9. *Some Condensation Products of* m-*Dialkylaminobenzaldehydes with Compounds containing Reactive Methylene Groups.*

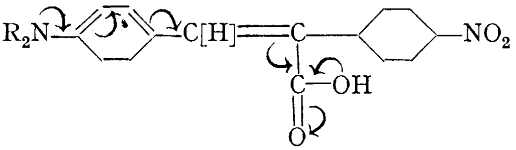
By Wesley Cocker and Denys G. Turner.

Stilbene-like compounds have been prepared from *m*-dialkylaminobenzaldehydes (Cocker and Harris, J., 1939, 1092) and 2:4-dinitrotoluene, *p*-nitrophenylacetic acid, *p*-nitrophenylacetonitrile, and 1-phenyl-3-methyl-5-pyrazolone. These compounds gave interesting shades on acetate silk, but their light-fastness was poor.

Condensation of the above aldehydes with α-picoline methiodide, quinaldine methiodide, 2-methylthiazole methiodide, and 2-methylbenzthiazole methiodide yielded dyes of little interest tinctorially, but spectrographic determinations now in progress will indicate their suitability as photographic sensitisers.

The condensation of carbonyl compounds with compounds containing reactive methylene groups has frequently been investigated (see Knoevenagel, *Ber.*, 1904, **37**, 4461, for references) and Pfeiffer (*Ber.*, 1915, **48**, 1796) and Dippy, Hogarth, Watson, and Williams (*J. Soc. Chem. Ind.*, 1937, 396T) found that the condensation products of *p*-dialkylaminobenzaldehydes with nitrotoluenes are valuable dyes for acetate silk (Soc. Chem. Ind. Basle, B.P. 396,893). It is now shown that *m*-dialkylaminobenzaldehydes (Cocker and Harris, *loc. cit.*) similarly condense with the greatest ease, with piperidine as catalyst, giving highly coloured stilbene derivatives.

The condensation of *p*-nitrophenylacetic acid with *p*-dimethylaminobenzaldehyde at 116° yields a substituted stilbene (Dippy *et al.*, *loc. cit.*), but its condensation with *m*-dialkylaminobenzaldehydes at 100° gives substituted cinnamic acids, which are readily decarboxylated by heating with piperidine at 140°, yielding the corresponding stilbenes.



The condensation of *p*-dimethylaminobenzaldehyde with *p*-nitrophenylacetic acid at 100° yields a stilbene and it appears that the difference in the course of the reactions of *m*- and *p*-dialkylaminobenzaldehydes is due to the greater ease of transmission of electrons, by the conjugated system, from the alkylamino-group in the para-position, thus facilitating decarboxylation of the cinnamic acid first formed in the condensation.

The highly coloured products from *m*-dialkylaminobenzaldehydes with 2 : 4-dinitrotoluene and *p*-nitrophenylacetonitrile dye acetate silk in bright shades, not fast to light.

The condensation of *m*-dialkylaminobenzaldehydes with the alkyl iodides of heterocyclic compounds containing a 2-methyl group yields highly coloured products, which dye acetate silk in bright shades; these, however, are rapidly discharged by acid, although they may be restored by treatment with alkali. The compounds, like those described by Smith (J., 1923, **123**, 2288; see also Mills and Smith, J., 1922, **121**, 2724), may be useful as photosensitising agents and are being examined from this aspect.

Experimental.

Condensation of m-*Dialkylaminobenzaldehydes with* 2 : 4-*Dinitrotoluene.*—2 : 4-*Dinitro-3′-dimethylaminostilbene.* A mixture of 2 : 4-dinitrotoluene (3 g.), *m*-dimethylaminobenzaldehyde (2·5 g.), and piperidine (0·25 c.c.) was heated under reflux on the water-bath for 24 hours. The almost solid mass was extracted with the minimum quantity of boiling benzene, from which the required *compound* (3·1 g.) separated in very dark red prisms, m. p. 205° (Found : C, 61·7; H, 5·1; N, 13·7. $C_{16}H_{15}O_4N_3$ requires C, 61·3; H, 4·8; N, 13·4%).

