

[CONTRIBUTION FROM THE MCPHERSON CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

## Synthesis and Properties of 4,5-Dimethylacridine and 1,4,5,8-Tetramethylacridine<sup>1</sup>

MELVIN S. NEWMAN AND WARREN H. POWELL\*

Received May 16, 1960

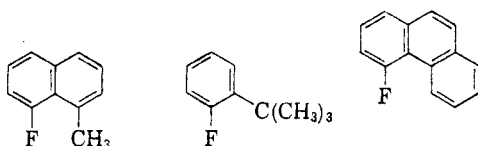
4,5-Dimethylacridine, II, and 1,4,5,8-tetramethylacridine, III, have been synthesized and shown to form salts with hydrogen chloride but not with boron trifluoride. These acridines also lack the irritating physiological effects possessed by acridine.

For a number of years the approximations listed below have been used here to estimate qualitatively steric effects of *ortho* substituents in aromatic compounds.

(1) A fused aromatic ring is equivalent to a methyl group. (F represents either a substituent on the ring or a nitrogen instead of a carbon if heterocyclic systems such as pyridine are under consideration).



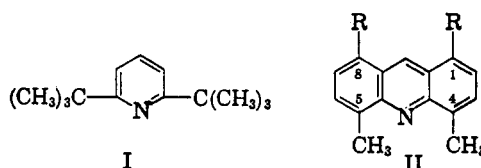
(2) Either (a) a fused aromatic ring containing a methyl group in the adjacent *peri*-position, or (b) two continuously angularly fused aromatic rings, is equivalent to a *t*-butyl group.



Recently the heats of activation for the reactions of a number of nitrogen-heterocyclic compounds with methyl iodide have been determined and the results interpreted with the aid of a similar hypothesis.<sup>3</sup>

The fact that 2,6-di-*t*-butylpyridine, I, will form a hydrochloride but will not interact with boron trifluoride has been established.<sup>4</sup> We have found that 4,5-dimethylacridine,<sup>5</sup> II, likewise fails to react with boron trifluoride or diborane. These facts indicate

that the second of the above mentioned hypotheses (2a) is valid. 1,4,5,8-Tetramethylacridine, III, was also synthesized and failed to react with boron trifluoride.



This expected result was not a foregone conclusion. Although it was realized that the in-plane (*i.e.*, plane of the pyridine ring) hindrance of the methyl groups of II would be at least as effective as that provided by the *t*-butyl group in I, one could not predict whether the out-of-plane hindrance of the *t*-butyl groups of I (which would be lacking in II) would prove to be of importance.

Another observation of interest in the field of electron donor-acceptor interactions is the fact that II forms a well defined *sym*-trinitrobenzene complex but fails to interact with boron trifluoride. The explanation is that the geometry of interaction of the two acceptors, *sym*-trinitrobenzene and boron trifluoride, with the donor 4,5-dimethylacridine, II, is different, the former making a layer type of complex whereas the latter requires in-plane complexing at the nitrogen. Nevertheless, it is true that, if II is used as the reference donor, *sym*-trinitrobenzene is a much stronger acceptor than boron trifluoride.

A fact of great interest concerning the physiological actions of II and III was noted. Neither II nor III caused any skin irritation or inflammation of the nose or eyes, whereas the parent acridine is quite bothersome. For example, on making a melting point determination with acridine on a heated stage device, the skin of the face became quite sensitive and severe lachrymatory effects were noted, whereas when either II or III was involved no inconvenience was noted. This observation suggests that the physiological properties of drugs containing the acridine nucleus (or for that matter, any heterocyclic nucleus where suitable steric effects might be introduced by appropriate substitution) might be significantly altered by substitution adjacent to the nitrogen (or other hetero atom).

(1) This research was supported in part by the Office of Ordnance Research, U. S. Army, under Contract No. DA-33-019-1910. Summer fellowships made possible by the E. I. du Pont de Nemours Company are also here gratefully acknowledged.

(2) The research herein reported was taken from the Ph.D. thesis of Warren H. Powell, December 1959.

