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4-BENZYL-2,6-DIMETHYLPYRIDINE, 1-BENZYLISOQUINOLINE, 9-BENZYLACRIDINE, AND CERTAIN RELATIVES

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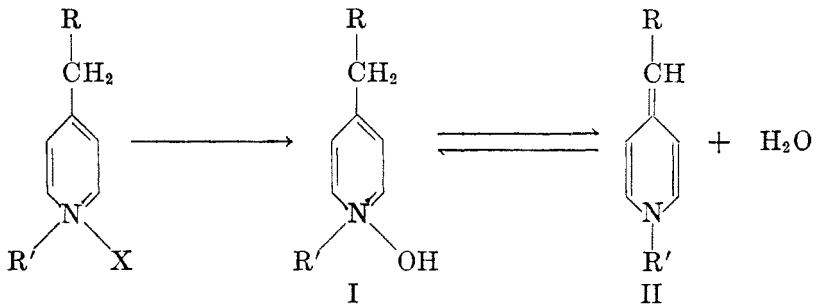
In his work on the quaternary hydroxides of six-membered nitrogenous heterocyclic bases formed from the corresponding quaternary halides by treatment with alkali, Decker regarded those having an alkyl group in α- or γ- relation to the ring nitrogen (I) as in equilibrium with what he termed an "anhydro base" (II). The hydroxides are generally colorless while the "anhydro bases" are yellow or orange (1, 2).



In the cases of α- and γ-(*p*-nitrobenzyl)pyridine (I, R = *p*-nitrophenyl) alkali treatment of the methiodide salt gave a deep blue color (3, 4, 5). This unusually strong color has been attributed either to increased activation of the methylene group or to *aci*-salt formation (3). No information is available as to the effect on the color of the anhydro base of other substituents in the benzene ring (R of II), or whether similar color phenomena accompany anhydro base formation in other heterocyclic series such as the isoquinolines or acridines when a *p*-nitrobenzyl group is the α- or γ- substituent. Some such cases have been examined in the present work.

The hitherto unreported 4-benzyl-2,6-dimethylpyridine (VI) has been prepared and various substituents introduced into the *p*-position of its benzyl radical. Of these products, those which contain one or more nitro groups produce the most marked color change under circumstances leading to anhydro base formation (Table I). A marked color change also accompanies anhydro base formation in the case of 1-(4-nitrobenzyl)isoquinoline (XVII) but the result is blood-red (rather than blue). Similar treatment of 9-(4-nitrobenzyl)acridine (XXI), however, gives only the yellow color usually observed from unsubstituted bases.

Under the usual conditions characteristic of Hantzsch condensation phenylacetaldehyde condensed smoothly with two moles of ethyl acetoacetate and one

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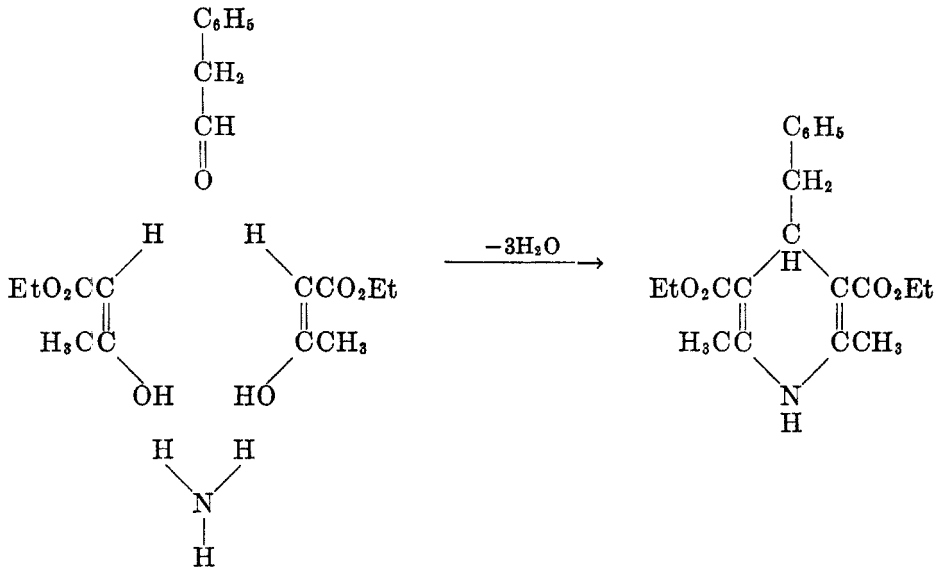
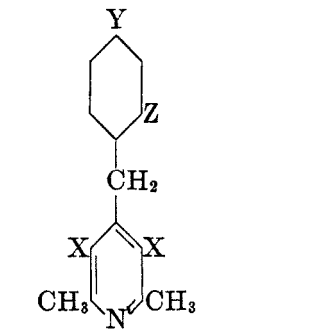
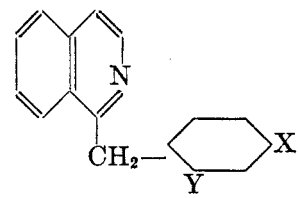
of ammonia in alcohol solution to give in excellent yield diethyl 4-benzyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (III). This was readily dehydrogenated by heating with sulfur (6) to diethyl 4-benzyl-2,6-dimethylpyridine-3,5-dicarboxylate (IV). Saponification of this ester led to the salt of a dibasic acid (V) which on distillation



