of each per gram) gave 14.1 g. (81% yield) of N-(3-pyridyl)-isobutyramide, m.p. 78–79°.

Anal. Calcd. for $C_9H_{12}ON_2$: C, 65.8; H, 7.4; N, 17.1. Found: C, 66.2; H, 7.1; N, 17.3

3-Phenylpyridine.—To a suspension of 20 g. (0.12 mole) of N-(3-pyridyl)-isobutyramide in 125 ml. of glacial acetic acid and 55 ml. of acetic anhydride, to which had been added 55 g. of anhydrous potassium acetate and 2 g. of phosphorus pentoxide, stirred at 0°, was added dropwise 8.0 g. (0.12 mole) of nitrosyl chloride (as a 25% solution in acetic anhydride). Stirring was continued for 10 minutes after the addition and the yellow solution was then poured into 500 ml. of ice and water and extracted with three 250-ml. portions of cold benzene. Anhydrous magnesium sulfate and sodium carbonate were added to the combined extracts which were maintained at 50° until gas evolution ceased. After filtering, the reaction mixture was heated under reflux for two hours, again treated with magnesium sulfate and sodium carbonate, filtered, and distilled to give 7.3 g. (39%) of 3-phenylpyridine, b.p. 117–118° (5 mm.), $n^{25}D$ 1.6123 (reported[5] b.p. 269–270° (749 mm.)).

Anal. Calcd. for $C_{11}H_9N$: C, 85.1; H, 5.9; N, 9.0. Found: C, 84.7; H, 5.9; N, 9.0.

The picrate, after crystallization from ethanol, melted at 159–160° (reported[5] m.p. 161–163.5°).

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Unit Cell Constants of α-Copper Phthalocyanine

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Although the dimorphism of copper phthalocyanine ($C_{32}H_{16}N_8Cu$) has been reported,[1] no unit cell constants have been published for the α (metastable) modification of the pigment. The β (stable) modification has been thoroughly discussed by Robertson.[2] In connection with another study we have had occasion to make an analysis of the structure of α-$C_{32}H_{16}N_8Cu$.

The material used was prepared from Solfast Sky Blue[3] by dissolving in 98% H_2SO_4, filtering to remove any residue, and precipitating α-$C_{32}H_{16}N_8Cu$ by pouring the solution slowly into a large volume of water. The dark blue precipitate was filtered with suction and thoroughly washed with

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(3) Sherwin-Williams Co. trademark for their brand of $C_{32}H_{16}N_8Cu$.