Anal. Calcd. for $C_9H_{10}N_4S$: C, 52.4; H, 4.9; N, 27.2. Found: C, 52.6; H, 5.0; N, 26.9.

2-Benzylmercapto-6-methyl-4-oxo-1,3,3a,7-tetrazaindene (XIX). A mixture of 20 g. of the triazole and 15 ml. of acetoacetic ester in 150 ml. of acetic acid was refluxed 5 hr. and then cooled. The solid was collected and recrystallized from ethanol. Yield, 15 g. of product, m.p. 252°.

Anal. Calcd. for $C_{13}H_{12}N_4OS$: C, 57.3; H, 4.4; N, 20.6. Found: C, 57.4; H, 4.5; N, 19.9.

6-Methyl-4-oxo-1,3,3a,7-tetrazaindene-2-thiol (XVII). To a solution of 6.5 g. of XIX in 200 ml. of liquid ammonia was added small pieces of sodium until the blue color persisted. The ammonia was allowed to evaporate at room temperature and the residue was dissolved in water, filtered, and the filtrate acidified with hydrochloric acid and chilled. The solid was collected and recrystallized from water. Yield, 4.3 g. of product, m.p. 287–288°.

Anal. Calcd. for $C_6H_6N_4OS$: C, 39.5; H, 3.3; N, 30.8. Found: C, 39.6; H, 3.3; N, 30.7.

A run in which acetic acid was used in place of hydrochloric acid for the neutralization yielded 3.5 g. of the sodium salt of the mercaptotetrazaindene, m.p. 310°, with decomposition.

Anal. Calcd. for $C_6H_5N_4OSNa$: C, 35.1; H, 2.9; N, 27.3. Found: C, 34.8; H, 2.7; N, 27.1.

7-Carbethoxy-6-methyl-2-methylmercapto-4-oxo-1,3,3a,7-tetrazaindene (XX). A solution of 5 g. of 6-methyl-2-methylmercapto-4-oxo-1,3,3a,7-tetrazaindene (XVIII) in 1 g. of sodium hydroxide and 50 ml. of water was evaporated to dryness *in vacuo* and to the residue was added 5 g. of ethyl chloroformate and 100 ml. of benzene. The mixture was stirred at room temperature for 24 hr., heated to boiling, filtered, and the filtrate chilled. The solid was collected and recrystallized from benzene. Yield, 2.5 g. of product, m.p. 190–191°.

Anal. Calcd. for $C_{10}H_{12}N_4O_3S$: C, 44.8; H, 4.5; N, 20.9. Found: C, 44.6; H, 4.4; N, 21.2.

7-Carbethoxy-6-methyl-4-oxo-1,3,3a,7-tetrazaindene (XXXV) A mixture of 5 g. of the sodium salt of 6-methyl-4-oxo-1,3,3a,-7-tetrazaindene (I), 10 ml. of ethyl chloroformate and 250 ml. of benzene was stirred 24 hr. at room temperature. The mixture was worked up as above to yield 2 g. of product, m.p. 182–183°, with decomposition.

Anal. Calcd. for $C_9H_{10}N_4O_3$: C, 48.6; H, 4.5; N, 25.2. Found: C, 48.5; H, 4.5; N, 24.8.

Dethiolation of 7-carbethoxy-6-methyl-2-methylmercapto-1,3,3a,7-tetrazaindene. A mixture of 2 g. of the tetrazindene XX, 2 teaspoons of Raney nickel, and 500 ml. of absolute ethanol was refluxed 4 hr. The mixture was filtered hot and the Raney nickel extracted with 500 ml. of hot alcohol. The combined alcohol solutions were evaporated to 25 ml. and chilled. Yield, 0.4 g. of 6-methyl-4-oxo-1,3,3a,7-tetrazaindene, (I).

Acknowledgment. We are indebted to Dr. D. W. Stewart and Miss T. J. Davis, Rochester, and Mr. B. S. Goode, Harrow, of these Laboratories, for the absorption spectra.

ROCHESTER 4, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE COLLEGE OF ARTS AND SCIENCES OF THE UNIVERSITY OF LOUISVILLE]

Pyridine Analogs of *p*-Terphenyl and *p*-Quaterphenyl

RICHARD H. WILEY, P. X. CALLAHAN, C. H. JARBOE, JR., J. T. NIELSEN, AND B. J. WAKEFIELD

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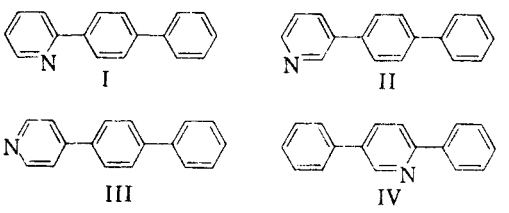
Four pyridine analogs of *p*-terphenyl and two of *p*-quaterphenyl have been synthesized for evaluation as scintillation solutes.

p-Terphenyl and its derivatives have been extensively studied as scintillation solutes.[1] A limitation on the usefulness of polyphenyls themselves for this purpose is their low solubility in toluene, the commonly used solvent. Although pyridine analogs of the polyphenyls offer a class of possible alternatives for use as scintillators, only a few such compounds are known. Of the twenty-five possible pyridine analogs of *p*-terphenyl, only four are reported in the literature. 4-(2-Pyridyl)biphenyl (I), 4-(3-pyridyl)biphenyl (II), and 4-(4-pyridyl)-biphenyl (III) have been synthesized by the reaction of the (*N*-nitrosoacetamidophenyl)pyridines with benzene.[2] The 2- and 4-isomers have also been prepared by the reaction of *p*-phenylbenzenediazonium chloride with pyridine.[2] An unseparated mixture of the six *p*-dipyridylbenzenes has been prepared[3] by the reaction of a mixture of diazotized



p-aminophenylpyridines with pyridine. None of the 2,5-diphenylpyridylpyridines or 2,5-dipyridylpyridines is known and no pyridine analogs of *p*-quaterphenyl are recorded. We wish to report at this time the results of a study of the synthesis and scintillation properties of some compounds of this type.

