3-(α-Methyl-p-bromophenacyl)-3-hydroxy-1-methyloxindole (Vb). A solution of 11.8 g. of *N*-methylisatin, 15.6 g. of *p*-bromopropiophenone,[3a,15] and 44 drops of diethylamine in 260 ml. of absolute ethanol, after standing at room temperature for several days, was partially evaporated and some water was added dropwise to precipitate 25.7 g. (97%) of Vb. After recrystallization from absolute ethanol it melted at 158–161°. λ_{max}, μ, 2.87s, 3.19w, 3.37w, 5.84s, 5.92s, 6.16s, 6.28m, 6.36m (shoulder), 6.66m, 6.78s, 6.86m, 7.00m.

Anal. Calcd. for $C_{18}H_{16}BrNO_2$: C, 57.77; H, 4.31. Found: C, 57.69; H, 4.44.

3-(α-Methyl-p-bromophenacylidene)-1-methyloxindole (VIb). (*cf.* ref. 6b). A mixture of 7.25 g. of Vb in 21.5 ml. of absolute ethanol and 43 ml. of conc. hydrochloric acid, upon standing overnight at room temperature, gave 3.7 g. (54%) of VIb. After recrystallization from benzene it melted at 226–227°. λ_{max} 261 mμ, ϵ 38,000; shoulder, 300 mμ, ϵ 8,000; μ, 5.84s, 5.93s, 6.05m, 6.18s, 6.28s, 6.70m, 6.78s, 7.02m.

Anal. Calcd. for $C_{18}H_{14}BrNO_2$: C, 60.69; H, 3.96. Found: C, 60.44; H, 4.04.

3-(α-Methyl-p-bromophenacyl)-1-methyloxindole (IIIb). Reduction (as for VIa) of 0.22 g. of VIb in 70% ethanol by 0.22 g. of sodium hydrosulfite gave 0.2 g. of IIIb. After recrystallization from ethanol it melted at 137–139° and was identified by mixture melting point with the product[4] of the action of acetic–conc. hydrochloric acid mixture on I. λ_{max}, 255 mμ, ϵ 26,900; μ, 3.25w, 3.40w, 5.84s, 5.95s, 6.18s, 6.28s, 6.48w (shoulder), 6.68s, 6.79s, 6.89m, 7.05w.

Anal. Calcd. for $C_{18}H_{16}BrNO_2$: C, 60.4; H, 4.5. Found: C, 60.1; H, 4.8.

Miscellaneous reactions. Only resinous product was obtained when the *trans*-methylanilide of (I) was subjected to the action of a 56:7 (by volume) mixture of acetic and conc. hydrochloric acids (refluxing for from 2 to 3 hr.); no VIb was isolated.

Numerous attempts to displace aniline or methylaniline or to force further reaction of the γ-anilino and methylanilinolactones (I) were unsuccessful; *e.g.*, heating the mixture at 150° for 2 hr., with or without added aniline or methylaniline hydrochloride (although in one case some VI was obtained), and heating a benzene solution saturated with dimethylamine and its hydrochloride.

Acknowledgment. We are indebted to Joseph P. Feifer for the determination of the infrared and two of the ultraviolet absorption spectra.

CHARLOTTESVILLE, VA.

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[15] A. Collet, *Compt. rend.*, **125**, 717 (1897); **126**, 1577 (1898).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DE PAUL UNIVERSITY]

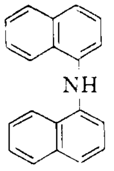
Formation of Tertiary Naphthylamines and Tetranaphthylhydrazines by *N*-Metallation[1]

EUGENE LIEBER[2] AND S. SOMASEKHARA

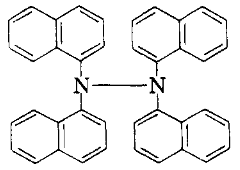
Received April 16, 1959

The discovery that the potassium metallation of 1,1′-dinaphthylamine (I) leads to significant yields of tetra(1-naphthyl)-hydrazine (II) has led to an extended study of the metallation of I and related secondary amines during which the syntheses of a number of tertiary amines have been achieved. Variation in the ratio of potassium to I and temperature did not increase the yields of II above 5%, the higher temperatures decreasing the yield. Diphenyl- and 2,2′-dinaphthylamines, respectively, failed to yield any evidence for hydrazine formation, under the conditions studied, while other related secondary amines gave only chromatogram fluorescent tests indicative of hydrazine formation. A free radical mechanism to account for I is proposed and discussed. The process is the reverse of the free radical dissociation of tetraarylhydrazines in solution.