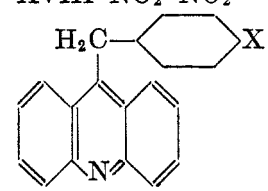
III



	X	Y	Z
IV	CO_2Et	H	H
V	CO_2H	H	H
VI	H	H	H
VII	H	NO_2	H
IX	H	NO_2	NO_2
X	H	NH_2	H
XI	H	NHAc	H
XII	H	OH	H
XIII	H	$NHCH_3$	H



XVI	H	H
XVII	NO_2	H
XVIII	NO_2	NO_2



XIX X = H
XXI X = NO_2

with lime in an inert atmosphere gave 4-benzyl-2,6-dimethylpyridine (VI). Mononitration of this base yielded 4-(4-nitrobenzyl)-2,6-dimethylpyridine (VII) in which the position of the nitro group was established by oxidation of VII [through the intermediate 4-(4-nitrobenzoyl)-2,6-dimethylpyridine VIII] to *p*-nitrobenzoic acid. Dinitration of VI or further nitration of VII yielded the same dinitro derivative, which is presumed to be 4-(2,4-dinitrobenzyl)-2,6-dimethylpyridine (IX). Reduction of VII with hydrogen and Adams' catalyst yielded 4-(4-aminobenzyl)-2,6-dimethylpyridine (X) which gave smoothly an acetyl derivative (XI), or after diazotization and appropriate hydrolysis the corresponding 4-(4-hydroxybenzyl)-2,6-dimethylpyridine (XII). On heating with methyl iodide, the primary amino group of (X) was partially methylated to 4-(4-methylaminobenzyl)-2,6-dimethylpyridine (XIII) which, however, was characterized only as its compound with one mole each of methyl iodide and hydrogen iodide (XIV).

TABLE I

METHIODIDES OF SUBSTITUTED 4-(R)-2,6-DIMETHYLPYRIDINES

R	M.P. UNCOR. OF METHIODIDE, °C.	COLOR	COLOR WITH ETHANOLIC KOH
Benzyl	150.5–152.0	Pink	Yellow
4-Nitrobenzyl	216–217	Yellow	Deep-blue
2,4-Dinitrobenzyl	210–211	Yellow	Deep-blue
4-Acetamino	193–194	White	Yellow
4-Methylamino	195–196	White	Yellow

The dehydrative cyclization of N-(β-phenylethyl)phenylacetamide with P_2O_5 (7) gave 1-benzyl-3,4-dihydroisoquinoline (XV), which upon dehydrogenation over palladium (7) served as a source of 1-benzylisoquinoline (XVI). Although both XV and XVI have previously been reported, our work led to the discovery that upon distillation of XV over potassium hydroxide cleavage occurs with resultant formation in excellent yield of both isoquinoline and toluene. Mononitration of 1-benzylisoquinoline (XVI) was effected by elimination of water from its nitrate salt and yielded 1-(4-nitrobenzyl)isoquinoline (XVII), in which the position of the nitro group was established by oxidation to *p*-nitrobenzoic acid. Dinitration of XVI led to a dinitro derivative (XVIII) in which the positions of the nitro groups have not been established but may, doubtless, be presumed to be *o*- and *p*- in the benzyl radical.

