EXPERIMENTAL[1]

2-Methacrylamido-3-methylbutyric acid (I). A mixture of 117 g. (1 mole) of *dl*-valine (Dow), 400 ml. of water and 80 g. (2 moles) of sodium hydroxide was stirred at 10–15° and 105 g. (1 mole) of methacrylyl chloride (Monomer and Polymer Co.) was added over a 1.5-hour period. The mixture was then treated with 1 mole of concentrated hydrochloric acid. The voluminous precipitate, which formed on standing, was removed by filtration, washed with water, and then recrystallized from benzene to give 141 g., a 75% yield, of I (m.p. 99–100°).

Anal. Calcd. for $C_9H_{15}NO_3$: C, 58.4; H, 8.10; N, 7.56. Found: C, 58.36; H, 8.08; N, 7.65.

2-Isopropenyl-4-isopropyl-2-oxazolin-5-one (II). The technique of Cleaver and Pratt[2] was employed for this closure. A mixture of 18.5 g. (0.1 mole) of I and 51 g. (0.5 mole) of acetic anhydride was added rapidly to 51 g. (0.5 mole) of acetic anhydride at 100°. The mixture was held at 100° for 10 min. and then distilled to give 6.8 g., a 40.5% yield, of II (b.p. 81°/10.5 mm., n_D^{30} 1.4550).

Anal. Calcd. for $C_9H_{13}NO_2$: C, 64.65; H, 7.78; N, 8.38. Found: C, 64.25; H, 7.68; N, 8.21.

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(1) All temperatures are uncorrected.

(2) C. S. Cleaver and B. C. Pratt, *J. Am. Chem. Soc.*, **77**, 1544 (1955).

Some Dimethylaminomethyl Derivatives of Polycyclic Aromatic Hydrocarbons

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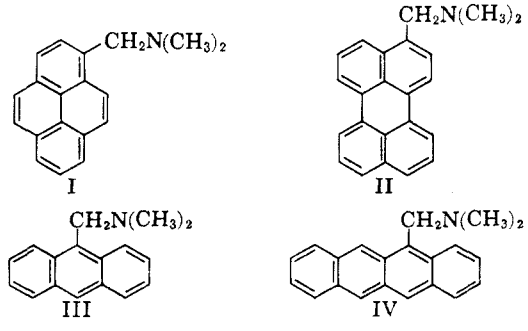
The preparation of dialkylaminomethylbenzenes from aromatic aldehydes and dialkylformamides by the Leuckart reaction has been described previously.[1] We wish to report the extension of the Leuckart reaction to the synthesis of the dimethylaminomethyl derivatives of pyrene, perylene, anthracene, and naphthacene (I–IV).



(1) (a) O. Wallach, *Ann.*, **343**, 54 (1905); (b) E. Staple and E. C. Wagner, *J. Org. Chem.*, **14**, 559 (1949); (c) M. Mousseron, R. Jacquier, and R. Zagdoun, *Bull. soc. chim.*, 974 (1953); (d) M. L. Moore, *Org. Reactions*, **5**, 301 (1952).

The corresponding aldehydes can be obtained readily by formylation of the hydrocarbons with *N*-methylformanilide or dimethylformamide and phosphorus oxychloride. Refluxing a solution of the aldehyde in dimethylformamide in the presence of formic acid gave fair to good yields of the desired compounds. When the reaction of pyrenecarboxaldehyde with dimethylformamide was carried out in the absence of formic acid, no product at all was obtained. The compounds were isolated as their hydrochlorides.

An alternative route *via* the corresponding chloromethyl derivatives is less satisfactory, because direct chloromethylation of such highly active polycyclic hydrocarbons often leads to diarylmethane-type compounds and bis(chloromethyl) derivatives.[2] When 9-(chloromethyl)anthracene was needed as an intermediate in some recent work, it was made by a three-step synthesis.[3]

EXPERIMENTAL

All melting points are uncorrected. The neutralization equivalents of the amine hydrochlorides were determined by titration with sodium hydroxide using phenolphthalein as indicator; the values are estimated to be accurate within 2 or 3%.