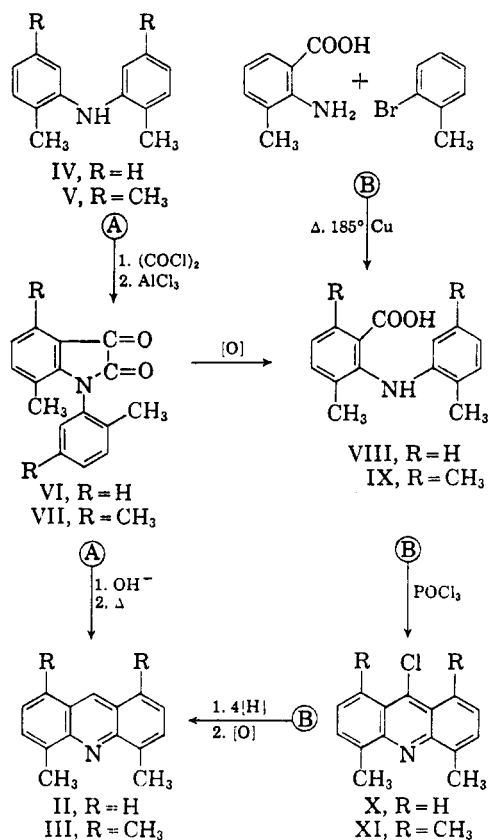
(3) J. Packer, J. Vaughan, and E. Wong, *J. Am. Chem. Soc.*, **80**, 905 (1958).

(4) H. C. Brown and B. Kanner, *J. Am. Chem. Soc.*, **75**, 3865 (1953).

(5) A. Albert and J. B. Willis, *J. Soc. Chem. Ind.*, **65**, 26 (1946). See also D. P. Craig, *J. Chem. Soc.*, 534 (1946) for a discussion of steric factors on ionization constants and ultraviolet spectra of 4,5-diaminoacridine and related compounds (called the 1,9-derivative in that paper).

In addition to 4,5-dimethylacridine, II, we have also prepared 1,4,5,8-tetramethylacridine, III, to obtain another example of a hindered base, to broaden our experience in acridine synthesis, and to supply Dr. M. Szwarc with a heterocyclic analog of 1,4,5,8-tetramethylantracene for studies on methyl affinities of aromatic compounds.<sup>6</sup>

Each of the two acridines, II and III, was synthesized by the two routes, A and B, summarized in the chart.



Di-*o*-tolylamine (IV) required for the synthesis of II via route A was prepared in 37% yield from formyl-*o*-toluidine and *o*-bromotoluene<sup>7</sup> while di-*o*-2,5-xylylamine (V) was obtained in 74% yield from 2,5-dimethylaniline and 2-bromo-*p*-xylene.<sup>8</sup> Conversion of IV and V to the isatins VI and VII followed by basic rearrangement and decarboxylation afforded II and III in 80% and 71% yields respectively.<sup>9</sup>

A quantity of II was also prepared in 56% yield from 3-methylanthranilic acid and *o*-bromotoluene

(6) M. Levy and M. Szwarc, *J. Am. Chem. Soc.*, **77**, 1949 (1955). The results of methyl affinity studies on II, III, and certain tetramethylantracenes will be reported by Dr. Szwarc.

(7) Compare H. Wieland and A. Süsler, *Ann.*, **392**, 176 (1912).

(8) See F. Scardiglin and J. D. Roberts, *J. Org. Chem.*, **23**, 629 (1958).

(9) See R. Stolle, *J. prakt. Chem. N.F.*, **105**, 137 (1922); P. Friedlander and K. Kunz, *Ber.*, **55**, 1597 (1922); J. Martinet and A. Dansette, *Bull. soc. chim. France*, **45**, 101 (1929).

essentially as described.<sup>5,10</sup> In a slight modification, the chloracridine, X, was converted into II by reduction to the corresponding 9,10-dihydroacridine with lithium aluminum hydride<sup>11</sup> (instead of Raney nickel and hydrogen<sup>6</sup>) followed by oxidation to II. Using this latter method of converting X to II, the overall yield of II from 3-methylantracenic acid and *o*-bromotoluene was 52%.

