

33. *The Preparation of Some Condensation Products of m-Dialkylaminobenzaldehydes with Compounds containing Reactive Methylene Groups, and an Investigation of their Suitability as Photographic Sensitisers.*

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A number of condensation products of 6-substituted quinaldine methiodides with *m*-dimethyl- and *m*-diethyl-aminobenzaldehydes have been prepared. The compounds and also those previously described (J., 1940, 57) are of little value as photographic sensitisers.

THE value as photographic sensitisers of the condensation products of *p*-dimethylaminobenzaldehyde and the methiodides of heterocyclic bases possessing a 2-methyl group is well known (Mills and Smith, J., 1922, **121**, 2724; Smith, J., 1923, **123**, 2288). Some of the corresponding *m*-dialkylamino-compounds have been described by the present authors (*loc. cit.*) and the preparation of 6-methyl-, 6-bromo-, and 6-methoxy-2-*m*-dimethylamino-styrylquinoline methiodides and also 6-methoxy- and 6-dimethylamino-2-*m*-diethylamino-styrylquinoline methiodides is now recorded. These compounds and the condensation products of *m*-dimethylaminobenzaldehyde with the methiodides of α -picoline, quinaldine, 2-methylthiazole and 2-methylbenzthiazole previously described (*loc. cit.*) have been investigated spectrographically.

Spectrographic investigation was performed with a wedge spectrograph. "Ilford Ordinary" (unsensitised) plates were bathed for 5 minutes in a solution of each dye (1 part of dye in 30,000 parts of 33% alcohol). The dried plates were then exposed for various times in the spectrograph.

Only 6-methyl-2-*m*-dimethylamino- and 6-dimethylamino-2-*m*-diethylamino-styrylquinoline methiodides showed any characteristics other than those of the control plates, and these compounds only showed the slightest increase of sensitivity in the direction of the red end of the spectrum.

This absence of photosensitising action is interesting and demonstrates the necessity for a fully conjugated system between the anionoid ($-NAlk_2$) and cationoid ($-N^+$) centres of the molecule such as exists in the *p*-dialkylamino-substituted compounds. Consequently

electromeric shifts of the type $Me_2\overset{\curvearrowright}{N}-\overset{\curvearrowleft}{C}=\overset{\curvearrowright}{C}-\overset{\curvearrowleft}{C}=\overset{\curvearrowright}{N}^+$ cannot take place. Thus, even though

there are two powerful anionoid centres in 6-bromo- and 6-methoxy-2-*m*-dimethylamino- and 6-methoxy- and 6-dimethylamino-2-*m*-diethylamino-styrylquinoline methiodides with the consequent electropolar effects, the existence alone of such strong electropolar effects is insufficient to produce sensitising action, and an electron transfer system is necessary.

All attempts to prepare 6-dimethylamino-2-*m*-dimethylaminostyrylquinoline methiodide were unsuccessful and some difficulty was experienced in the preparation of the corresponding 6-methoxy-compound until the *m*-dimethylaminobenzaldehyde was twice steam-distilled in strongly alkaline conditions, followed by careful distillation in a vacuum. On the other hand, *m*-diethylaminobenzaldehyde condensed readily with 6-methoxy- and 6-dimethylamino-quinaldine methiodides, and this appears contrary to the usually accepted views on the Knoevenagel reaction. It can only be assumed that the aldehyde had developed some anti-catalyst on keeping.

EXPERIMENTAL.

2-m-Dimethylaminostyryl-6-methylquinoline Methiodide.—A mixture of 6-methylquinaldine methiodide (2 g.), *m*-dimethylaminobenzaldehyde (1 g.), alcohol (40 c.c.), and piperidine (1 c.c.) was refluxed for 6 hours and cooled. The crystalline deposit, after being washed with a little alcohol and with ether, crystallised from alcohol in small blue-black prisms (0.5 g.), *m. p.* 253° (Found : C, 58.5; H, 5.3. $C_{21}H_{23}N_2I$ requires C, 58.5; H, 5.3%). It gave an intense purple solution in alcohol and its absorption spectrum displayed a strong band with a maximum at 5670 Å. and a smaller one at 2980 Å.

6-Bromo-2-m-dimethylaminostyrylquinoline methiodide, similarly prepared from 6-bromoquinaldine methiodide (1.79 g.) (Bartow and McCollum, *J. Amer. Chem. Soc.*, 1904, **26**, 704), *m*-dimethylaminobenzaldehyde (0.7 g.), alcohol (30 c.c.), and piperidine (0.5 c.c.), crystallised from a large volume of methyl alcohol in long purple prisms (1.3 g.), *m. p.* 244.5° (Found : C, 48.7; H, 3.9. $C_{20}H_{26}N_2BrI$ requires C, 48.5; H, 4.0%). The dye gave a red solution in alcohol and its absorption curve showed two maxima at 2550 Å. and 3910 Å.