We have recently reported[4] the synthesis of 2,5-diphenylpyridine (IV), m.p. 174°, by the reaction of phenyllithium with 3-phenylpyridine. The structure of the product was proved by an alterna-

(1) F. N. Hayes, D. G. Ott, V. N. Kerr, and B. S. Rogers, *Nucleonics* **13**, #12, 38 (1955).

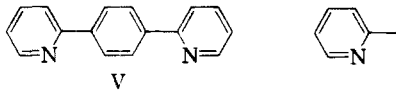
(2) I. M. Heilbron, D. H. Hey, and A. Lambert, *J. Chem. Soc.*, 1279 (1940).

(3) A. H. Cook, I. M. Heilbron, D. H. Hey, A. Lambert, and A. Spinks, *J. Chem. Soc.*, 404 (1943).

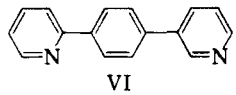
(4) R. H. Wiley, C. H. Jarboe, P. X. Callahan, and J. T. Nielsen, *J. Org. Chem.*, **23**, 780 (1958).

tive synthesis involving permanganate oxidation of 3-phenylbenzo(f)quinoline. Complete details of these experiments are given here. The *p*-dimethylamino analog has been prepared using *p*-dimethylaminophenyllithium to evaluate the effect of the dimethylamino group on scintillation properties. The 3-phenylpyridine used in these reactions was prepared by a new method. Cyclohexanone was treated with 3-pyridyllithium[5] and the product was dehydrated to give 3-(1-cyclohexenyl)pyridine in 77% yield. Dehydrogenation with sulfur or, better, with palladium on alumina at 360° gave 3-phenylpyridine in 50% yield.

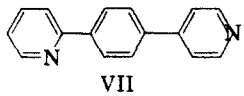
We have synthesized and characterized three *p*-dipyridylbenzenes (V, VI, VII). *p*-Nitroaniline was diazotized and treated with pyridine[6] and



V



VI



VII

the resulting 2-, 3-, and 4-(*p*-nitrophenyl)pyridines were separated by fractional crystallization of the bases and their salts. The structures of the (*p*-nitrophenyl)pyridines have been established.[6] The *p*-nitrophenylpyridines were reduced to the corresponding *p*-aminophenylpyridines with tin and hydrochloric acid. If three *p*-dipyridylbenzenes could be isolated from the reaction of each of the *p*-aminophenylpyridines with pyridine, the structures of the six isomeric products would be established. We have isolated three compounds from these reactions and some conclusions as to their structures have been established.

From the reaction of 2-(*p*-aminophenyl)pyridine we have isolated two compounds, m.p. 147–148° and 196–197°; from 3-(*p*-aminophenyl)pyridine one compound, m.p. 131–132°, and from 4-(*p*-aminophenyl)pyridine one compound, m.p. 196–197°. Elementary analyses confirmed that these compounds are dipyridylbenzenes. The two materials, m.p. 196–197°, were identical on the basis of mixed melting points and infrared absorption characteristics. From the starting materials involved, this product can be only *p*-di-(2,4-pyridyl)-benzene (VII). The other two products can be tentatively assigned 2-substituted structures since homolytic substitution of the pyridine ring normally takes place in the 2-position[2,3,7,8] and the 3-isomer is usually most difficult to isolate.[2,8] It is probable, therefore, that the compound, m.p. 147–148°, is *p*-di-(2,2-pyridyl)benzene (V) and that the compound, m.p. 131–132°, is *p*-di-(2,3-pyridyl)benzene (VI).

The physical properties of these dipyridylbenzenes are consistent with the assigned structures. Thus, the melting points of the 2,2- and 2,3-isomers are both lower than that of the 2,4- isomer. The 4-isomer is generally the highest melting of a series.[8] The ultraviolet spectrum of the 2,2-isomer (m.p. 147–148°) differs greatly from that of *p*-terphenyl, whereas those of the other compound are less different. Pyridine analogs of *p*-polyphenyls also show abnormalities when 2-pyridyl nuclei are present. The ultraviolet spectra are discussed in more detail below. The infrared spectra of the *p*-dipyridylbenzenes are complex and do not provide further information on the identity of the isomers. Detailed studies have been made[9–11] of the infrared spectra of substituted pyridines in the 1600 cm.$^{-1}$ to 1000 cm.$^{-1}$ region (chloroform solution). The correlations so established are useful in simple cases but are of little value for structural assignments in compounds with more than one type of pyridine substitution. The *p*-dipyridylbenzenes show strong bands in the 900 cm.$^{-1}$ to 600 cm.$^{-1}$ regions (potassium bromide disk), which can be assigned to out of plane hydrogen vibrations. Although assignments consistent with those for simple pyridines can be made, these are not sufficiently characteristic to serve as a proof of structure. These infrared spectra are discussed in more detail below.