The conventional method (8) of heating together phenylacetic acid, diphenylamine, and zinc chloride provided 9-benzylacridine (XIX), whose nitrate (XX) readily dehydrated to 9-(4-nitrobenzyl)acridine (XXI), in whose structure the position of the nitro group was demonstrated by formation of *p*-nitrobenzaldehyde on chromic acid oxidation. Oxidation of XXI gave the corresponding ketone, to be regarded as 9-(4-nitrobenzoyl)acridine (XXII).

EXPERIMENTAL

2,6-Dimethylpyridine Series

Diethyl 4-benzyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (III). Phenylacetaldehyde (12 g. = 0.1 mole), ethyl acetoacetate (27 g. = 0.2 mole) in absolute ethanol containing 1.7 g. (0.1 mole) of dry ammonia were mixed in a pressure bottle which was sealed and stood at room temperature for 24 hours. Concentration of the alcoholic solution gave 23.5 g. (71% yield) of yellow solid which, after recrystallization from 75% methanol, gave colorless needles, m.p. 117–118° uncor.; recorded, 115° (9), 119° (6).

Diethyl 4-benzyl-2,6-dimethyl-3,5-dicarboxylate (IV). The dihydro compound (III, above) (18 g.) mixed with sublimed sulfur (1.68 g.) was heated in a test tube at 200°, the molten contents being efficiently stirred to facilitate evolution of hydrogen sulfide. Reaction was generally complete in 30 minutes. The oily product from several runs in which a total of 71 g. of dihydro compound had been used gave, upon fractionation, 57 g. (80% yield) of pale yellow oil, b.p. 199–204° at 10 mm. On standing, or when seeded, the oil solidified, and recrystallization from ethyl acetate gave transparent plates, m.p. 47.0–48.5°; recorded, 46° (6).

4-Benzyl-2,6-dimethylpyridine-3,5-dicarboxylic acid (V). The diethyl ester (IV) (40 g.) was saponified with potassium hydroxide (60 g.) in absolute ethanol (200 ml.). The solution was refluxed for 5 hours, during which the yellow potassium salt gradually separated. After filtration of this solid, additional material was obtained by concentration of the filtrate. Subsequent crops of salt became increasingly hygroscopic due to contamination with free alkali, making exact determination of yield impracticable, but the hydrolysis appears to be quantitative. This economical and convenient method of isolation is preferred to that of precipitation by addition of large volumes of ether (10).

The salt so obtained was dissolved in water and made neutral to litmus. Upon addition of two equivalents of 12 *N* hydrochloric acid, a white precipitate formed and redissolved in the hot solution. After decolorizing with charcoal and cooling, the acid was obtained as a white solid, m.p. 257–258° uncor., with evolution of carbon dioxide.

Anal. Calc'd for $C_{16}H_{15}NO_4$: N, 4.91; Neut. Equiv., 142.5.
Found: N, 4.98, 5.16; Neut. Equiv., 138.

4-Benzyl-2,6-dimethylpyridine (4-benzyl-2,6-lutidine) (VI). The acid (V) was decarboxylated by heating its dipotassium salt (10 g.) with calcium hydroxide (20 g.). A combustion tube of Corning 172 Pyrex tubing (19 mm. inside x 25 mm. outside diameter) supported horizontally in a V-shaped trough and heated with three burners served very satisfactorily after ordinary Pyrex tubing had been found insufficiently heat-resistant. A passage was left along the top of the charge to permit free flow of gases. After flushing out the charged tube with nitrogen, full heat was applied, the top of the tube being covered with asbestos board. The distillate was condensed in a flask cooled by flowing water. Accumulated distillates from potassium salt obtained from 48 g. of phenylacetaldehyde were combined, dried in ether over potassium hydroxide and fractionated, giving 24 g. of 4-benzyl-2,6-lutidine, b.p. 167–169° at 17 mm., n_D^{25} 1.5686 as a colorless oil with pale yellow-blue fluorescence. This result represents a 30% over-all yield from phenylacetaldehyde.

