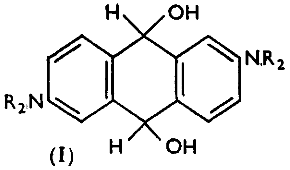
431. *The Action of Tin and Hydrochloric Acid on* p-*Dialkylaminobenzaldehydes. Part II.* The Preparation of Some New Anthracenes.*

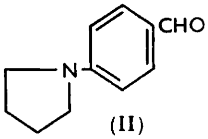
By JACK W. RASBURN and FREDERICK H. C. STEWART.

The reaction of *p*-dialkylaminobenzaldehydes with tin and hydrochloric acid to give 2 : 6-bisdialkylaminoanthracenes has been extended to include several 2-substituted *p*-dimethylaminobenzaldehydes. Certain steric aspects of the reaction are also discussed.

IN Part I it was shown that *p*-dialkylaminobenzaldehydes react with tin and hydrochloric acid to form 2 : 6-bisdialkylamino-9 : 10-dihydro-9 : 10-dihydroxyanthracenes (I) which are then reduced by the stannous chloride present to 2 : 6-bisdialkylaminoanthracenes. The behaviour of a diol (I) depends markedly on the nature of the dialkylamino-group. Thus the diethylamino-compound (I; $R = Et$) was less readily reduced than the dimethylamino-analogue (I; $R = Me$). This effect, which was ascribed to steric inhibition of resonance in the former diol, has now been examined further in the case of 1-*p*-formylphenylpyrrolidine (II) in which steric interference between the dialkylamino-group and the



(I)



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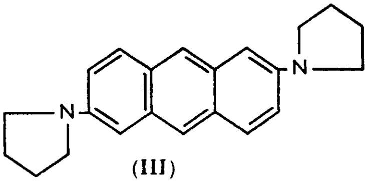

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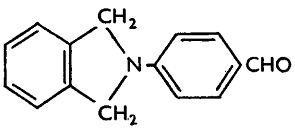

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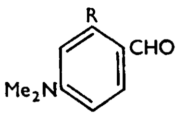

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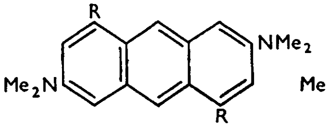

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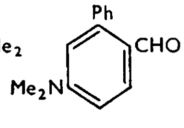

(VII)

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* Part I, Stewart, *J.*, 1957, 1026.

aromatic nucleus should be reduced owing to the rigidity imposed by the heterocyclic ring. In fact, the aldehyde (II) reacted readily with tin and hydrochloric acid to give 2 : 6-dipyrrolidinoanthracene (III) in 57% yield. Under the same conditions *p*-diethylaminobenzaldehyde gave only a trace of 2 : 6-bisdiethylaminoanthracene, the main product being unreduced diol (I; R = Et), while *p*-dimethylaminobenzaldehyde gave 2 : 6-bisdimethylaminoanthracene in some 35% yield. An attempt to apply the reaction to 2-*p*-formylphenyl*iso*indoline (IV) was unsuccessful owing to its very low solubility.

While it is thus clear that the reaction is very sensitive to relatively minor steric effects at the dialkylamino-group nothing is known regarding similar influences at the aldehyde function. Consequently, the effect of various substituents *ortho* to the aldehyde group in *p*-dimethylaminobenzaldehyde has now been investigated.

The aldehydes (V; R = Me, OMe, Cl) react readily with tin and hydrochloric acid, to give the corresponding anthracenes (VI; R = Me, OMe, Cl) in yields of 40—55%. These results indicate that the reaction is virtually unaffected by moderate steric hindrance at the aldehyde group. A particularly interesting compound in this connection is 4-dimethylamino-2-phenylbenzaldehyde (VII). With this aldehyde intramolecular condensation at the 2′-position to form a fluorene derivative was a possible mode of reaction. The steric effect of the bulky phenyl group might also be expected to facilitate such condensation rather than the alternative intermolecular diol-forming reaction. However, the aldehyde (VII) gave 2 : 6-bisdimethylamino-4 : 8-diphenylanthracene in 37% yield. There was no indication of the simultaneous formation of a fluorene derivative.

The mechanism and applications of this reaction are being further investigated.

EXPERIMENTAL

Preparation of p-*Dialkylaminobenzaldehydes.*—The aldehydes were prepared from the dialkylanilines by the *NN*-dimethylformamide–phosphorus oxychloride procedure of Campaigne and Archer.[1] The mixture was poured with stirring into a large excess of cold water; the product separated slowly. Neutralization with sodium acetate [1] was found to be unnecessary in most cases and tended to yield an inferior product.

The substituted dimethylanilines which were required were prepared by the trimethyl phosphate method of Thomas, Billman, and Davies [2] which was found to be more uniformly satisfactory than the various methods described elsewhere.

The following aldehydes are new.

2-p-*Formylphenyl*iso*indoline* (IV), obtained from 2-phenyl*iso*indoline [3] as a buff powder after recrystallisation from benzene–light petroleum (b. p. 60—80°), had m. p. 176—177° (70%). When sublimed *in vacuo* and recrystallised from benzene–light petroleum, it formed light yellow needles, m. p. 176·5—177° (Found : C, 80·9; H, 5·7. $C_{15}H_{13}ON$ requires C, 80·7; H, 5·8%).

1-p-*Formylphenylpyrrolidine* (II), prepared (69%) from 1-phenylpyrrolidine,[4] recrystallised from light petroleum (b. p. 80—100°) in plates, m. p. 84·5—85·5° (Found : C, 75·3; H, 7·05; N, 8·2. $C_{11}H_{13}ON$ requires C, 75·4; H, 7·5; N, 8·0%).