Several attempts have been made to provide further confirmation of the identity of the supposed 2,2- and 2,3-isomers by degradation or by alternative synthesis. The 2,2-isomer (m.p. 147–148°) was recovered unchanged after heating with alkaline permanganate for 48 hours. In order to facilitate oxidation of the central ring, the compound was nitrated and the nitro-compound was reduced to the amine. Permanganate oxidation of the amine gave insufficient amounts of pyridinecarboxylic acids to be identified. Attempted synthetic routes utilized 2-(*p*-bromophenyl)pyridine and 2-(*p*-iodophenyl)pyridine prepared from 2-(*p*-aminophenyl)pyridine.[8] 2-(*p*-Bromophenyl)pyridine did not react with lithium. It has been reported that this compound does not form a Grignard reagent.[3] The aryllithium was formed normally, however, by metal exchange between *n*-butyllithium and 2-(*p*-bromophenyl)pyridine, but reaction of the *p*-(2-pyridyl)phenyllithium with pyridine gave only tars from which no identifiable products could be isolated. *p*-Di-(2,2-pyridyl)benzene was not

(5) H. Gilman and S. M. Spatz, *J. Am. Chem. Soc.*, 62, 446 (1940).

(6) J. W. Haworth, I. M. Heilbron, and D. H. Hey, *J. Chem. Soc.*, 349 (1940).

(7) D. H. Hey, J. M. Stirling, and G. H. Williams, *J. Chem. Soc.*, 3963 (1955).

(8) E. C. Butterworth, I. M. Heilbron, and D. H. Hey, *J. Chem. Soc.*, 357 (1940).

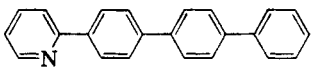
(9) A. R. Katritzky and J. N. Gardner, *J. Chem. Soc.*, 2198 (1958).

(10) A. R. Katritzky and A. R. Hands, *J. Chem. Soc.*, 2202 (1958).

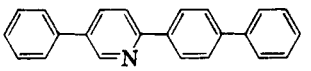
(11) A. R. Katritzky, A. R. Hands, and R. A. Jones, *J. Chem. Soc.*, 3165 (1958).

formed by mixed Ullman reactions[12] between 2-(*p*-bromophenyl)pyridine or 2-(*p*-iodophenyl)-pyridine and 2-bromopyridine. Even under conditions which converted the 2-bromopyridine to a tarry product, halophenylpyridine could be recovered. An attempt to synthesize 1-(2-pyridyl)-4-(4-methylpyridyl)benzenes by coupling diazotized 2-(*p*-aminophenyl)pyridine with γ-picoline gave tars.

Two pyridine analogs of *p*-quaterphenyl have been synthesized: 4-(2-pyridyl)-*p*-terphenyl (VIII) and 2-(4-biphenylyl)-5-phenylpyridine (IX). Nitration of biphenyl with concentrated nitric acid



VIII



IX

at 45° gave 4,4′-dinitrobiphenyl.[13] This was reduced to 4-amino-4′-nitrobiphenyl with sodium polysulfide[14] and the product was diazotized and coupled with pyridine. The only product isolated was 4-nitro-4′-(2-pyridyl)biphenyl, m.p. 214–215° (lit.[2] m.p. 213°). This compound was reduced to the amine with stannous chloride[2] and the amine was acetylated. Treatment of the 4-acetamido-4′-(2-pyridyl)biphenyl with nitrosyl chloride gave 4-(*N*-nitrosoacetamido)-4′-(2-pyridyl)biphenyl. This compound with benzene gave 4-(2-pyridyl)-*p*-terphenyl (VIII), m.p. 269–270°. 2-(4-Biphenylyl)-5-phenylpyridine (IX) was prepared by a method similar to that used for 2,5-diphenylpyridine. Metal exchange between *n*-butyllithium and 4-bromobiphenyl gave 4-biphenyllithium, which with 3-phenylpyridine gave the product m.p. 274–275°.

Scintillation data for some of the compounds described above and for some related compounds are recorded in Table I. The general conclusion drawn from these results is that while the introduction of a pyridine nucleus into a polyphenyl does increase its solubility in toluene, this advantage is overshadowed by a great reduction in scintillation response. The reduction is greater for a non-terminal pyridine (as in 2,5-diphenylpyridine and 2-(4-biphenylyl)-5-phenylpyridine than for a terminal pyridine (as in 4-(2-pyridyl)biphenylyl)-5-phenylpyridine. As was expected,[15] the introduction of a *p*-dimethylamino group into 2,5-diphenylpyridine produced a pronounced increase in scintillation response.