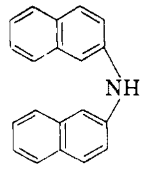
In a preliminary communication Lieber[3] reported that a significant yield of tetra(1-naphthyl)-hydrazine (II) was obtained during an attempt to prepare the potassium salt of 1,1′-dinaphthylamine (I) by heating I under reflux with potassium in xylene.



I



II



III

In the same reaction, methylation experiments offered evidence that the potassium salt of I was not the intermediate involved in the formation of II. Further experiments with I using potassium in boiling xylene, with the exclusion of atmospheric oxygen, verified the formation of II, the yields being about the same (5%). Reagents such as potassium butoxide, potassium methoxide, and potassium amide, used under a variety of conditions, failed to produce any detectable amount of the potassium salt of I. In order to examine further the novel conversion of I to II, an extended study of the potassium metallation of I and related secondary amines was undertaken during the course of which the syntheses of a number of tertiary amines was achieved.

The metallation of I was carried out at various temperatures ranging from 110° to 200°. The experimental data revealed that the potassium salt of I was formed in good yields at lower temperatures.

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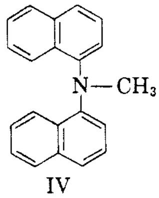
[1] This investigation was sponsored by the Basic Research Group, Corps of Engineers, U. S. Army, Fort Belvoir, Va. The authors gratefully acknowledge this assistance.

[2] Present address: Roosevelt University, Chicago 5, Ill., to whom all correspondence should be addressed.

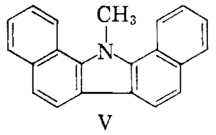
[3] E. Lieber and S. Somasekhara, *Chem. and Ind.*, 1262 (1958).

At higher temperatures the reaction was accompanied by extensive decomposition forming unworkable tars. The effect of increasing the molar ratio of potassium to I, in refluxing xylene, had no effect on the yield of II, in all cases approximately 5% of product being obtained. When the above reaction was repeated with 2,2'-dinaphthylamine (III), no evidence could be found for the formation of the corresponding hydrazine, although an exhaustive search was made for it by techniques which could reveal trace amounts. An explanation for this curious contradiction of anticipation is discussed below. The behaviors of other secondary amines, *N*-methyl-, *N*-ethyl-, and *N*-phenyl-1-naphthylamine and *N*-phenyl-2-naphthylamine and diphenylamine, with metallic potassium under experimental conditions that led to II, were studied. In no case could the corresponding tetrasubstituted hydrazine be isolated. However, with the exception of diphenylamine it was demonstrated, by chromatographic fluorescent techniques in comparison with authentic specimens of the hydrazines,[4] that the tetrasubstituted hydrazines were indeed formed, albeit in quantities too small for isolation. Diphenylamine, unlike the other secondary amines studied, yielded its potassium salt under a variety of experimental conditions, and in no case, could evidence be obtained for the formation of tetraphenylhydrazine under the experimental conditions studied.

Heydrich[5] and Herz[6] have shown that some difficulty accessible tertiary amines can be synthesized by treating the alkali metal salts of secondary amines with aromatic halides. Heydrich[5] allowed molten diphenylamine to react with metallic sodium to obtain the sodium salt of diphenylamine. Herz,[6] on the other hand, used aniline as a solvent for obtaining the potassium salt of diphenylamine. In the present study solvents such as toluene, xylene, and decalin were employed. With the exception of diphenylamine, the experimental data indicates that the potassium salts of the secondary amines studied were thermally unstable above 110°. In all cases evidence for metallation was sought by the usual procedure of methylation (or ethylation). In the case of diphenylamine, benzylation was employed since the resulting tertiaryamine had been reported previously.[7] The melting point of *N*-methyl-*N*-phenyl-2-naphthylamine (88-90°) was found to be at variance with that previously reported[8] (52-53°). The methylation of *N*-methyl- and *N*-ethyl-1-naphthylamine, respectively, led to liquid tertiary amines which were therefore characterized as picrates. In an attempt to prepare *N*-methyl-1,1'-dinaphthylamine by the zinc chloride dehydration of *N*-methyl-1-naphthylamine with 1-naphthol, a high melting (188–190°) product was obtained which did not correspond to the *N*-methyl-1,1'-dinaphthylamine (IV) (melting point, 143–144°), prepared by methylation of the potassium salt of I. Analysis suggests that this product is *N*-methyl-1,3-dibenzo (a,i) carbazole, V:

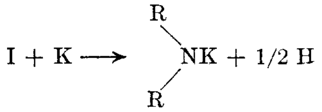


IV



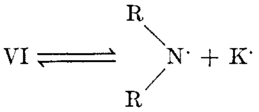
V

In order to account for the formation or nonformation of a tetrasubstituted hydrazine it is suggested that the potassium salts of the secondary amines under scrutiny, being more or less thermally unstable, are capable of homolytic dissociation to produce free radicals:



$$\mathrm{I} + \mathrm{K} \longrightarrow \begin{matrix} R \\ \diagdown \\ \quad \mathrm{NK} \\ \diagup \\ R \end{matrix} + 1/2\ \mathrm{H}$$

VI
(R = 1-Naphthyl)



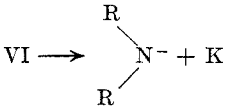
$$\mathrm{VI} \rightleftharpoons \begin{matrix} R \\ \diagdown \\ \quad \mathrm{N}^{\cdot} \\ \diagup \\ R \end{matrix} + \mathrm{K}^{\cdot}$$

VII
(R = 1-Naphthyl)

It is also possible that potassium could generate the free radical in the following manner:

$$\mathrm{I} + \mathrm{K} \longrightarrow \mathrm{VII} + \mathrm{KH}$$

The tetranaphthylhydrazine (II) is then produced by recombination of VII. However, the electronic deficiency of VII and related substances could be satisfied by bonding to carbon, leading to more complicated products and thus account for the unworkable tars formed in many cases. A theory based on the acidic properties of the secondary amines studied, which would in turn involve the relative stabilities of the potassium salts, is not too satisfactory since the differences in the acidic properties are probably very small or nonexistent. On the other hand, heterolytic cleavage of the potassium salts, *e.g.*,



$$\mathrm{VI} \longrightarrow \begin{matrix} R \\ \diagdown \\ \quad \mathrm{N}^{-} \\ \diagup \\ R \end{matrix} + \mathrm{K}^{+}$$

could be the concurrent and major process and would account for the alkylations carried out.

The dissociation of tetraarylhydrazines in solution into diarylnitrogen free radicals is a well

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[4] E. Lieber and S. Somasekhara, *J. Org. Chem.*, **24**, 1775 (1959).

[5] C. Heydrich, *Ber.*, **18**, 2156 (1885).

[6] R. Herz, *Ber.*, **23**, 2541 (1890).

[7] R. D. Desai, *J. Ind. Inst. Sci. (India)*, **7**, 235 (1924); *Chem. Abstr.*, **19**, 2645 (1925).

[8] German Patent 96402, *Chem. Centr.*, **69**, II, 240 (1898).

known phenomenon.[9,10] Schlenk and Marcus[11] have shown that tetraphenylhydrazine in dry ether reacts slowly with potassium to yield the potassium salt of diphenylamine:

$$R_2NNR_2 + 2\,K \longrightarrow 2\,R_2NK\ (R = C_6H_5)$$

This is the only reaction reported in the literature which bears some relationship to the potassium metal induced formation of I. It is obvious that the observation of Schlenk and Marcus[11] and the present study bear an inverse relationship to one another even though this investigation has been unable to detect any reversal of the Schlenk and Marcus[11] process. This latter can only proceed by a free radical mechanism. The present observations with 1,1′-dinaphthylamine, and related secondary amines, however, suggest that the process should be reversible. Studies to this end are being continued.