4-*Dimethylamino-2-phenylbenzaldehyde* (VII), prepared (50%) from 3-dimethylaminodiphenyl,[5] formed a white powder which was sufficiently pure for further use (m. p. 55—56°). It recrystallised from light petroleum (b. p. 60—80°) in plates, m. p. 55—56° (Found : C, 80·2; H, 6·7; N, 6·2. $C_{15}H_{15}ON$ requires C, 80·0; H, 6·6; N, 6·2%).

4-*Dimethylamino-2-methoxybenzaldehyde* (V; R = OMe), obtained from *NN*-dimethyl-*m*-anisidine [6] and purified by distillation, had b. p. 190—192°/7 mm., m. p. 58—60° (48%), and recrystallised from light petroleum (b. p. 60—80°) in needles, m. p. 61—62° (Found: C, 67·0;

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[1] Campaigne and Archer, *J. Amer. Chem. Soc.*, 1953, **75**, 989.
[2] Thomas, Billman, and Davies, *ibid.*, 1946, **68**, 895.
[3] Scholtz, *Ber.*, 1898, **31**, 628.
[4] Sommers, *J. Amer. Chem. Soc.*, 1956, **78**, 2439.
[5] Groenewoud and Robinson, *J.*, 1934, 1692.
[6] Reverdin and Luc, *Ber.*, 1914, **47**, 1541.

H, 7·5; N, 7·9. $C_{10}H_{13}O_2N$ requires C, 67·0; H, 7·3; N, 7·8%). The *semicarbazone* formed needles (from ethanol), m. p. 234—235° (Found: C, 55·9; H, 6·7; N, 23·6. $C_{11}H_{16}O_2N_4$ requires C, 55·9; H, 6·8; N, 23·7%). The monoaldehyde was accompanied by higher-melting colourless needles (from ethanol), m. p. 157—158° (16%), probably 4-*dimethylamino*-6-*methoxy*iso*phthaldehyde* (Found: C, 63·45; H, 6·4; N, 6·8. $C_{11}H_{13}O_3N$ requires C, 63·75; H, 6·3; N, 6·8%).

Preparation of 2 : 6-*Bisdialkylaminoanthracenes.*—The general procedure was that described in Part I. The *p*-dialkylaminobenzaldehyde (1 part) was dissolved in diluted hydrochloric acid (60 parts; 1 : 1 v/v), and granulated tin (4 parts) added. The mixture was kept at 20—30° until most of the metal had dissolved (1—2 weeks). The precipitated tin salt was then separated and treated with alkali to liberate the crude anthracene, which was dried and recrystallised from an appropriate solvent. In this manner the following 2 : 6-bisdialkylaminoanthracenes were prepared.

2 : 6-*Bisdimethylamino*-4 : 8-*dimethylanthracene* (VI; R = Me), from 4-dimethylamino-2-methylbenzaldehyde,[7] formed golden-yellow needles [from benzene–ethanol (1 : 2)], m. p. 175—176° (39%) (Found: C, 81·4; H, 8·7; N, 9·4. $C_{20}H_{24}N_2$ requires C, 82·1; H, 8·2; N, 9·5%).

4 : 8-*Dichloro*-2 : 6-*bisdimethylaminoanthracene* (VI; R = Cl) (48%), from 2-chloro-4-dimethylaminobenzaldehyde,[8] recrystallised from benzene (charcoal) in yellow elongated plates (opaque on storage), m. p. 205·5—206·5° (Found: C, 64·8; H, 5·7. $C_{18}H_{18}N_2Cl_2$ requires C, 64·9; H, 5·4%).

2 : 6-*Bisdimethylamino*-4 : 8-*dimethoxyanthracene* (VI; R = OMe) (55%), from 4-dimethylamino-2-methoxybenzaldehyde, crystallised in yellow needles [from benzene–ethanol (1 : 2)], m. p. 206—207° (Found: C, 73·8; H, 6·9; N, 8·7. $C_{20}H_{24}O_2N_2$ requires C, 74·0; H, 7·5; N, 8·6%).

2 : 6-*Bisdimethylamino*-4 : 8-*diphenylanthracene* (VI; R = Ph) (37%), from 4-dimethylamino-2-phenylbenzaldehyde (VII), formed pale yellow needles, m. p. 173·5—174·5°, from benzene–ethanol (charcoal) (Found: C, 86·4; H, 6·8; N, 6·6. $C_{30}H_{28}N_2$ requires C, 86·5; H, 6·8; N, 6·7%).

2 : 6-*Dipyrrolidinoanthracene* (III), from 1-*p*-formylphenylpyrrolidine (II), formed light yellow needles, m. p. 315—318° (57%), from boiling benzene (in which it was rather sparingly soluble). Recrystallised from benzene (charcoal) it had m. p. 315—317° (Found: C, 83·1; H, 7·95; N, 8·95. $C_{22}H_{24}N_2$ requires C, 83·5; H, 7·65; N, 8·85%).

Solutions of these anthracenes exhibited a strong blue fluorescence. Treatment of each with hydrogen peroxide and hydrochloric acid under the conditions described in Part I produced a thermolabile red colour. This reaction appears to be characteristic of 2 : 6-bisdialkylaminoanthracenes.

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[7] Duff, *J.*, 1945, 276.
[8] Ullmann and Frey, *Ber.*, 1904, **37**, 864.