6-Methoxy-2-m-dimethylaminostyrylquinoline Methiodide.—*6-Methoxyquinaldine methiodide*. References to this compound have not been found and those to the free base are scanty. Kozlov and Gimpel'vich (*J. Gen. Chem. U.S.S.R.*, 1936, **6**, 1341) prepared an oil, apparently 6-methoxyquinaldine, *b. p.* 176—179°/33 mm., from *p*-anisidine and acetylene in presence of cuprous and mercuric chlorides, using toluene as solvent. The following method gives the quinaldine as a white crystalline solid. *p*-Anisidine (19 g.), dissolved in concentrated hydrochloric acid, was heated for 4 hours on the water-bath with paraldehyde (25 g.). The product was cooled and poured into a large excess of dilute alkali solution, the tarry deposit extracted with ether, and the extract dried over sodium sulphate and fractionated. The fraction, *b. p.* 240—280°, was dissolved in hydrochloric acid and treated at 0° with an excess of sodium nitrite. After extraction with ether, the aqueous layer was basified, heated for 2 hours on the water-bath, cooled, and again extracted with ether. This extract was dried, the solvent removed, and the dark residue fractionated in a vacuum. The required 6-methoxyquinaldine (10 g.) was a light yellow oil, *b. p.* 138—139°/5 mm., which rapidly solidified on cooling in ice; it then readily crystallised with little loss from light petroleum (*b. p.* 40—60°) in colourless, transparent tablets, *m. p.* 64—65° (Found : C, 76.2; H, 6.3. $C_{11}H_{11}ON$ requires C, 76.3; H, 6.3%). The

methiodide crystallised from alcohol, in which it was sparingly soluble, in pale yellow needles, m. p. 238° (decomp.) (Found : C, 45·7; H, 4·6. $C_{12}H_{14}ONI$ requires C, 45·7; H, 4·4%).

The methiodide (2·1 g.), suspended in alcohol (30 c.c.), was refluxed for 1 hour with *m*-dimethylaminobenzaldehyde (1 g.), piperidine being used as catalyst. After a few minutes red crystals of *6-methoxy-2-m-dimethylaminostyrylquinoline methiodide* were obtained. After cooling, these were collected, washed with alcohol and ether, and recrystallised from a large bulk of methyl alcohol, forming long, red, felted prisms, m. p. 235° (decomp.) (Found : C, 56·8; H, 4·9. $C_{21}H_{23}ON_2I$ requires C, 56·5; H, 5·2%). The dye gave an orange solution in alcohol, and an absorption curve with a maximum at 3925 Å. and lower maxima at 3150 Å. and 2825 Å.

6-Methoxy-2-m-diethylaminostyrylquinoline methiodide crystallised from a large volume of methyl alcohol in dark red needles or long prisms with a violet reflex, m. p. 240° (decomp.) (Found : C, 58·3; H, 6·0. $C_{23}H_{27}ON_2I$ requires C, 58·2; H, 5·7%).

6-Dimethylamino-2-m-diethylaminostyrylquinoline Methiodide.—*6*-Dimethylaminoquinaldine methiodide (A) was prepared by Barbier's method (*Bull. Soc. chim.*, 1920, **27**, 427), who separated it from its isomer, quinaldinetetramethylammonium iodide (B), by fractional crystallisation from alcohol. He described (A) as red-orange crystals, m. p. 230°, and (B) as pale orange leaflets, m. p. 190°. We found that (A) crystallised from alcohol in deep orange needles, m. p. 268—269°, and (B) from the same solvent in colourless plates, m. p. 199—200°. However, when the latter compound was heated at 200—205° for 10 minutes, it isomerised to compound (A) and then gave m. p. and mixed m. p. 268—269°. The best method of separation was by crystallisation from hot water, in which (B) was readily soluble and (A) only sparingly soluble [Found : (A) C, 47·6; H, 5·2; I, 38·1; (B) C, 47·7; H, 5·1. Calc. for $C_{13}H_{17}N_2I$: C, 47·6; H, 5·2; I, 38·6%].

All attempts to condense (A) or (B) with *m*-dimethylaminobenzaldehyde were unsuccessful. (B) was recovered quantitatively unchanged as expected, and (A) gave a deep green solution from which a dark micro-crystalline powder was obtained. Recrystallisation from alcohol effected no apparent purification and analysis indicated the substance to be largely (A). By treatment with charcoal in hot alcohol (A) was recovered in almost pure condition.

6-Dimethylamino-2-m-diethylaminostyrylquinoline methiodide crystallised from dilute alcohol in long, deep red prisms or needles with a bronze lustre, m. p. 220—221° (Found : C, 59·3; H, 6·5. $C_{24}H_{30}N_3I$ requires C, 59·1; H, 6·2%).

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