TABLE I

SCINTILLATION DATA[a]

Compound	R.P.H.[b]	Concentration g./l.	Solubility g./l. in toluene at 25°
p-Terphenyl[c]	0.94	3	8
4-(2-Pyridyl)biphenyl[c]	0.12	3	...
2,5-Diphenylpyridine	<0.10	3	13
2-(*p*-Dimethylaminophenyl)-5-phenylpyridine	0.94	3	...
p-Di(2,4-pyridyl)benzene	<0.10	3	...
p-Quaterphenyl	...	...	<1
4-(2-Pyridyl)-*p*-terphenyl	0.70	1.02	1.02
2-(4-biphenylyl)-5-phenylpyridine	0.41	1.8	1.8

[a] Data obtained by Dr. F. N. Hayes and co-workers. [b] Pulse height relative to solution of 3 g./l. of 2,5-diphenyloxazole in toluene. [c] See ref. (15).

Ultraviolet absorption data have been recorded[16] for the 4-pyridylbiphenyls. The synthesis of further analogs of *p*-terphenyl makes possible some further correlations of the spectra of these compounds. Relevant information is recorded in Table II. It has been pointed out[16] that the spectra of the pyridine analogs of biphenyl and terphenyl are generally similar to those of the hydrocarbons but show a tendency to absorb at slightly longer wave lengths. Compounds containing 2-pyridine rings

TABLE II

ULTRAVIOLET ABSORPTION SPECTRA

Compound	λ_{max} mμ	log ε	Solvent[a]	Ref.
Biphenyl	250	4.26	E	17
2-Phenylpyridine	245.5	4.10	E	16
	275.5	4.05		
3-Phenylpyridine	246	4.24	E	16
	275sh			
4-Phenylpyridine	257	4.20	E	16
2,2′-Bipyridine	237	4.04	H	16
	281	4.16		
4,4′-Bipyridine	238.5	4.10	H	16
p-Terphenyl	276	4.45	H	16
4-(2-Pyridyl)biphenyl	292	4.66	H	16
4-(3-Pyridyl)biphenyl	279	4.49	H	16
4-(4-Pyridyl)biphenyl	279	4.53	H	16
2,5-Diphenylpyridine	271	4.20	E	
	289.5	4.24		
p-Di(2,2-pyridyl)benzene	262	4.34	M	
	295	4.64		
p-Di(2,3-pyridyl)benzene	260sh		M	
	290	4.57		
p-Di(2,4-pyridyl)benzene	255sh		M	
	290	4.46		
2-(4-Biphenylyl)-5-phenylpyridine	280sh	4.47	M	
	307	4.63		

[a] The letters stand for the following solvents: E, ethanol; H, hexane; M, methanol.

(12) F. H. Burstall, *J. Chem. Soc.*, 1666 (1938).

(13) H. C. Gull and E. E. Turner, *J. Chem. Soc.*, 494 (1929).

(14) R. Belcher, A. J. Nutten, and W. I. Stephen, *J. Chem. Soc.*, 1334 (1953).

(15) F. N. Hayes *et al.*, *Survey of Organic Compounds as Primary Scintillation Solutes; a Status Report, U.S.A.E.C.*, 1958.

(16) A. E. Gillam, D. H. Hey, and A. Lambert, *J. Chem. Soc.*, 364 (1941).

(17) A. E. Gillam and D. H. Hey, *J. Chem. Soc.*, 1170 (1939).

TABLE III

INFRARED MAXIMA IN THE 900 CM.$^{-1}$ TO 650 CM.$^{-1}$ REGION

Normal range of vibrations[a]	One Hydrogen 900–860 cm.$^{-1}$	Two Hydrogens 860–800 cm.$^{-1}$	Three Hydrogens 810–750 cm.$^{-1}$	Four Hydrogens 770–735 cm.$^{-1}$	Five Hydrogens 770–730, 710–695 cm.$^{-1}$
Compound					
Pyridine					750
2-Picoline				755	
3-Picoline			790		
4-Picoline		800			
3-Phenylpyridine			807m		753vs(707s)-693s
4-(2-Pyridyl)biphenyl		846s		784m	752vs(708m)-682 vs
4-(4-Pyridyl)biphenyl		842s, 804s			761vs(701s)-688vs
2,5-Diphenylpyridine	904w	834m			749vvs(734s)-681vs
2-(4-Biphenylyl)-5-phenylpyridine	907m	856w, 827vs	780w		756vvs(749sh)-685vs
p-Di(2,2-pyridyl)benzene		861s		770vvs	(744w, 720w)
p-Di(2,3-pyridyl)benzene		848m	795m	774vs	(740w, 724w, 703s)
p-Di(2,4-pyridyl)benzene		860m, 818vs		779vvs	(738m, 711s)

[a] Bands in parentheses correlated with presence of pyridine nucleus. See ref. (18).

were however, abnormal. Thus, for example, 2,2′-bipyridine showed two absorption maxima. 4-(2-Pyridyl)biphenyl absorbed at a much longer wave length than did the 3-pyridyl- and 4-pyridyl-isomers. The fact that the *p*-dipyridylbenzene which has been assigned the 2,2 structure give two maxima, one at the same wave length as that of the absorption maximum of 4-(2-pyridyl)biphenyl, tends to confirm its identity. The other two isomers synthesized have very similar spectra with a pronounced maximum at the same wave length as that of 4-(2-pyridyl)biphenyl, and a shoulder at lower wave length. This suggests that both have one 2-substituted and one other pyridine ring and hence tends to confirm the identity of the supposed 2,2-isomer. 2,5-Diphenylpyridine has maxima both at the "normal" *p*-terphenyl frequency and at the "abnormal" 2-pyridine analog frequency.