The aldehydes were prepared according to methods described in the literature.[4–7] The melting point of crude 5-naphthacenecarboxaldehyde (m.p. 157–161°) agreed better with the data for analytically pure material reported by Buu-Hoï and Lavit[8] (m.p. 164°) than by Martynoff[7] (m.p 148°). Buu-Hoï and Eckert[9] reported they could use dimethylformamide in place of *N*-methylformanilide for the preparation of 1-pyrenecarboxaldehyde. We found that a fair yield of 1-pyrenecarboxaldehyde could be obtained with dimethylformamide by heating the reaction mixture for 3 hr. at 105°.

As an example for the synthesis of the amines the preparation of *N,N*-dimethyl-1-pyrenemethylamine hydrochloride is described. The hydrochlorides of *N,N*-dimethyl-3-perylenemethylamine, *N,N*-dimethyl-9-anthracenemethylamine, and *N,N*-dimethyl-5-naphthacenemethylamine were made in a similar fashion (Table I).

N,N-Dimethyl-1-pyrenemethylamine hydrochloride. A mixture of 11.5 g. (0.05 mole) of 1-pyrenecarboxaldehyde, 27.5 g. (0.38 mole) of dimethylformamide, and 2.5 ml. of 90% formic acid was refluxed for 4 hr. at about 150°. After removal of the excess of dimethylformamide and formic acid by distillation the residual oil was dissolved in ethyl ether, dried over sodium sulfate, and filtered. Introduction of gaseous hydrogen chloride into the ethereal solution pre-

(2) G. M. Badger and C. W. Cook, *J. Chem. Soc.*, 802 (1939).

(3) W. T. Hunter, J. S. Buck, F. W. Gubitz, and C. H. Bolen, *J. Org. Chem.*, **21**, 1512 (1956).

(4) H. Vollmann, H. Becker, M. Corell, and H. Streeck, *Ann.*, **531**, 1 (1937).

(5) L. F. Fieser, J. L. Hartwell, J. E. Jones, J. H. Wood, and R. W. Bost, *Org. Syntheses*, **Coll. Vol. III**, 98 (1955).

(6) N. P. Buu-Hoï and C. T. Long, *Rec. trav. chim.*, **75**, 1221 (1956).

(7) M. Martynoff, *Compt. rend.*, **238**, 249 (1954).

(8) N. P. Buu-Hoï and D. Lavit, *Rec. trav. chim.*, **76**, 674 (1957).

(9) N. P. Buu-Hoï and B. Eckert, *Rec. trav. chim.*, **74**, 1119 (1955).

TABLE I

PHYSICAL DATA, ANALYSES, AND YIELDS OF DIMETHYLAMINOMETHYL DERIVATIVES

Compound		Analyses C	H	N	Cl	Neutral Equivalent	Color	M.P.[a]	Yield, %[b]
I	Found.[b]	77.00	6.43	4.70		299[b]	White	270–277[b]	72
	Calcd.:	77.14	6.13	4.74		296			
II[d]	Found.[e]	79.68	5.67	4.10	10.00	346[b]	Yellow	290–305[e]	50
	Calcd.:	79.90	5.79	4.05	10.25	346			
III	Found:[c]	75.30	6.67	5.33		275[b]	White	241–242[c]	81
	Calcd.:	75.12	6.67	5.15		272			
IV[d,f]	Found:[e]	77.62	6.19	4.24	10.30	319[e]	Yellow-brown	220–237[e]	61
	Calcd.:	78.36	6.27	4.35	11.02	322			

[a] All samples melted with decomposition. [b] Crude product. [c] After recrystallization from a mixture of concentrated hydrochloric acid and water (1:1) with the aid of charcoal. [d] After removal of the excess of dimethylformamide and formic acid a solid remained. Most of this solid was soluble in a very large amount of ethyl ether. A solid by-product, corresponding in weight to about 20% of the aldehyde used as starting material, was insoluble and was discarded. [e] The sample had been purified by dissolving the material in a very large amount of hot water, filtration, and addition of hydrochloric acid to the filtrate. [f] The analytical data indicate the presence of an impurity. However, there is little doubt that the product has predominantly the assigned structure.

cipitated 10.7 g. (72%) of white *N,N*-dimethyl-1-pyrenemethylamine hydrochloride, m.p. 270–277° with decomposition; it had a neutral equivalent of 299 (Calcd. 296).