The synthesis of III in 41–43% yield from IX was effected similarly. The tetramethyldiphenylamine-2-carboxylic acid used, IX, was prepared in 92% yield by oxidation of the isatin (VII). Since the preparation of the isatin (VII) was a step in route A, this synthesis of III actually involved a combination of routes A and B.

To summarize our experiences with the syntheses of II and III, we believe that route A is by far the more convenient.

#### EXPERIMENTAL<sup>12</sup>

**Di-*o*-tolylamine, IV.** A mixture of 25.0 g. of *N*-formyl-*o*-toluidine,<sup>13</sup> 34.0 g. of redistilled *o*-bromotoluene, 13.8 g. of anhydrous potassium carbonate, 100 ml. of nitrobenzene, and 1 g. of catalytic copper<sup>14</sup> was refluxed for 50 hr. The cooled black reaction mixture was steam distilled. Ether-benzene was added to the cooled residue and the whole mixture filtered. After the usual treatment, the black residue was distilled to yield 25.7 g. of yellow oil, b.p. 130–170°/2 mm. This oil was refluxed with a 1:1 mixture of glacial acetic and concentrated hydrochloric acids for 10 hr. and the resulting solution poured into 200 ml. of ice water. An ether benzene extract of the bluish semi-solid was worked up in the usual manner. Distillation through a 12" column packed with glass helices gave 14.2 g. (43%) of a colorless oil, b.p. 145–170°/4 mm. Recrystallization of this partly solidified material from Skellysolve F afforded 13.5 g. (37%) of IV as colorless crystals, m.p. 46–48°, suitable for further work.

**Di-*o*-2,5-xylylamine (V).** This amine was prepared from 2,5-xylylidine and 2-bromo-*p*-xylene essentially as described.<sup>8</sup> V was obtained as colorless crystals, m.p. 51–53°, in 65% yield. Two recrystallizations from Skellysolve F followed by a microdistillation gave the analytical sample, m.p. 53.4–54.8° corr.

*Anal.* Calcd. for C<sub>16</sub>H<sub>19</sub>N: C, 85.3; H, 8.5; N, 6.2. Found: C, 85.0; H, 8.6; N, 6.2.

(10) A. Albert and W. Gledhill, *J. Soc. Chem. Ind.*, **64**, 169 (1945).

(11) This reagent has been used to reduce 9-chlorophenanthridine to 9,10-dihydrophenanthridine. See G. M. Badger, J. H. Seidler, and B. Thomson, *J. Chem. Soc.*, 3207 (1951); W. C. Wooten and R. L. McKee, *J. Am. Chem. Soc.*, **71**, 2946 (1949).

(12) All melting points are uncorrected unless otherwise stated. All microanalyses are by Galbraith Microanalytical Laboratories, Knoxville, Tenn. The term 'worked up in the usual manner' means that an ether-benzene (3:2 by volume) solution of the products was washed successively with a saturated solution of sodium chloride and then filtered through a layer of anhydrous magnesium sulfate. The solvents were then removed by distillation. Skellysolve F, b.p. 35–55° and Skellysolve B, b.p. 65–69°, are aliphatic hydrocarbon solvents.

(13) T. T. Tyson, *Org. Syntheses*, Coll. Vol. III, 479 (1955).

(14) R. Brewster and T. Groenig, *Org. Syntheses*, Vol. **14**, 67 (1934).

(15) M. Battagay, H. Silberman, and J. Fisher, *Chemie und Industrie, Spec. No.*, **27**, 525 (1932) report the pure material to melt at 52–53°, and boil at 192°/23 mm.

Reworking the mother liquor gave an additional 6.2 g. (9%) of V as follows: The solvent was removed by distillation and the hydrochloride salt precipitated from dry ether with anhydrous hydrogen chloride. The salt was decomposed with water and the product worked up as described above.