Infrared absorption maxima and their approximate intensities for some pyridine analogs of polyphenyls and some related compounds in the 900 cm.$^{-1}$ to 650 cm.$^{-1}$ region are given in Table III. Maxima in this region have been correlated[18] with out of plane vibrations of different numbers of adjacent hydrogen atoms in aromatic nuclei. The ranges in which the maxima normally fall are indicated in the Table III. While it is generally easy to correlate bands in the spectra of known compounds with the number of adjacent hydrogen atoms present, it is less easy to deduce the structure of an unknown compound from the maxima. For example, the band at 800 cm.$^{-1}$ in 4-picoline is clearly due to the vibration of two adjacent hydrogens but a band at this frequency in an unknown compound might be due to two or to three adjacent hydrogens. Correlation appears to be particularly difficult when pyridine, as well as benzene nuclei are present, as in these cases bands may be found at the extremes of, or outside, their normal ranges. A band in the 710–730 cm.$^{-1}$ range has been correlated with a pyridine nucleus.[18] The proposed correlations for the maxima given by the analogs of the polyphenyls are indicated by their positions in Table III.

EXPERIMENTAL

Ultraviolet spectra were measured with a Beckman DK-2 recording spectrophotometer using spectral grade methanol or ethanol as solvent. Infrared spectra were run on a Baird recording double beam spectrometer in potassium bromide disks unless otherwise stated. Melting points were measured in open capillaries and are uncorrected. The authors are indebted to Drs. F. N. Hayes, D. G. Ott, and Miss E. Hansbury of the Los Alamos Laboratories for the pulse height measurements.[1] Analyses by Micro Tech Laboratories, Skokie, Ill.

3-(1′-Cyclohexenyl)pyridine. *n*-Butyllithium was prepared from lithium (4.4 g.) and 1-bromobutane (40 g.) in 350 ml. of dry ether. The mixture was cooled in a Dry ice–acetone bath and to it was added 3-bromopyridine (30 g.) and cyclohexanone (28.6 g.). After 3 hr., the reaction mixture was warmed to room temperature, poured onto ice water, and steam distilled to remove reactants. The residue was extracted with ether and the ether extracts dried and distilled to give a crude product, b.p. 266–268°. Refractionation gave 21 g. (77%) of the product, b.p. 98–101°/2 mm. n_D^{25} 1.5683.

Anal. Calcd. for $C_{11}H_{13}N$: C, 82.97; H, 8.23. Found: C, 82.68; H, 8.35.

3-Phenylpyridine. By dehydrogenation with sulfur. Sulfur (4.5 g.) and 3-(1-cyclohexenyl)pyridine (12.0 g.) were heated under reflux for 2 hr. The mixture was distilled to give 4.5 g. (39%) of 3-phenylpyridine, b.p. 273–274°, n_D^{25} 1.6142 (lit.[19] b.p. 117–118°/5 mm.; n_D^{25} 1.6123).

By dehydrogenation over palladized alumina. A Pyrex tube (6 mm. × 40 cm.) was packed with alumina pellets (1 × 3 mm.; 15 g.) on which 0.5 g. of palladium had been precipitated. The tube was heated electrically to 360°. Nitrogen was passed through the tube at a rate of 25 ml./min. (at exit). 3-(1-Cyclohexenyl)pyridine was distilled into the nitrogen stream and the product was condensed at the exit of the tube. Fractionation gave 0.5 g. (50%) of 3-phenylpyridine from 1 g. of 3-(1-cyclohexenyl)pyridine.

(18) L. J. Bellamy, *The Infra red Spectra of Complex Molecules*, 2nd. ed., Wiley, New York, 1958.

(19) C. P. Farley and E. L. Eliel, *J. Am. Chem. Soc.*, **78**, 3481 (1956).

3-Phenylpyridine was also prepared by oxidation of benzo(f)quinoline with permanganate, followed by decarboxylation of the product;[20-22] and by coupling *N*-nitrosoacetanilide with pyridine.[19]

2-Phenylbenzo(f)quinoline. A solution of phenyllithium prepared from 0.15 g. of lithium and 1.6 g. of bromobenzene in 150 ml. of ether was added to a solution of 2.55 g. of benzo(f)quinoline in 150 ml. of dry ether in an atmosphere of nitrogen. The mixture was stirred for 10 hr., and poured into excess cold dilute hydrochloric acid. The ether layer was evaporated and the residue was recrystallized three times from dilute hydrochloric acid to give the hydrochloride of the product, m.p. 215–225° (dec.). The free base (2.4 g.; 80%) was liberated by treating the hydrochloride with dilute aqueous sodium hydroxide and recrystallized from ethanol, m.p. 188–188.5° (lit.[23] m.p. 188°).

2,5-Diphenylpyridine. From 3-phenylpyridine. A solution of phenyllithium in ether (150 ml.) prepared from bromobenzene (2.71 g.) was added to a solution of 3-phenylpyridine (2.50 g.) in dry ether (150 ml.). The mixture was stirred for 24 hr. at room temperature. Water (30 ml.) was added and ether was removed and the residue recrystallized from ethanol to give 2,5-diphenylpyridine (0.95 g.; 26%), m.p. 174–175° (undepressed on admixture with material prepared from 2-phenylbenzo(f)quinoline; see below).