4-Benzyl-2,6-lutidine picrate. Orange rods, m.p. 142–143° uncor.

Anal. Calc'd for $C_{20}H_{18}N_4O_7$ (*i.e.*, $C_{14}H_{15}N \cdot C_6H_3N_3O_7$): N, 13.15.
Found: N, 12.9, 13.2.

4-Benzyl-2,6-lutidine methiodide. Lustrous pink or yellow flakes from alcohol-ether, m.p. 150.5–152.0° uncor.

Anal. Calc'd for $C_{15}H_{18}IN$ (*i.e.*, $C_{14}H_{15}N \cdot CH_3I$): N, 4.13; I, 37.4.
Found: N, 4.50; I, 37.9.

4-(4-Nitrobenzyl)-2,6-dimethylpyridine (VII). 4-Benzyl-2,6-lutidine (VI) (10 g.) was shaken in a separatory funnel with 30 ml. of 2 *N* nitric acid saturated with sodium nitrate. The lower aqueous layer was drawn off and the upper layer (presumably the base nitrate)

was shaken with ether (20 ml.), then added dropwise with stirring to concentrated sulfuric acid (35 ml.) cooled in an ice-bath. The sulfuric acid solution was brought to 50° for 5 minutes, poured onto ice, made neutral with sodium carbonate, and extracted with benzene. Decolorization and evaporation of the solvent gave a crude product, m.p. 132–135°; recrystallization from alcohol with addition of water gave (40% yield) white needles of m.p. 135.5–136.5° uncor.

Anal. Calc'd for $C_{14}H_{14}N_2O_2$: N, 11.6. Found: N, 11.5, 11.6.

4-(4-Nitrobenzyl)-2,6-dimethylpyridine methiodide. Yellow crystals from ethanol, m.p. 216–217° uncor.

Anal. Calc'd for $C_{15}H_{17}IN_2O_2$: N, 7.28; I, 33.1.
Found: N, 7.40; I, 33.4.

4-(4-Nitrobenzoyl)-2,6-dimethylpyridine (VIII). A small sample of the above nitro compound (VII) (0.55 g.) suspended in boiling water (40 ml.) was slowly treated with 5% aqueous potassium permanganate, each addition of oxidant being made only when its predecessor had been almost consumed. The total time involved was 22 hours, after which the excess permanganate was decolorized with ethanol and the hot solution filtered. From the aqueous filtrate on cooling, and from benzene extraction of the manganese dioxide cake, there was obtained 0.2 g. of the desired ketone.

Anal. Calc'd for $C_{14}H_{12}N_2O_3$: N, 10.95. Found: N, 10.8, 10.9.

From the aqueous filtrate on concentration and acidification there was also obtained 0.11 g. of *p*-nitrobenzoic acid, m.p. 235–236°, alone or mixed with an authentic sample.

4-(4-Aminobenzyl)-2,6-dimethylpyridine (X). A solution of 4-(4-nitrobenzyl)-2,6-lutidine (VII) (3.43 g.) in 95% ethanol (70 ml.) together with platinum oxide (47 mg.) was shaken with hydrogen at atmospheric pressure and room temperature. After the theoretical amount of hydrogen for reduction of the nitro group had been taken up, rate of absorption of gas sharply decreased. After filtering off the catalyst and evaporating the solvent, there remained 2.8 g. (93% yield) of product recrystallization of which from 40% methanol gave colorless needles, m.p. 132–133° uncor.

Anal. Calc'd for $C_{14}H_{16}N_2$: N, 13.2. Found: N, 13.0, 13.4.

4-(4-Acetaminobenzyl)-2,6-dimethylpyridine (XI). This was obtained from the above base (X) with acetic anhydride; m.p. 145–146° uncor.

Anal. Calc'd for $C_{16}H_{18}N_2O$: N, 11.0. Found: N, 10.9, 11.0.