*1-o-Tolyl-7-methylisatin*, VI.<sup>9</sup> A solution of 12.3 g. of IV in 60 ml. of purified carbon disulfide<sup>16</sup> was added dropwise (40 min.) to a stirred, gently refluxing solution of 9.0 g. of oxalyl chloride in 45 ml. of carbon disulfide. The evolution of hydrogen chloride was rapid. The yellow solution was refluxed (1 hr.) and the solvent and excess oxalyl chloride completely removed under reduced pressure. Then 100 ml. of carbon disulfide was added followed by 26.6 g. of anhydrous aluminum chloride portionwise (15 min.). As the black complex separated, stirring became impossible but refluxing was continued for 1 hr. After stripping off the solvent, the complex was decomposed with crushed ice followed by dilute hydrochloric acid. After the usual treatment, the red solid was recrystallized from benzene-cyclohexane (3:5) to yield 14.6 g. (93%) of VI as red needles, m.p. 172–174°. The analytical sample, m.p. 172.6–173.9° corr., was prepared by recrystallization from benzene-cyclohexane.

*Anal.* Calcd. for C<sub>18</sub>H<sub>13</sub>NO<sub>2</sub>: C, 76.5; H, 5.2; N, 5.6. Found: C, 76.4; H, 5.3; N, 5.8.

*1-(2,5-Dimethylphenyl)-4,7-dimethylisatin*, VII.<sup>9</sup> Similarly, V was converted to VII using 45.0 g. of V in 300 ml. of carbon disulfide and 33.1 g. of oxalyl chloride in 180 ml. of carbon disulfide. Cyclization to VII was effected in 200 ml. of carbon disulfide with 94.0 g. of aluminum chloride. Recrystallization from cyclohexane gave 53.4 g. (96%) of VII as red needles, m.p. 140–142°. The analytical sample, m.p. 141.5–142.0° corr., was prepared by recrystallization from cyclohexane.

*Anal.* Calcd. for C<sub>18</sub>H<sub>17</sub>NO<sub>2</sub>: C, 77.4; H, 6.1; N, 5.0. Found: C, 77.7; H, 6.3; N, 5.2.

*2',6-Dimethyldiphenylamine-2-carboxylic acid*, VIII. This compound was prepared from 3-methylantranilic acid,<sup>17</sup> 65.8 g. and *o*-bromotoluene, 114.5 g., as described<sup>10</sup> except that 26 hr. of heating was needed to obtain a 75% yield of VIII as light tan crystals, m.p. 186–187°.<sup>18</sup>

The methyl ester, m.p. 67.5–68.5°<sup>19</sup> was prepared with diazomethane<sup>20</sup> in 90% yield. The analytical sample, m.p. 68.2–68.9° corr., was prepared by two recrystallizations from methanol.

*Anal.* Calcd. for C<sub>18</sub>H<sub>17</sub>NO<sub>2</sub>: C, 75.3; H, 6.7; N, 5.5. Found: C, 75.5; H, 6.5; N, 5.6.

*2',3',5',6'-Tetramethyldiphenylamine-2-carboxylic acid* IX. A mixture of 8.0 g. of VII, 16.0 g. of potassium hydroxide, and 145 ml. of water was heated at 60° until the red solid turned to a yellow suspension (1 hr.). Then 10 ml. of 30% hydrogen peroxide was added in two portions 2 hr. apart. Stirring at 60° was continued (3 hr.) and the clear yellow solution cooled and acidified with crushed ice and concentrated hydrochloric acid. The crude brown solid, 7.5 g. (97%) m.p. 194–197° dec., obtained by filtration was dissolved in hot 10% potassium carbonate which was cooled and extracted with two portions of ether-benzene. The basic aqueous phase was treated with charcoal and acidified with concentrated hydrochloric acid to yield 7.1 g. (92%) of IX as a white powder, m.p. 197–199° dec., suitable for further

(16) Purified by shaking for eight hours with anhydrous aluminum chloride followed by distillation.

(17) Synthesized from 3-methylphthalic anhydride by the Schmidt reaction. See H. R. Barkenmeyer, M. S. Thesis, The Ohio State University, 1952.

(18) Purification was effected by treatment of a slightly basic solution (potassium carbonate) with charcoal, followed by acidification and two recrystallizations (charcoal) of the crude acid from benzene. Compare ref. 10.