Anal. Calcd. for $C_{17}H_{13}N$: C, 88.28; H, 5.67; N, 6.06. Found: C, 88.09, 88.18; H, 5.79, 5.89; N, 6.12, 6.10.

From 2-phenylbenzo(f)quinoline. Finely divided 2-phenylbenzo(f)quinoline (1.6 g.) was suspended in a solution of sodium hydroxide (0.87 g.) in water (700 ml.). The solution was heated to 90–100°, potassium permanganate (2.26 g.) was added in portions and the suspension was stirred at 90–100° for 4 days. The suspension was filtered and the filtrate was made neutral to phenolphthalein with dilute sulfuric acid and concentrated to 2.5 ml. Ethanol (40 ml.) was added, and the precipitated potassium sulfate was removed by filtration. The solution was evaporated to dryness and the residue was recrystallized from benzene to give 3-(*o*-carboxyphenyl)-6-phenyl-2-carboxypyridine (1.6 g. 85%), m.p. 196° (dec.) (lit.[24] m.p. 196°). pK_a 5.62, pK_b 8.16. Mol. wt.: Calcd., 319; found (by titration), 320.5.

3-(*o*-Carboxyphenyl)-6-phenyl-2-carboxypyridine (1.5 g.) was heated to 200° for 25 min. Carbon dioxide was evolved. The residue was recrystallized from ethanol to give 5-(*o*-carboxyphenyl)-2-phenylpyridine (1.2 g.; 92%), m.p. 195–196° (depressed to 140–151° on admixture with 3-(*o*-carboxyphenyl)-6-phenyl-2-carboxypyridine).

Anal. Calcd. for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76. Found: C, 78.40; H, 4.68.

5-(*o*-Carboxyphenyl)-2-phenylpyridine (0.3 g.) was ground with a large excess of copper dust, and the mixture was heated to redness in a copper test tube. The residue was extracted with benzene. The benzene was evaporated and the residue was recrystallized from ethanol to give 2,5-diphenylpyridine (0.2 g.; 60%), m.p. 174°.

Ultraviolet absorption: λ_{max} 271 mμ (log ε, 4.20), 289.5 mμ (log ε, 4.24). Relative pulse height <0.10.

2-(p-Dimethylaminophenyl)-5-phenylpyridine. A solution of *p*-dimethylaminophenyllithium prepared from *p*-dimethylaminobromobenzene (2 g.) was added to a solution of 3-phenylpyridine in dry ether. The reaction mixture was allowed to stand for 3 days in an atmosphere of nitrogen and was then poured into excess dilute hydrochloric acid. The ether was evaporated and the solution was neutralized with aqueous sodium hydroxide and extracted four times with 50-ml. portions of hot benzene. The benzene was evaporated, and the residue was recrystallized from ethanol to give 2-(*p*-dimethylaminophenyl)-5-phenylpyridine, (0.39 g.; 15%), m.p. 201°.

Anal. Calcd. for $C_{19}H_{18}N_2$; C, 83.17; H, 6.61. Found: C, 83.12; H, 6.96.

Ultraviolet absorption: λ_{max} 240.5 mμ (log. ε, 3.88), 335 mμ (log ε, 4.32).

Relative pulse height 0.94.

p-Nitrophenylpyridines. A mixture of *p*-nitrophenylpyridines was prepared by the coupling of diazotized *p*-nitroaniline and pyridine using the method previously described.[6] Fractional recrystallization of the hydrochlorides and of the nitrates gave 2-(*p*-nitrophenyl)pyridine (36% yield from *p*-nitroaniline) m.p. 130–131° (lit.[6] m.p. 130–131°) and 3-(*p*-nitrophenylpyridine (15% yield), m.p. 146–147° (lit.[6] m.p. 146–147°). Fractions thought to contain a high proportion of the 4-isomer were combined and converted to the picrates. These were readily separated by fractional recrystallization from acetone into a more soluble picrate, m.p. 157–160° (mainly the 2-isomer; lit.[6] m.p. 168°) and a less soluble picrate, m.p. 225–227° (dec.) (lit.[6] m.p. for picrate of 4-(*p*-nitrophenyl)pyridine, 228–229°). Treatment of the less soluble picrate with aqueous sodium hydroxide gave 4-(*p*-nitrophenyl)pyridine (5% yield from *p*-nitroaniline), m.p. 122–124° (lit.[6] m.p. 122–123°).

p-Aminophenylpyridines. The 2-, 3- and 4-(*p*-nitrophenyl)-pyridines were reduced to the corresponding *p*-aminophenylpyridines with tin and hydrochloric acid,[25] in 86%, 60%, and 40% yields respectively. 2-(*p*-Aminophenyl)pyridine, m.p. 96–97° (lit.[25] m.p. 97–98°); 3-(*p*-aminophenyl)pyridine, m.p. 99–101° with water of crystallization, 116–118° anhydrous (lit.[25] m.p. 102–104°; 116–118°); 4-(*p*-aminophenyl)pyridine, m.p. 232–233° (lit.[25] m.p. 232–234°).

p-Dipyridylbenzenes. From 2-(p-aminophenyl)pyridine. 2-(*p*-Aminophenyl)pyridine (14.5 g.) was dissolved in concentrated hydrochloric acid (55 ml.) and water (25 ml.). The solution was cooled to 0° (some hydrochloride crystallized) and the temperature was kept below 5° while a solution of sodium nitrite (7.0 g.) in water (15 ml.) was added slowly, with stirring. The solution was stirred for 15 min. and added to pyridine (250 ml.) with stirring at such a rate that the temperature of the solution was maintained at 35–40°. The solution was heated to 80° for 30 min., cooled, and poured into cold water (2.5 l.). The resulting suspension was filtered and the solid was washed free from pyridine with cold water and air dried. The product (16 g.), m.p. 110–136°, was dissolved in ethanol (70 ml.). A small amount of insoluble material was discarded. The solution was progressively concentrated and diluted with water to give four fractions of crystalline material, m.p. 150–153° (1.6 g.), 159–163° (0.6 g.), 123–125° (7.8 g.) and 103–108° (1.2 g.): total weight 11.2 g.