4-(4-Acetaminobenzyl)-2,6-dimethylpyridine methiodide. White crystals from ethanol, m.p. 193–194° uncor.

Anal. Calc'd for $C_{17}H_{21}IN_2O$: N, 7.07. Found: N, 7.78.

4-(4-Methylamino)-2,6-dimethylpyridine methiodide hydriodide (XIV). 4-(4-Aminobenzyl)-2,6-dimethylpyridine (0.5 g.) with methyl iodide (4 ml.) in a sealed tube at 90° for 6 hours effected monomethylation of the amino group, subsequently quaternizing on one nitrogen and forming the hydriodide salt on the other. The product (0.3 g.) formed white crystals, m.p. 195–196° uncor.

Anal. Calc'd for $C_{16}H_{22}I_2N_2$: C, 38.7; H, 4.44.
Found: C, 38.4, 38.7; H, 4.55, 4.72.

4-(4-Hydroxybenzyl)-2,6-dimethylpyridine (XII). Diazotization of 4-(4-aminobenzyl)-2,6-lutidine (X) (0.7 g.) was carried out in 16% sulfuric acid (40 ml.) by addition at 0° of sodium nitrite (0.23 g.) in water (5 ml.). More water (20 ml.) was added and the solution heated for 2 hours at 100°. The solution was made alkaline with sodium carbonate and extracted with ether. Evaporation of the ether gave a solid which, after purification from alcohol by addition of water, gave 0.4 g. (57% yield) of product which was finally raised to m.p. 163–164° uncor.

Anal. Calc'd for $C_{14}H_{15}NO$: N, 6.58. Found: N, 6.66, 6.66.

4-(2,4-Dinitrobenzyl)-2,6-dimethylpyridine (IX). 4-Benzyl-2,6-lutidine (VI) (3 g.) dissolved in concentrated sulfuric acid (17 ml.) was treated dropwise with fuming nitric acid (1.5 ml., *d*, 1.5) with cooling. After two hours at room temperature the solution was poured onto ice, made alkaline with sodium carbonate and extracted with benzene. Concentration

of the solvent gave 2.2 g. (50% yield) of product which on recrystallization from benzene gave white needles, m.p. 139.5° uncor.

Anal. Calc'd for $C_{14}H_{13}N_3O_4$: N, 14.6. Found: N, 14.1, 14.2.

The melting point of this compound was not depressed when mixed with the product of treatment of 4-(4-nitrobenzyl)-2,6-lutidine (0.25 g.) in concentrated sulfuric acid (5 ml.) with concentrated nitric acid (0.4 ml., *d*, 1.42) at 70° for 1 hour, followed by usual isolation.

4-(2,4-Dinitrobenzyl)-2,6-dimethylpyridine methiodide. Yellow crystals from ethanol, m.p. 210–211° uncor.

Anal. Calc'd for $C_{15}H_{16}IN_3O_4$: N, 9.79. Found: N, 10.2.

Isoquinoline Derivatives

1-Benzyl-3,4-dihydroisoquinoline (XV). This base was obtained from N-(2-phenylethyl)phenylacetamide (11), m.p. 92–93° uncor. by dehydrative cyclization essentially according to Späth (7). The amide (20 g.) dissolved in boiling tetralin (400 ml.) was treated with phosphorus pentoxide (40 g.); after 15 minutes a second equal portion (40 g.) of phosphorus pentoxide was added and boiling continued for 15 more minutes. The tetralin was decanted from the brown residue, to which water was then very carefully added. All of the solid was finally dissolved with a total of 300 ml. of water. A second layer of tetralin was then removed and the phosphoric acid layer extracted with ether to remove the last traces. By neutralizing the acid solution with solid sodium hydroxide the dihydro base was liberated as a brown oil. After drying in ether over potassium hydroxide fractionation gave the base (15.5 g., 84% yield), b.p. 195–198° at 2 mm., n_D^{25} 1.6167. The corresponding picrate showed m.p. 173.5–175°; recorded, 182° uncor. (11), 173–175° (7), 174–175° (12).

