Journal of Chromatography, 77 (1973) 455–457
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CHROM. 6554

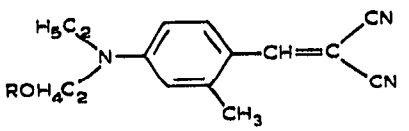
Note

Problems arising during the chromatographic purification of some monoazo and styryl disperse dyes

We have reported previously[1] some problems encountered during the purification of some monoazo disperse dyes by column chromatography. During investigations subsequent to this, additional difficulties in both selection of appropriate chromatographic techniques and of isolation of dyestuffs from chromatographic media were observed and these are reported below.

Styryl dyestuffs

The susceptibility to hydrolysis on alumina columns of N-β-acyloxyaminoazobenzenes and related dyes has been described[1]. More complete dyestuff degradation was found to occur in attempts to purify a series of styryl disperse dyestuffs, typified by 2-methyl-4-(N-ethyl-N-β-hydroxyethyl)amino-β,β-dicyanostyrene (I, R = H) (Ia). Dissolution of this dyestuff, application to an alumina column (Laporte, Type H,



I

100–200 mesh) and development with a benzene–acetone (4:1) solvent mixture gave, in the initial stages, a rapidly eluting yellow band (impurity) and retention of the more strongly adsorbed yellow dye Ia. During further elution of this, a darkening of colour occurred and after 1.5–2 h, the yellow zone had become deep reddish orange and remained stationary on further elution. Extraction of the zone with acetone gave a dark brown resinous material, the mass spectrum of which showed no recognisable P^+ and indicated the presence of compounds up to mol. wt. 471; no mass peak corresponding to Ia (mol. wt 245) was present.

β,β-Dicyanostyrenes are known to be sensitive to degradation under alkaline conditions, *e.g.*, as may occur in their application to textile substrates. Acidification of the alumina used in the chromatographic purification was found to prevent effectively decomposition of the dyestuffs. Use of excess acid did, however, greatly reduce the band resolution, resulting in inefficient purification of the crude dyestuff. Optimum conditions were found using a slurry of activated alumina (500 g), benzene (500 c.c.) and glacial acetic (10 c.c.) to prepare the column. Using this medium, no degradation of dyestuff occurred during development of the column and band resolution was satisfactory, the required dyestuff Ia separating completely from impurities of both lower and higher R_F values.

Alternative chromatographic purification without dyestuff degradation was

also effected by preparative layer chromatography using silica gel (Kieselgel 60 $PF_{254+366}$, Merck) and development with benzene. Ia and a range of analogous dyestuffs were satisfactorily purified by this method.

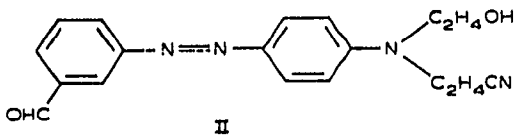
Whilst Ia reacted with various acylating agents giving reaction products which were essentially homogeneous, the crude reaction of Ia with methanesulphonyl chloride showed two principal yellow zones on chromatographic purification on alumina. A higher R_F zone yielded[2] 2-methyl-4-(N-ethyl-N-β-chloroethyl)amino-β,β-dicyanostyrene, m.p. 132–133°, and the lower, apparently homogeneous zone, on extraction from either alumina or silica gel with ethanol, gave a residue showing two yellow components on TLC examination (Eastman Chromagram sheets, Silica Gel, Type 6060; benzene–acetone 95:5) at R_F values 0.36 and 0.62. Isolation of the lower R_F zone by elution from an alumina column gave a yellow oil, showing one spot at R_F 0.36; after crystallisation from ethanol, TLC indicated two spots at R_F 0.36 and 0.62. This product, redissolved in ethanol and refluxed, showed a gradual increase in the intensity of the spot at R_F 0.62, a decrease in intensity of the spot at R_F 0.36 and the appearance of a further yellow product at R_F 0.17. These were identified[2] by mass spectrometry and elemental analysis as:

R_F 0.17 Ia R = H
R_F 0.36 Ib R = SO_2CH_3
R_F 0.62 Ic R = C_2H_5

These results indicate that the methyl sulphonyl ester, Ib, is converted, in boiling ethanol, by hydrolysis to Ia, and by ester–ester exchange, to Ic. Similar chromatographic separation of the crude dyestuff and extraction of the lower R_F zone with a non-ethanolic solvent, *e.g.*, acetone or benzene–acetone mixtures, afforded only Ib. Careful selection of solvents from which pure dyes containing $-(CH_2)_nOSO_2Alk$ groups are extracted from chromatographic media is therefore necessary.

Aminoazobenzene dyestuffs

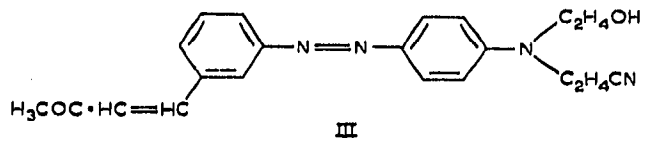
Similar solvent effects were also observed during the purification of the dyestuff II. Thus, the crude dyestuff obtained by diazotisation of 3-aminobenzaldehyde



II

and coupling to N-β-hydroxyethyl-N-β-cyanoethylaniline, was partially purified on an activated alumina column using benzene–acetone (90:10) as eluent; the principal orange zone, after extraction with ethanol, was separated from trace impurities by preparative layer chromatography on 2-mm-thick silica gel plates (Kieselgel 60 $PF_{254+366}$, Merck) using benzene–acetone (95:5) as eluent. The principal orange-brown zone gave, on extraction with methanol, yellow needles, m.p. 104°, showing, on a mass spectrum, P^+ at *m/e* 362 and not at *m/e* 322 as expected for II. The mass spectrum showed characteristic fragmentations[3] for dyes containing the coupling

component residue of II, indicating structural modifications to have occurred in the diazo residue of II during the chromatographic purification. High resolution mass measurement gave a molecular structure $C_{21}H_{22}N_4O_2$, compatible with III.



III

Chromatographic purification, but eliminating acetone from the solvent used during elution, gave a yellow product, m.p. 93–94°, corresponding to the required product II. The corresponding crude dye from 4-aminobenzaldehyde gave similar results, *viz.*, from chromatographic separations using solvents containing acetone, the "acetone adduct", m.p. 187°, and from non-acetone-containing solvents, the aldehyde-substituted dye of type II, m.p. 143–144°.

Conclusions

Choice of chromatographic media for the purification of styryl disperse dyes is shown to lead to dyestuff degradation under conditions which are acceptable with disperse dyes of other chromophoric systems; optimum pH conditions for satisfactory purification of these dyestuffs are reported.

Careful selection of solvents may be necessary for both elution during a chromatographic separation, and in the extraction of dyestuffs from chromatographic media after separation has been effected. The results reported give examples of modification of dyestuff structure both during the chromatographic purification process (as in the aminoazobenzenes containing aldehyde groups) and during the isolation of homogeneous zones after completion of chromatography (as in Ic).

The authors thank the Science Research Council (M.W.) and Yorkshire Chemicals Ltd. (H.P.M.) for the award of research studentships.

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Received December 29th, 1972