(19) This material appeared to be dimorphic. It melted first at 61–62°, then if cooled and remelted, at 67.5–68.5°.

(20) F. Arndt, *Org. Syntheses*, Coll. Vol. II, 165 (1943).

work. Two recrystallizations from benzene-Skellysolve B gave the analytical sample, m.p. 197.5–199.0° dec.

*Anal.* Calcd. for C<sub>17</sub>H<sub>13</sub>NO<sub>2</sub>: C, 75.8; H, 7.1; N, 5.2 neut. equiv., 269. Found: C, 75.8; H, 7.1; N, 5.3, neut. equiv., 268, 271.

The methyl ester, m.p. 126–128°, was prepared in 91% yield with diazomethane.<sup>20</sup> Several recrystallizations from alcohol gave the analytical sample, m.p. 127.2–128.3° corr.

*Anal.* Calcd. for C<sub>18</sub>H<sub>15</sub>NO<sub>2</sub>: C, 77.8; H, 6.5; N, 4.8. Found: C, 77.6; H, 6.7; N, 5.0.

*9-Chloro-4,5-dimethylacridine*, X. The compound was prepared from VIII, 43.6 g., as described<sup>10</sup> in quantitative crude yield. The separation of the desired chloroacridine, X, from its hydrolysis product, 4,5-dimethylacridone, XII, was accomplished by chromatography over alumina (Fisher) using Skellysolve B as developer. Recrystallization from Skellysolve F afforded X as yellow, silky needles, m.p. 149–151°, in 89% yield.

Further elution of the column with chloroform followed by recrystallizations from chloroform-Skellysolve B gave 2.5 g. (6%) of 4,5-dimethylacridone (XII) m.p. 232–233°, the hydrolysis product of X. The analytical sample, m.p. 233.6–234.9° corr., was prepared by recrystallization from benzene-Skellysolve B.

*Anal.* Calcd. for C<sub>18</sub>H<sub>13</sub>NO: C, 80.9; H, 5.9; N, 6.2. Found: C, 80.7; H, 5.7; N, 6.3.

*9-Chloro-1,4,5,8-tetramethylacridine*, XI. A mixture of 7.0 g. of IX and 70 ml. of phosphorus oxychloride was refluxed (90 min.) at 120° (bath temperature). After the usual work-up<sup>10</sup> the crude product, 6.2 g., m.p. 150–180°, was purified by chromatography on alumina to yield 3.9 g. (56%) of XI as yellow needles, m.p. 170.0–171.5°. The analytical sample, m.p. 171.5–172° corr., was prepared by rechromatography on alumina with Skellysolve B followed by recrystallization from Skellysolve B.

*Anal.* Calcd. for C<sub>17</sub>H<sub>13</sub>NOCl: C, 75.7; H, 6.0; N, 5.2; Cl, 13.1. Found: C, 75.7; H, 5.9; N, 5.2; Cl, 13.0.

Further elution of the column with chloroform gave, after recrystallization from benzene, 1.7 g. (26%) of 1,4,5,8-tetramethylacridone, XIII, m.p. 220–221°, the hydrolysis product of XI. The analytical sample, m.p. 220.4–221.4° corr., was prepared by recrystallization from benzene.

*Anal.* Calcd. for C<sub>17</sub>H<sub>17</sub>NO: C, 81.2; H, 6.8; N, 5.6. Found: C, 81.1; H, 6.8; N, 5.7.

*4,5-Dimethylacridine*, II.<sup>5</sup> A. From *1-o-tolyl-7-methylisatin* (VI). A solution of 47.0 g. of VI in 500 ml. of 10% potassium hydroxide solution was refluxed for 12 hr. The cooled reaction mixture was poured into crushed ice and concentrated hydrochloric acid. Extraction of the orange mixture with ether-benzene (3:2) followed by the usual work-up gave, in two portions, 46.5 g. (99%) of 4,5-dimethylacridine-9-carboxylic acid as a yellow solid, m.p. 229–234° dec., sufficiently pure for further work.