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Pyridoxine *N*-Oxide[1]

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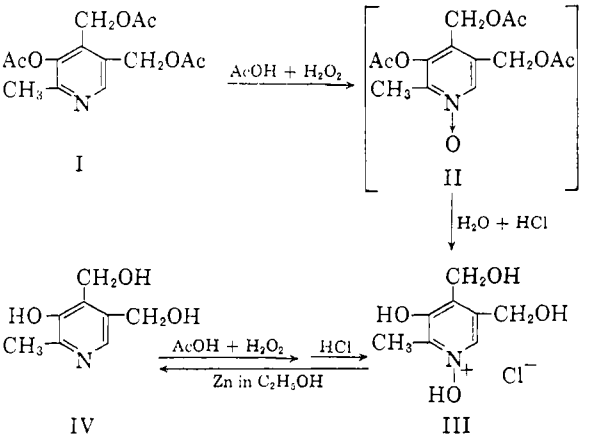
Upon treatment with acetic acid–hydrogen peroxide, a variety of pyridine derivatives form *N*-oxides.[2] It seemed possible, in a similar manner, to convert pyridoxine (IV) to pyridoxine *N*-oxide (III), which is of interest because of the following two possibilities: (a) pyridoxine *N*-oxide (III) may act as an antimetabolite, or (b) pyridoxine *N*-oxide (III) may serve as a source of vitamin B_6 *in vivo*. It has been reported that pyridine *N*-oxide was reduced to pyridine by baker's yeast, although an analogous reaction did not occur with 4-picoline *N*-oxide.[3]

In the present study, 3,4,5-triacetylpyridoxine (I) was treated with a mixture of glacial acetic acid and hydrogen peroxide at 37° for 72 hr., or at 60–70° for 8 hr. The intermediate, possibly 3,4,5-triacetylpyridoxine *N*-oxide (II), was hydrolyzed by refluxing in 65% ethanol containing 4.5% hydrogen chloride. The resulting product contained a considerable amount of pyridoxine. A longer reaction time and the use of an oxidation mixture which consisted of acetic acid–acetic anhydride–hydrogen



I II III IV

peroxide failed to complete the oxidation. The *N*-oxide hydrochloride (III), however, was far more soluble than pyridoxine hydrochloride in 1-propanol, 2-propanol, and 1-butanol and could thus be purified by solvent fractionation. Pyridoxine (IV) was regenerated from pyridoxine *N*-oxide (III) upon refluxing in 95% ethanol in the presence of zinc dust. The identity of the reduced material was established by mixed melting point with an authentic specimen of pyridoxine, paper chromatography, and the biological activity to support growth of *Saccharomyces carlsbergensis*. For paper chromatography, the solvent systems reported by Rodwell *et al.*[4] and Snyder *et al.*[5] were satisfactory.

Free pyridoxine base (IV) also formed pyridoxine *N*-oxide (III), although the yield was considerably lower. It has been shown that under certain conditions, a portion of pyridoxine is oxidized to pyri-

(1) This work was supported by research grant No. A-257 from the National Institutes of Health, U. S. Public Health Service, Department of Health, Education, and Welfare.
(2) E. Ochiai, *J. Org. Chem.*, **18**, 534 (1953).
(3) A. May, *Enzymologia*, **18**, 142 (1957).
(4) V. W. Rodwell, B. E. Volcani, M. Ikawa, and E. E. Snell, *J. Biol. Chem.*, **233**, 1548 (1958).
(5) J. Q. Snyder and S. H. Wender, *Arch. Biochem. Biophys.*, **46**, 465 (1953).