EXPERIMENTAL[12,13]

N-Methyl-1,1′-dinaphthylamine (IV). (a) *By metallation in toluene.* To 2.7 g. (0.01 mol.) of 1,1′-dinaphthylamine dissolved in dry toluene (20 ml.) was added 0.5 g. (0.0125 mol.) of potassium cut into small pieces. The reaction mixture was stirred and refluxed for 2 hr. in a nitrogen atmosphere while the reaction mixture turned reddish brown. After cooling and treatment with methyl iodide (8.5 g., 0.06 mol.) the reaction mixture was allowed to stand overnight, then filtered hot, and concentrated *in vacuo*. The brown oily residue was dissolved in benzene and chromatographed over alumina. From the benzene elutes a yellow solid melting at 140–143° was obtained; yield, 1.5 g. (52%). Recrystallization from benzene-ethanol gave pale yellow needles, m.p., 143–144°.

Anal. Calcd. for $C_{21}H_{17}N$: C, 89.04; H, 6.00; N 4.95; Found: C, 88.74; H, 5.98; N, 4.78.

(b) *By metallation in liquid ammonia.* Potassium (0.34 g., 0.0087 mol.) was dissolved in dry liquid ammonia (40 ml.). On addition of 1,1-dinaphthylamine (2 g., 0.0074 mol.) a vigorous evolution of hyrdogen occurred and an orange-red solid separated almost immediately. The ammonia was allowed to evaporate and the solid residue was treated in the cold with methyl iodide (11.4 g., 0.08 mol.). When the initial vigor of reaction subsided, the mixture was gently refluxed for 3 hr. The reaction mixture was filtered hot and the precipitate washed with hot benzene (25 ml.). The filtrate and the washings were combined, concentrated to a small volume (15 ml.) and chromatographed on a 20-in. column of alumina with benzene as eluent. The benzene elute (60 ml.) was concentrated to small volume (5 ml.) and diluted with ethanol to obtain a yellow powder, m.p., 140°, yield, 1.2 g. (55%). Recrystallization was effected as above yielding pale yellow needles, melting at 143–144°. By mixed melting point, this was shown to be identical with IV obtained in (a).

(c) *By metallation in xylene. Formation of tetra(1-naphthyl)-hydrazine* (II). To 2.7 g. (0.01 mol.) of 1,1′-dinaphthylamine dissolved in 25 ml. of dry xylene was added 0.4 g. (0.01 mol.) of potassium. The reaction mixture was stirred and refluxed in an atmosphere of deoxygenated dry nitrogen for 4 hr. producing a tarry solid material. After filtration, the filtrate was concentrated *in vacuo,* diluted with benzene, decolorized with charcoal and chromatographed on alumina. The benzene elutes were concentrated and diluted with petroleum ether to obtain 120 mg. of a yellow solid melting around 130°. This was purified by repeated dissolution in acetone and precipitation with ethanol to obtain a yellow crystalline powder, m.p. 235°. Mixture melting point with an authentic specimen[3] of II showed no depression. The yield of II was 5%.

Repetition of the above experiment in the presence of air did not effect the nature of the reaction product, a 5% yield of II being obtained. Attempts to react the tarry material, *in situ,* with methyl iodide, failed to yield a methylation product. Rather II was repeatedly obtained in about 5% yields. Using 4, 6, and 10 mol. of potassium to 1 mol. of 1,1′-dinaphthylamine was without effect in increasing the yield of II above 5%. Increasing the reaction temperature to 193° (refluxing in decalin) decreased the yield of II to 2–3%.

(d) *By reaction of N-methyl-1-naphthylamine with 1-naphthol in the presence of zinc chloride. Formation of N-methyl-1,2-dibenzo (a, i) carbazole* (V). A mixture of *N*-methyl-1-naphthylamine (5 g., 0.032 mol.), 1-naphthol (5 g., 0.035 mol., ammonium chloride (5 g.), and freshly fused zinc chloride (5 g.) was gently heated to melting and held at that state for 15 min. On cooling, the dark brown cake was triturated with water and then extracted with benzene, filtered, washed with 10% potassium hydroxide (twice), water, 2*N* hydrochloric acid (twice), and finally with water. The benzene layer was separated, concentrated, and subjected to chromatographic separation. The first fraction yielded a very pale yellow solid (1.1 g., 12%) melting about 180°. Recrystallization from benzene-alcohol gave colorless needles melting at 188–190°. It was identified as V by analysis.