The methyl ester, m.p. 123–124°, was prepared (diazomethane) in 87% yield. The analytical sample, m.p. 123.6–124.4° corr., was prepared by two recrystallizations from Skellysolve B.

*Anal.* Calcd. for C<sub>17</sub>H<sub>13</sub>NO<sub>2</sub>: C, 77.0; H, 5.7; N, 5.3. Found: C, 76.7; H, 5.9; N, 5.2.

The crude acid, 20.8 g., was heated at 240–250° (15 min.) while carbon dioxide was rapidly evolved. The cooled residue was purified by chromatography on alumina to yield 14.9 g. (87%) of II as yellow needles, m.p. 77.5–77.9° corr.<sup>5</sup>

B. From *9-Chloro-4,5-dimethylacridine*, X. 1. *Catalytic reduction*. Reduction of X over Raney nickel at room temperature and an initial hydrogen pressure of 45 p.s.i., followed by potassium dichromate-dilute sulfuric acid oxidation as reported<sup>5</sup> gave an 83% yield of II as yellow needles, m.p. 78–79°, on recrystallization from methanol.

2. *Reduction with lithium aluminum hydride*. A solution of 24.2 g. of X in 400 ml. purified tetrahydrofuran<sup>21</sup> was added

(21) Purified by shaking with phosphorus pentoxide followed by distillation from lithium aluminum hydride.

dropwise (90 min.) under nitrogen to a stirred slurry of 19.0 g. of lithium aluminum hydride in 100 ml. purified tetrahydrofuran and the resulting mixture refluxed for 45 hr. The excess of hydride was decomposed by cautious addition of a tetrahydrofuran-water mixture (1:1) to the cooled solution. After addition of an excess of dilute hydrochloric acid, the crude product, m.p. 84–95° (20.5 g.) was isolated and oxidized as reported<sup>6</sup> to yield 18.8 g. (91%) of crude II, m.p. 72–77°. Recrystallization from methanol (charcoal) gave, in two crops, 16.0 g. (77%) of II as yellow needles, m.p. 78–79°.

The trinitrobenzene complex of II was prepared and crystallized from absolute ethanol to give 1.74 g. (86%) of complex as yellow needles, m.p. 137.5–139.5°. Recrystallization from absolute ethanol gave the analytical sample, m.p. 138.8–140.4° corr.

*Anal.* Calcd. for  $C_{21}H_{16}N_4O_6$ : C, 60.0; H, 3.8. Found: C, 60.2; H, 3.5.

*1,4,5,8-Tetramethylacridine, III. A. From 1-(2,5)-Xylyl-4,7-dimethylisatin, VII.* A solution of 10.0 g. of VII in 150 ml. of water containing 20.0 g. of potassium hydroxide was refluxed for 305 hr. The cooled reaction mixture was acidified with ice and concentrated hydrochloric acid. The orange powder, obtained by filtration, was triturated with hot benzene and the residue dissolved in hot 10% potassium carbonate solution, treated with charcoal, and acidified with concentrated hydrochloric acid to yield 7.9 g. (79%) of 1,4,5,8-tetramethylacridine-9-carboxylic acid as an orange powder, m.p. 229–233° dec., sufficiently pure for the next step.

The methyl ester, m.p. 126.0–127.5° was prepared (diazomethane) in 91% yield. Two recrystallizations from alcohol gave the analytical sample, m.p. 127.2–128.3° corr.

*Anal.* Calcd. for  $C_{19}H_{19}NO_2$ : C, 77.8; H, 6.5; N, 4.8. Found: C, 77.6; H, 6.7; N, 5.0.

The crude acid, 7.8 g., was treated as above (II-A) to yield 6.2 g. (94%) of III as yellow needles, m.p. 187–189°. The analytical sample, m.p. 188.7–189.2° corr., was prepared by recrystallization from Skellysolve B followed by sublimation.

*Anal.* Calcd. for  $C_{17}H_{17}N$ : C, 86.8; H, 7.3; N, 6.0. Found: C, 86.7; H, 7.3; N, 6.2.