When the ether extract from a ring closure such as described above was distilled from potassium hydroxide pellets, an unexpected cleavage occurred with formation of isoquinoline and toluene in good yield, as shown in the following example. Half of the ether solution from a typical cyclization on distillation without potassium hydroxide gave 8.9 g. of 3,4-dihydroisoquinoline. The other half was concentrated over potassium hydroxide pellets in a Claisen flask from which (after ether removal) raising of bath temperature to 200° caused distillation over about an hour of a colorless liquid. Refractionation of this material gave 2.5 g. of toluene, b.p. 107–110° confirmed by neutral permanganate oxidation to benzoic acid. Reduction of pressure to 5 mm. then yielded a second distillate (3.8 g., b.p. 95° at 5 mm.) which was shown to be isoquinoline by preparation of the corresponding methiodide and picrate and direct comparison with authentic samples. The picrate was also confirmed by satisfactory analyses for nitrogen and for neutralization equivalent.

1-Benzylisoquinoline (XVI). Samples of 1-benzyl-3,4-dihydroisoquinoline (XV) were dehydrogenated over palladium black at 190° as previously reported (7), yielding 1-benzylisoquinoline, b.p. 160–162° at 2 mm.; corresponding picrate, m.p. 179–181° uncor. [recorded, 184–185° cor. (13), 184° cor. (14), 182° (7, 12), 182–184° (15), 176° (16)].

This base (1 g.) with methyl iodide (10 ml.) in a sealed tube at 100° for 10 minutes gave benzylisoquinoline methiodide (1.8 g.) which recrystallized from alcohol as pale yellow crystals, m.p. 229–231° uncor.; recorded 248° cor. (14).

Anal. Calc'd for $C_{17}H_{16}IN$: N, 3.88. Found: N, 4.02, 4.07.

1-(4-Nitrobenzyl)isoquinoline (XVII). 1-Benzylisoquinoline (XVI) (3 g.) was mononitrated by essentially the same procedure used for 4-benzyl-2,6-lutidine (VI). The orange oil comprising the crude product distilled at 218–220° at 1.5 mm. and gave 1.85 g. = 51% yield. Subsequent solidification slowly occurred, after which recrystallization from dilute ethanol yielded white needles, m.p. 85–86°.

Anal. Calc'd for $C_{16}H_{12}N_2O_2$: N, 10.6. Found: N, 10.7, 11.2.

After conversion of this compound to its methiodide and oxidation of a boiling aqueous solution of the latter with potassium permanganate, there was isolated *p*-nitrobenzoic acid, m.p. 233–235°, which did not depress the melting point of an authentic sample.

1-(2,4-Dinitrobenzyl)isoquinoline (XVIII). 1-Benzylisoquinoline (XVI) (1.5 g.) was dinitrated by solution in concentrated sulfuric acid (12 ml.) and treatment at room tempera-

ture with concentrated nitric acid (1.5 ml., *d*, 1.42). After standing for one hour, pouring onto ice and working up there resulted 0.26 g. (12% yield) of crude product, recrystallization of which from 50% ethanol gave yellow flakes, m.p. 160–162° uncor.

Anal. Calc'd for $C_{16}H_{11}N_3O_4$: N, 13.6. Found: N, 13.4, 13.8.

Acridine Derivatives

9-Benzylacridine (XIX). This material was prepared from phenylacetic acid, diphenylamine, and fused zinc chloride by heating at 190–200° for 24 hours as described in the literature (8); yield 21%; from benzene it separated as yellow crystals, m.p. 174–175° uncor.; recorded 173° (8, 17).

9-Benzylacridinium nitrate (XX). 9-Benzylacridine, on boiling with 3 *N* nitric acid for 10 minutes did not dissolve, and the only apparent change was an increase in the hardness of the yellow solid. Recrystallization of the material by solution in glacial acetic acid and reprecipitation with dry ether gave yellow needles of 9-benzylacridine nitrate, m.p. 167–168° uncor.

Anal. Calc'd for $C_{20}H_{16}N_2O_3$: N, 8.44. Found: N, 8.38, 8.40.