Anal. Calcd. for $C_{21}H_{15}N$: C, 89.69; H, 5.34; N, 4.98; Found: C, 89.76; H, 4.79; N, 4.64.

The subsequent chromatographic fractions yielded only contaminated material from which no definite substance could be obtained. Attempts to cyclize *N*-methyl-1,1′-dinaphthylamine to the carbazole by the same technique led only to recovery of the starting material in diminished yield.

N-Methyl-2,2′-dinaphthylamine. Metallation and methylation of 2,2′-dinaphthylamine was carried out as described in (a). The yield of *N-methyl-2,2′-dinaphthylamine was 50%,* crystallized from benzene-alcohol as pale brown fragile needles, m.p., 115–117° (lit.[14] 139–140°, and 123–124°[15]).

Anal. Calcd. for $C_{21}H_{17}N$: N, 4.95; Found: N, 4.68.

Metallation and methylation in liquid ammonia as described in (b) increased the yield of product to 68% identified as *N-methyl-2,2′-dinaphthylamine* by mixed melting point. When the metallations and attempted methylations were carried out in refluxing xylene only unworkable tars were obtained. Repeated and exhaustive chromatographic separation failed to yield any trace of tetra(2-naphthyl)-hydrazine.

N-Methyl-N-phenyl-1-naphthylamine. From 4.4 g. (0.02 mol.) of *N*-phenyl-1-naphthylamine by procedure (a) was obtained 3.5 g. (75%) of a pale brown powder, which on repeated crystallizations from ethanol gave a constant m.p. of 52–53°.

Anal. Calcd. for $C_{17}H_{15}N$: N, 6.01; Found: N, 6.27.

N-Methyl-N-phenyl-1-naphthylammonium chloride was obtained, in quantitative yield, by passing dry hydrogen chloride into a benzene solution of the base; m.p., 118–121°.

Anal. Calcd. for $C_{17}H_{16}NCl$: N, 5.20; Found: N, 5.58.

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(9) J. E. Leffler, *The Reactive Intermediates of Organic Chemistry,* Interscience Publishers, Inc., New York, 1956, 66.

(10) C. Walling, *Free Radicals In Solution,* John Wiley and Sons, Inc., New York, 1957, 524.

(11) W. Schlenk and E. Marcus, *Ber.,* **47,** 1673 (1914).

(12) Melting points are uncorrected.

(13) Microanalyses by Drs. C. Weiler and F. B. Strauss, Oxford, England.

(14) C. Ris, *Ber.,* **20,** 2619 (1887).

(15) O. Kym, *Ber.,* **23,** 2460 (1890).

Repetition of the potassium metallation experiments with *N*-phenyl-1-naphthylamine at higher temperatures (refluxing xylene and decalin) led only to unworkable tars.

N-Methyl-N-phenyl-2-naphthylamine was obtained by procedure (a) in 33% yield, m.p. 88–90° (lit.[8] 52–52°).

Anal. Calcd. for $C_{17}H_{15}N$: N, 6.01; Found: N, 6.35.

Higher temperature experiments gave only unworkable tars.

N,N-Dimethyl-1-naphthylammonium picrate. A mixture of *N*-methyl-1-naphthylamine (3.1 g., 0.02 mol.), potassium (1.6 g., 0.04 mol.) and xylene (10 ml.) was refluxed and stirred for 4 hr. in a continuous stream of purified dry nitrogen to give a suspension of a greenish yellow solid. The reaction mixture was cooled and treated overnight with methyl iodide (11.4 g., 0.08 mol.) at room temperature the mixture was warmed, filtered, and the precipitate washed with hot benzene (10 ml.). The filtrate and washings were combined and concentrated. The concentrate was treated with an excess of a saturated solution of picric acid in ethanol. A yellow crystalline solid was obtained melting at 144–145° (lit.[16] m.p. 145°); yield, 4.2 g. (53%).

Anal. Calcd. for $C_{18}H_{16}N_4O_7$: N, 14.00. Found: N, 14.04.

After chromatography of the combined filtrates and washings, and development of the bands, fluorescent examinations show bands identical with those produced by an authentic specimen[3] of *sym*-dimethyl-di(1-naphthyl)hydrazine.

N-Methyl-N-ethyl-1-naphthylammonium picrate. By the same procedure as described above, 3.4 g. (0.02 mol.) of *N*-ethyl-1-naphthylamine gave 4.15 g. (50%) of a picrate melting at 146°.