Dyeing experiments were made with this and the following substances, which were obtained finely divided by pouring boiling alcoholic solutions into a large excess of cold water. The dried precipitate (0·25 g.) was triturated with 2 c.c. of Turkey-red oil and introduced into 120 c.c. of water containing 0·25 g. of Lux soap. The solution was warmed to 40°, 4 g. of acetate silk fabric introduced, and the temperature then maintained at 70—80° for 90 minutes, with periodical stirring. The fabric was rinsed in cold water, and a portion dried. A further portion was brightened by immersion in 0·5% lactic acid solution for 30 minutes, followed by rinsing and drying.

2 : 4-Dinitro-3′-dimethylaminostilbene gave orange solutions and imparted a pale yellow shade to acetate silk. The dye-bath was almost discharged. When the dyed fabric was exposed for 24 hours to bright sunlight, the colour was largely discharged.

2 : 4-*Dinitro*-3′-*diethylaminostilbene*, similarly prepared from *m*-diethylaminobenzaldehyde (3 g.), 2 : 4-dinitrotoluene (3. g.), and piperidine (0·25 c.c.) (6 hours' heating), formed very dark red prisms (3·8 g.), m. p. 153° (Found : C, 63·5; H, 5·35; N, 12·4. $C_{18}H_{19}O_4N_3$ requires C, 63·4; H, 5·8; N, 12·3%). It gave a pale pinkish-yellow shade on acetate silk, but its light-fastness was poor, although rather better than that of the lower homologue.

2 : 4-*Dinitro*-3′-*dipropylaminostilbene* (60% yield) formed long, dark red, pointed prisms, m. p. 132° (Found : C, 65·3; H, 6·0. $C_{20}H_{23}O_4N_3$ requires C, 65·0; H, 6·2%). Its shade on acetate silk was brown-yellow, but the discharge of the dye bath was not very good.

2 : 4-*Dinitro*-3′-*dibenzylaminostilbene*.—*m*-Dibenzylaminobenzaldehyde (5 g.), 2 : 4-dinitrophenylacetic acid (3·8 g.), and piperidine (0·25 c.c.), heated on the water-bath for 24 hours, yielded a viscous mass. After extraction with alcohol the residue crystallised from petroleum (b. p. 100—120°) in orange-red prisms (1·6 g.), m. p. 163° (Found : C, 72·6; H, 5·2; N, 8·9. $C_{28}H_{23}O_4N_3$ requires C, 72·3; H, 5·0; N, 9·0%). It gave pale champagne shades on acetate silk.

Condensations with p-*Nitrophenylacetonitrile*.—3-*Dimethylamino*-α-4′-*nitrophenylcinnamonitrile*. A mixture of *m*-dimethylaminobenzaldehyde (2·5 g.), *p*-nitrophenylacetonitrile (2·7 g.), and piperidine (0·25 c.c.) was heated on the water-bath for 3 hours. The solid product, recrystallised from boiling benzene, gave the required *compound* (3·7 g.) in large, dark red, transparent prisms, m. p. 162·5° (Found : C, 69·6; H, 5·2. $C_{17}H_{15}O_2N_3$ requires C, 69·6; H, 5·1%). The rich golden-yellow shades produced on acetate silk faded to primrose-yellow after about 16 hours in bright sunlight.

3-*Diethylamino*-α-4′-*nitrophenylcinnamonitrile*, similarly prepared (yield, theoretical), formed small, dark red prisms, m. p. 136° (Found : C, 71·1; H, 6·0. $C_{19}H_{19}O_2N_3$ requires C, 71·0; H, 5·9%). It gave orange-yellow shades on acetate silk, which rapidly faded in bright sunlight.

3-*Dipropylamino*-α-4′-*nitrophenylcinnamonitrile* (maximum yield, 65%, obtained after 8 hours' heating) crystallised from benzene in orange-red prisms, m. p. 108° (Found : C, 71·8; H, 6·5. $C_{21}H_{23}O_2N_3$ requires C, 72·2; H, 6·5%). Its shade on acetate silk was bright yellow, rapidly fading in sunlight.

3-*Diallylamino*-α-4′-*nitrophenylcinnamonitrile* separated, on cooling (yield, 90%), in long, bright orange prisms, m. p. 82° (Found : C, 73·1; H, 5·6. $C_{21}H_{19}O_2N_3$ requires C, 73·0; H, 5·5%), from a hot alcoholic extract (charcoal) of the dark red tarry product obtained by heating together *m*-diallylaminobenzaldehyde and *p*-nitrophenylacetonitrile in presence of piperidine for 8 hours on the water-bath. It gave extremely bright yellow shades on acetate silk, but after 16 hours' accelerated fading under the ultra-violet lamp the fabric was almost white.