9-(4-Nitrobenzyl)acridine (XXI). 9-Benzylacridinium nitrate (XX) (1.68 g.) was dissolved in concentrated sulfuric acid (20 ml.). The solution was brought to 50°, poured over ice, and made alkaline with concentrated ammonium hydroxide. The resultant pink solid was separated, dissolved in boiling absolute ethanol (110 ml.), decolorized with carbon, and reprecipitated by addition of water (40 ml.) as lustrous golden flakes, 1.4 g. = 75% yield, m.p. 195–198° uncor.

Anal. Calc'd for $C_{20}H_{14}N_2O_2$: N, 8.92. Found: N, 9.16, 9.24.

9-(4-Nitrobenzyl)acridine methiodide. 9-(4-Nitrobenzyl)acridine (0.2 g.) with methyl iodide (10 ml.) in a sealed tube heated for 20 minutes gave deep red rods of quaternary salt (0.12 g.) which did not melt up to 250°. The yield was not increased by longer heating. The salt was sparingly soluble in water but gave an immediate precipitate with silver nitrate solution.

Anal. Calc'd for $C_{21}H_{17}IN_2O_2$: I, 27.9. Found: I, 28.0.

9-(4-Nitrobenzyl)acridine (XXII). 9-(4-Nitrobenzyl)acridine (0.5 g.) in glacial acetic acid (10 ml.) containing sodium dichromate (0.4 g.) was refluxed for 2 hours. Water (40 ml.) was then added, precipitating a gummy solid which on recrystallization from alcohol gave yellow crystals (0.01 g.), m.p. 226–228° uncor.

Anal. Calc'd for $C_{20}H_{12}N_2O_3$: N, 8.53. Found: N, 8.61.

Unlike the isomeric nitroacridones (18) this material gave no color with alcoholic alkali.

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SUMMARY

1. A hitherto unreported base, 4-benzyl-2,6-dimethylpyridine, has been synthesized and characterized.

2. The color reactions produced by alcoholic alkali upon the quaternary salts of 4-(4-nitrobenzyl)-2,6-dimethylpyridine, 1-(4-nitrobenzyl)isoquinoline, and 9-(4-nitrobenzyl)acridine have been compared.

3. Including those above 20 new compounds have been characterized.

4. 1-Benzyl-3,4-dihydroisoquinoline, when distilled with alkali, has been found to split into good yields of toluene and isoquinoline.

BIBLIOGRAPHY

(1) DECKER AND KLAUSER, *Ber.*, **37**, 520 (1904).
(2) DECKER, *Ber.*, **38**, 2493 (1905).
(3) KOENIGS, KÖHLER, AND BLINDOW, *Ber.*, **58**, 933 (1925).

(4) TSCHITSCHIBABIN, KUINDSHI, AND BENEWOLENSKAJA, *Ber.*, **58,** 1580 (1925).
(5) BRYANS AND PYMAN, *J. Chem. Soc.*, 549 (1929).
(6) AYLING, *J. Chem. Soc.*, 1014 (1938).
(7) SPÄTH, BERGER, KUNTARA, *Ber.*, **63,** 139 (1930).
(8) DECKER AND HOCK, *Ber.*, **37,** 1564 (1904).
(9) JEAURENAUD, *Ber.*, **21,** 1783 (1888).
(10) KIRCHNER, *Ber.*, **25,** 2786 (1892).
(11) DECKER, KROPP, HOYER, AND BECKER, *Ann.*, **395,** 305 (1913).
(12) PICTET AND KAY, *Ber.*, **42,** 1977 (1909).
(13) DECKER AND PSCHORR, *Ber.*, **37,** 3397 (1904).
(14) FORSYTH, KELLY, AND PYMAN, *J. Chem. Soc.*, **127,** 1662 (1925).
(15) VON BRAUN AND NELLES, *Ber.*, **70,** 1767 (1937).
(16) BERGMANN AND ROSENTHAL, *J. prakt. Chem.*, (2) **135,** 276 (1932).
(17) BUU-HOÏ, AND LECOCQ, *Rec. trav. chim.*, **64,** 250 (1945); *Chem. Abstr.*, **40,** 4068 (1946).
(18) ULLMANN AND BADER, *Ann.*, **355,** 328 (1907).