The fraction m.p. 159–163° was chromatographed on acid alumina (Woelm, Grade I) using dry benzene as solvent. The chromatogram consisted of several colored and/or fluorescent bands which were eluted with benzene/ethanol mixtures. Ethanol (1%)/benzene eluted a blue fluorescent band; evaporation of the eluate gave an almost colorless, crystalline solid, (14 mg.), m.p. 146–148°. Ethanol (5%)/benzene eluted intermediate colored bands and a yellow-fluorescent band; evaporation of the eluate gave brown tars and semisolids (from the intermediate bands) and a yellow crystalline solid, (50 mg.), m.p. 191–193° (from the fluorescent band). Higher proportions of ethanol eluted further tarry materials.

Chromatography of the other fractions gave similar results but with different proportions of the two crystalline products. The intermediate fractions and the tarry residues were combined and rechromatographed. Tars, and further small amounts of the materials already isolated, were obtained but no additional compounds.

(20) Z. H. Skraup and A. Cobenzyl, *Monatsh.*, **4**, 450 (1884).

(21) Z. H. Skraup and A. Cobenzyl, *Monatsh.*, **4**, 442 (1884).

(22) Z. H. Skaup and A. Cobenzyl, *Monatsh.*, **4**, 456 (1884).

(23) O. Döbner and P. Knutze, *Ann.* **248**, 133 (1888).

(24) R. Ciusa, *Gazz. chim. ital.*, **46**, I, 139 (1916).

(25) R. Forsyth and F. L. Pyman, *J. Chem. Soc.*, 2912 (1926).

Compound (V) m.p. 146–148° (estimated yield 30%) was recrystallized from acetonitrile to give white platelets, m.p. 147–148°.

Anal. Calcd. for $C_{16}H_{12}N_2$: N, 12.06. Found: 12.16.

Ultraviolet absorption. λ_{max} 262 mμ (log ε, 4.34), 295 mμ (log ε, 4.64).

The compound m.p. 191–193° (estimated yield 5%) was recrystallized from toluene, giving *p*-di-(2,4-pyridyl)benzene (VII), m.p. 196–197° (undepressed on admixture with material from 4-(*p*-aminophenyl)pyridine).

Anal. Calcd. for $C_{16}H_{12}N_2$: N, 12.06. Found: 12.23.

Ultraviolet absorption. λ_{max} 255 mμ (shoulder), 290 mμ (log ε, 4.46). Relative pulse height <0.10.

From 3-(p-aminophenyl)pyridine. 3-(*p*-Aminophenyl)pyridine (anhydrous; 5.5 g.) was diazotized and coupled with pyridine as described above for 2-(*p*-aminophenyl)pyridine. The product was recrystallized from aqueous ethanol to give two fractions each having m.p. ~120° (indefinite) (combined weight 4.5 g.). The fractions were combined and the mixture (0.50 g.) was chromatographed as described above. Ethanol (1%)/benzene eluted a pale orange, crystalline solid (0.29 g.; estimated yield 35%), m.p. 126–128.5°. Rechromatography of materials from the remainder of the eluate gave further small amounts of this material but no additional pure compounds. The crystalline product was recrystallized from acetonitrile to give the pure *p*-dipyridylbenzene (VI) as white crystals, m.p. 131.5–132°.

Anal. Calcd. for $C_{16}H_{12}N_2$: N, 12.06. Found: N, 12.04.

Ultraviolet absorption. λ_{max} 260 mμ (shoulder), 290 mμ (log ε, 4.57).

From 4-(p-aminophenyl)pyridine. 4-(*p*-Aminophenyl)pyridine (0.8 g. was diazotized and coupled with pyridine as described above for 2-(*p*-aminophenyl)pyridine. The product (0.6 g.) had m.p. 187–194°. The product (112 mg.) was chromatographed as described above. Ethanol (3%)/benzene eluted an almost white, crystalline solid (51 mg.; estimated yield 24%), m.p. 196–197° (VII) (undepressed on admixture with material from 2-(*p*-aminophenyl)pyridine) with infrared spectrum identical with that of material from 2-(*p*-aminophenyl)pyridine. Rechromatography of materials from the remainder of the eluate gave further small amounts of *p*-di(2,4-pyridyl)benzene and a little higher-melting material. All attempts to obtain a pure compound from this material were unsuccessful.