Anal. Calcd. for $C_{19}H_{18}N_4O_7$: N, 13.53. Found: N, 13.50.

Chromatographic banding and fluorescent examination gave bands suggestive of a tetrasubstituted hydrazine.

Repetition of the same procedure on the ethylation of *N*-methyl-1-naphthylamine gave a 46% yield of a picrate, m.p., 146°, shown by mixed melting point to be identical with *N-methyl-N-ethyl-1-naphthylammonium picrate.*

N-Benzyl-diphenylamine. A mixture of diphenylamine (3.4 g., 0.02 mol.), potassium (0.8 g., 0.02 mol.) and xylene (20 ml.) was refluxed and stirred in a continuous stream of purified dry nitrogen for 4 hr. when a suspension of a pale yellow solid was obtained. The reaction mixture was cooled and allowed to react with benzyl chloride (2.6 g., 0.02 mol.) at room temperature overnight, warmed, and filtered. The filtrate was concentrated to a small volume (6 ml.). On dilution with petroleum ether, 2 g. (44%) of a crystalline solid melting at 84–86° was obtained. Recrystallization from ethanol gave needles, m.p., 88° (lit.[7] 88–88.5°).

Anal. Calcd. for $C_{19}H_{17}N$: N, 5.41; Found: N, 5.63.

Repeated experiments and exhaustive chromatographic separations in attempts to find evidence for the formation of *tetraphenylhydrazine* were negative.

CHICAGO 14, ILL.

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[16] H. H. Hodgson and J. H. Crook, *J. Chem. Soc.*, 1500 (1936).

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, UNION CARBIDE CHEMICALS CO., SOUTH CHARLESTON, W. VA.]

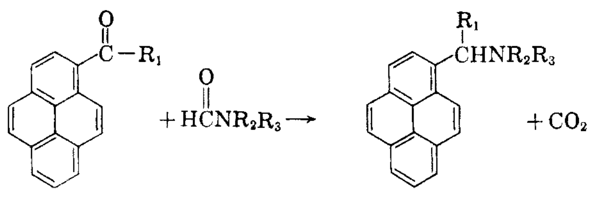
(Aminoalkyl)pyrenes

E. MARCUS AND J. T. FITZPATRICK

Received August 12, 1959

The synthesis of a variety of 1-pyrenemethylamines is described. Most of the compounds were prepared by the Leuckart reaction from the corresponding carbonyl derivative of pyrene and a formamide in the presence of formic acid. Some others were made by catalytic reduction of the imines obtained from 1-pyrenecarboxaldehyde and a primary amine. 1-Pyrenemethylamine was obtained best by reduction of the oxime.

During our study of derivatives of polycyclic hydrocarbons we became interested in the synthesis of 1-pyrenemethylamines. A convenient method for the preparation of such compounds appeared to be the Leuckart reaction.[1]



In the reaction of pyrenecarboxaldehyde with dialkylformamides good yields were obtained when the nitrogen of the dialkylamine part was attached to two methyl or ethyl groups, or when it was part of a heterocyclic system; with higher alkyl groups lower yields were realized. With monoalkylformamides or unsubstituted formamide and pyrenecarboxaldehyde the desired products could also be obtained, but only in low yields; the reaction proceeded further to give large amounts of bis- and tris(pyrenemethyl)amines. The monosubstituted pyrenemethylamines could be made more easily by catalytic hydrogenation of the imines derived from the aldehyde and the corresponding amines. The unsubstituted pyrenemethylamine was prepared best by catalytic reduction of the oxime.

With acetylpyrene and dialkylformamides (we investigated the reaction with dimethylformamide in the presence of formic acid as well as magnesium chloride) the desired reaction did not occur at all. Acetylpyrene reacted fairly well with a monosubstituted formamide and very well with formamide itself; formation of bis- and tris(α-methyl-1-pyrenemethyl)amines was of no importance.

In benzoylpyrene the steric hindrance around the carbonyl group is apparently significant enough, that the reaction even with unsubstituted formamide proceeds only very slowly.

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[1] E. Marcus and J. T. Fitzpatrick, *J. Org. Chem.*, **24**, 1031 (1959).