*B. From 9-Chloro-1,4,5,8-tetramethylacridine, XI. 1. By reduction with Raney nickel and hydrogen.* XI was converted

to III, m.p. 188–189°, in 76% yield as described above for the conversion of X to II.

*2. By reduction with lithium aluminum hydride.* Reduction of XI with lithium aluminum hydride as described above for II followed by oxidation<sup>6</sup> with potassium dichromate and sulfuric acid yielded III as yellow needles, m.p. 187.5–189.0°, in 74% yield.

The trinitrobenzene complex of III was prepared by mixing a hot solution of 1.20 g. of III in 20 ml. benzene and a hot solution of 1.10 g. of trinitrobenzene in 10 ml. of benzene and boiling for 5 min. Thorough chilling produced 2.10 g. (92%) of orange needles, m.p. 179–181°. Two recrystallizations from benzene gave the analytical sample, m.p. 180.6–182.0° corr.

*Anal.* Calcd. for  $C_{23}H_{20}N_4O_6$ : C, 61.6; H, 4.5; N, 12.6. Found: C, 61.9; H, 4.6; N, 12.5.

*Heats of reaction of bases with boro trifluoride and diborane.* The heats of reaction were approximated by noting the temperature rise of 10.0 ml. of a dry thiophene-free benzene solution of 0.002 mole of the base at the same initial temperature when treated with an excess of boron trifluoride (from a cylinder) or diborane (generated by dropwise addition of a solution of sodium borohydride in redistilled diglyme to a solution of redistilled boron trifluoride etherate in redistilled diglyme). Nitrogen was used to sweep the system before and after each run. Two runs were made with each base and the results agreed to within 1°. The results are listed in Table I.

TABLE I  
HEATS OF REACTION OF BASES

Compound	$\Delta T_{BF_3}$ , °	$\Delta T_{B_2H_6}$ , °
Benzene (blank run)	-0.5	1.9
Pyridine	9.3	5.4
2,4,6-Collidine	8.3	4.4
Acridine	7.9	4.5
4,5-Dimethylacridine, II	-0.4	0.1
1,4,5,8-Tetramethylacridine <sup>a</sup>	-0.7	...

<sup>a</sup> Concentration was only 0.001 mole/10 ml. because of low solubility in benzene.

COLUMBUS 10, OHIO

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF KANSAS]

## Condensation of *N*-Phenylbenzimidyl Chloride with Hydrogen Cyanide and Heterocyclic Bases

PAUL DAVIS AND WILLIAM E. McEWEN

Received June 15, 1960

The hydrochlorides of 1-( $\alpha$ -phenyliminobenzyl)-1,2-dihydroquinonitrile, 1-( $\alpha$ -phenyliminobenzyl)-1,2-dihydroquinonitrile and 2-( $\alpha$ -phenyliminobenzyl)-1,2-dihydroisoquinonitrile are obtained by reaction of *N*-phenylbenzimidyl chloride and hydrogen cyanide with pyridine, quinoline, and isoquinoline, respectively. The pyridine adduct gives benzaldehyde, aniline and picolinic acid on acid hydrolysis and the amide of picolinic acid on nitrobenzene oxidation. The quinoline adduct affords benzaldehyde, aniline, and quinaldic acid on acid hydrolysis, and quinaldonitrile is produced by nitrobenzene oxidation. The isoquinoline adduct behaves in an analogous manner, giving benzaldehyde, aniline, and isoquinaldic acid on acid hydrolysis and 1-eyanoisoquinoline on oxidation with nitrobenzene.

As part of an investigation of the effect of various amines on the preparation of *N*-phenylbenzimidyl cyanide, Mumm, Volquartz, and Hesse<sup>1</sup>

found that a reaction of *N*-phenylbenzimidyl chloride (I) with anhydrous hydrogen cyanide in the presence of quinoline led to the formation of an addition compound,  $C_{23}H_{18}N_3Cl$ . This product was thought to be 1-( $\alpha$ -phenyliminobenzyl)-1,2-dihydroquinonitrile hydrochloride (II) in analogy

(1) O. Mumm, H. Volquartz, and H. Hesse, *Ber.*, **47**, 751 (1914).