Condensations with p-*Nitrophenylacetic Acid*.—3-*Dimethylamino*-α-4′-*nitrophenylcinnamic acid*. A mixture of *m*-dimethylaminobenzaldehyde (2·5 g.), *p*-nitrophenylacetic acid (3 g.), and piperidine (0·25 c.c.) was heated on the water-bath for 16 hours. The solid product was recrystallised twice from benzene, the required *compound* being obtained (1·7 g.) in long orange-yellow prisms, m. p. 215·5° (Found : C, 65·2; H, 5·0; N, 9·6. $C_{17}H_{16}O_4N_2$ requires C, 65·4; H, 5·1; N, 9·0%). The compound had little affinity for acetate silk. It was readily soluble in warm 3N-caustic soda or sodium carbonate; on cooling, the sodium salt was deposited in bronze plates readily soluble in water or alcohol.

3-Dimethylamino-α-4′-nitrophenylcinnamic acid (1 g.) was heated with piperidine (0·5 c.c.) at 140—145° for ½ hour. The product was extracted with caustic soda solution, washed with water, dried, and crystallised twice from alcohol, 4-*nitro*-3′-*dimethylaminostilbene* being obtained in long, deep orange prisms, m. p. 145—145·5° (Found : C, 71·7; H, 6·0. $C_{16}H_{16}O_2N_2$ requires C, 71·6; H, 6·0%). It gave very bright lemon-yellow shades on acetate silk.

3-*Diethylamino*-α-4′-*nitrophenylcinnamic acid*. The oily product obtained by heating *m*-diethylaminobenzaldehyde with *p*-nitrophenylacetic acid and a trace of piperidine for 7 hours on the water-bath was shaken with warm dilute caustic soda solution, and the alkaline solution extracted with ether. The aqueous layer was neutralised with dilute acetic acid and the tar produced was washed with water and dissolved in the minimum quantity of warm benzene. On long standing, this solution deposited orange prisms, m. p. 173° (Found : C, 66·9; H, 6·0. $C_{19}H_{20}O_4N_2$ requires C, 67·0; H, 5·9%). On decarboxylation as described above, the *acid* gave 4-*nitro*-3′-*diethylaminostilbene*, which crystallised from alcohol in orange-red needles or long prisms, m. p. 97° (Found : C, 72·7; H. 6·7. $C_{18}H_{20}O_2N_2$ requires C, 73·0; H, 6·8%). Its shade on acetate silk was similar to those of its homologues.

3-*Dipropylamino-α-4'-nitrophenylcinnamic acid.* The product of heating *m*-dipropylaminobenzaldehyde and *p*-nitrophenylacetic acid for 24 hours on the water-bath with piperidine as catalyst was crystallised from benzene, yielding 1·7 g. of transparent, bright yellow prisms, m. p. 180·5° (Found : C, 68·5; H, 6·4. $C_{21}H_{24}O_4N_2$ requires C, 68·5; H, 6·5%). The properties of this *acid* were similar to those of the lower homologue. On decarboxylation it gave 4-*nitro*-3'-*dipropylaminostilbene*, which crystallised from alcohol in orange-yellow needles, m. p. 79° (Found : C, 73·75; H, 7·4. $C_{20}H_{24}O_2N_2$ requires C, 74·1; H, 7·4%). This gave a bright yellow shade on acetate silk.

Condensation with 1-*Phenyl*-3-*methyl*-5-*pyrazolone*.—A mixture of *m*-dimethylaminobenzaldehyde (2·5 g.), phenylmethylpyrazolone (3·0 g.), and piperidine (0·25 c.c.) was heated on the water-bath for 6 hours, the dark red mass extracted with boiling benzene, the extract concentrated and cooled, and the deposited crystals recrystallised from high-boiling ligroin; 1-*phenyl*-4-3'-*dimethylaminobenzylidene*-5-*pyrazolone* was obtained (2·3 g.) in deep red needles or long prisms, m. p. 117° (Found : C, 74·7; H, 6·6. $C_{19}H_{19}ON_3$ requires C, 74·8; H, 6·2%). It dyed acetate silk a very pale ivory shade, and this retained its colour even after many hours under the ultra-violet lamp.