4-Nitro-4'-(2-pyridyl)biphenyl. Biphenyl (60 g.) was nitrated with concentrated nitric acid at 45°[13] to give 4,4'-dinitrobiphenyl (29 g.; 31%), m.p. 225–230° (lit.[13] m.p. 239–243°). 4,4'-Dinitrobiphenyl (29 g.) was reduced to 4-amino-4'-nitrobiphenyl (13 g.; 52%), m.p. 201–203° (lit.[14] m.p. 198°) with aqueous sodium polysulfide.[14] 4-Amino-4'-nitrobiphenyl (13 g.) was dissolved in glacial acetic acid (80 ml.) and the solution was cooled to 10°. Finely divided sodium nitrite (3.9 g.) was added over 15 min. with vigorous stirring with the temperature below 15°. The solution was stirred for 15 min. and added to pyridine (200 ml.) at such a rate that the temperature was maintained at 35–40°. The solution was heated on a steam bath for 30 min. and poured into water (1500 ml.). The solution was filtered and the solid was washed and air-dried. The product (14.5 g.) was systematically fractionally recrystallized from toluene. The only 4-nitro-4'-pyridylbiphenyl isolated was the 2-isomer (1.9 g.; 11%), m.p. 214–215° (lit.[2] m.p. 213°).

4-(2-Pyridyl)-p-terphenyl. 4-Nitro-4'-(2-pyridyl)biphenyl (1.7 g.) was reduced by stannous chloride in hydrochloric acid[2] to 4-amino-4'-(2-pyridyl)biphenyl (1.1 g.; 73%), m.p. 192–193° (lit.[2] m.p. 191–192°). 4-Amino-4'-(2-pyridyl)biphenyl (1.1 g.) was acetylated with acetic anhydride[2] to give 4-acetamido-4'-(2-pyridyl)biphenyl, (0.9 g.; 70%), m.p. 235–237° (lit.[2] m.p. 236–237°).

4-Acetamido-4'-(2-pyridyl)biphenyl (0.9 g.) was suspended in glacial acetic acid (5 ml.) and acetic anhydride (3 ml.). Anhydrous potassium acetate (1 g.) and phosphorus pentoxide (few mg.) were added. The solution was cooled to 5° and stirred as a mixture of redistilled nitrosyl chloride (0.6 g.) and acetic anhydride (0.6 g.) was added dropwise. The solution was stirred for 15 min. and poured into ice water (50 ml.). The mixture was extracted with benzene (50 ml.), treated with sodium carbonate, and again extracted with benzene (50 ml.). The benzene extracts were combined, washed once with water, and allowed to stand overnight over anhydrous sodium sulfate. The benzene was distilled and the residue (0.8 g.) was chromatographed on acid alumina. Ethanol (2%)/benzene eluted material which was recrystallized from benzene to give 4-(2-pyridyl)-*p*-terphenyl (0.10 g.; 11%). Further recrystallization gave pure material, m.p. 269–270°.

Anal. Calcd. for $C_{23}H_{17}N$: C, 89.86; H, 5.58. Found: C, 89.80; H, 5.72.

Relative pulse height 0.70 at 1.02 g./l. (saturated solution).

2-(p-Biphenylyl)-5-phenylpyridine (IX). The reaction was carried out in a dry box. Lithium (0.14 g.) was suspended in dry ether (200 ml.) in an atmosphere of nitrogen. The suspension was cooled to −65° and 1-bromobutane (1.37 g.) was added dropwise to the stirred mixture. 4-Bromobiphenyl (2.33 g.) was added and the mixture was stirred at −65° for 30 min. 3-Phenylpyridine (1.5 g.) was added and the mixture was allowed to warm to room temperature and stand overnight. Water was added and the mixture was extracted with benzene. The organic layer was removed and concentrated. The product was recrystallized from benzene to give 2-(4-biphenylyl)-5-phenylpyridine (0.5 g.; 17%), m.p. 274–275°.

Anal. Calcd. for $C_{23}H_{17}N$: C, 89.86; H, 5.58. Found: C, 90.09; H, 5.55.

Ultraviolet absorption. λ_{max} 280 mμ (shoulder; log ε, 4.47), 307 mμ (log ε, 4.63).

Relative pulse height 0.41 at 1.8 g./l. (saturated solution).

Note on nomenclature. Compounds I, II, and III have been named as pyridylbiphenyls to provide an element of consistency in this discussion by treating the pyridine rings as substituents where possible. Chemical Abstracts has indexed these as biphenylylpyridines with a cross reference under pyridylbiphenyl. Compounds IV and IX are exceptions named as substituted pyridines to provide simple names. The pyridylterphenyl name for VIII conforms to the principle of naming the compound as a derivative of the largest parent (Chemical Abstracts rule 70). Compounds V, VI, and VII present a special nomenclature problem. They cannot easily be named as substituted pyridines, nor is there any reason for doing so as they are rather obviously disubstituted benzenes. The problem is to indicate in a concise and definitive name the positions of the benzene and pyridine linkages. The name 1-(2-pyridyl)-4-(4-pyridyl)-benzene (for VII) is clear but hardly concise and somewhat labored. 2,2-*p*-Phenylenebispyridine (for V) is concise but the phenylene system is not a commonly used basis for systematic names of di-substituted benzenes, and it also provides no association with the terphenyl concept involved in our present discussion. It has been used in Chemical Abstracts for dipyrrylbenzene with a cross reference. *p*-Di-(2,4-pyridyl)benzene (for VII) is concise and definitive and follows Chemical Abstracts indexing principles for di-substituted benzenes.

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