Condensations with Methiodides of Heterocyclic Bases containing Reactive 2-*Methyl Groups*.—2-m-*Dimethylaminostyrylpyridine methiodide.* A solution of *m*-dimethylaminobenzaldehyde (2·5 g.), α-picoline methiodide (4 g.), and piperidine (0·5 c.c.) in alcohol (50 c.c.), heated under reflux on the water-bath for 6 hours, soon became deep red and finally deposited crystals. The alcohol was distilled off, and the residue recrystallised from methyl alcohol, the required *compound* (2·5 g.) being obtained in deep orange prisms, m. p. 237° (Found : C, 51·5; H, 5·2. $C_{16}H_{19}N_2I$ requires C, 52·5; H, 5·2%). It gave a reddish-yellow solution in alcohol and imparted a vivid lemon-yellow shade to acetate silk.

2-m-*Diethylaminostyrylpyridine methiodide*, similarly prepared from *m*-diethylaminobenzaldehyde, formed orange-red prisms, m. p. 208°, from methyl alcohol (Found : C, 53·8; H, 5·8. $C_{18}H_{23}N_2I$ requires C, 54·8; H, 5·8%). It gave an orange-coloured solution in alcohol and imparted a rich orange-yellow shade to acetate silk.

2-m-*Dipropylaminostyrylpyridine methiodide* was obtained by refluxing a solution of *m*-dipropylaminobenzaldehyde (2 g.), α-picoline methiodide (2·4 g.), and piperidine (0·3 c.c.) for 8 hours on the water-bath. Recrystallised from methyl alcohol, it gave large, deep red, transparent prisms (1·3 g.), m. p. 192° (Found : C, 56·4; H, 6·2. $C_{20}H_{27}N_2I$ requires C, 56·9; H, 6·4%). It produced orange shades on acetate silk.

2-m-*Dimethylaminostyrylquinoline methiodide.* A solution of *m*-dimethylaminobenzaldehyde (2·7 g.), quinaldine methiodide (5·3 g.), and piperidine (0·5 c.c.) in alcohol (50 c.c.) was refluxed on the water-bath; a deep purple colour developed immediately and after 5 hours a black crystalline solid was deposited. This was recrystallised from methyl alcohol, and the *dye* obtained (2 g.) in clusters of minute purple or black prisms, m. p. 261° (Found : C, 57·25; H, 4·8; $C_{20}H_{21}N_2I$ requires C, 57·7; H, 5·0%). It dyed silk a pale mauve-pink shade.

2-m-*Dimethylaminostyrylthiazole methiodide.* A mixture of *m*-dimethylaminobenzaldehyde (2·5 g.), 2-methylthiazole methiodide (4 g.; 1·1 mols.), and piperidine (0·6 c.c.) in alcohol (60 c.c.) was refluxed for 4 hours, a portion of the alcohol distilled off, and the mixture cooled. The crystals deposited were recrystallised from methyl alcohol and obtained (1·1 g.) as small, bright red prisms, m. p. 218° (Found : C, 44·1; H, 4·4 $C_{14}H_{17}N_2IS$ requires C, 45·1; H, 4·6%). The *compound* gave golden-yellow shades on acetate silk.

2-m-*Dimethylaminostyrylbenzthiazole methiodide* was prepared in 21% yield by the method described for the previous compound and recrystallised from boiling water and then from methyl alcohol, from which long purple-brown prisms were deposited, m. p. 205° (Found : C, 50·2; H, 4·9. $C_{18}H_{19}N_2IS$ requires C, 51·1; H, 4·5%). It gave beige shades on acetate silk.

2-m-*Diethylaminostyrylbenzthiazole methiodide.* The product obtained by heating *m*-diethylaminobenzaldehyde and 2-methylbenzthiazole methiodide in alcoholic solution for 6 hours deposited a considerable amount of dark red tarry material. The supernatant liquor was poured off and concentrated. The crystals deposited were recrystallised from methyl alcohol, and the required *compound* obtained in small brown prisms, m. p. 188° (Found : C, 53·1; H, 4·8. $C_{20}H_{23}N_2IS$ requires C, 53·3; H, 5·1%).

The authors are indebted to the Chemical Society for a grant.

UNIVERSITY COLLEGE, EXETER. [*Received, September* 15*th*, 1939.]