

CHROM. 4635

### Thin-layer chromatographic studies of some dianilino quinones

Triphenodioxazines which are the oxidised form of the dioxazine have excellent properties, especially high fastness against photochemical degradation. This makes them useful for dyeing cotton, plastics, lacquers and rubber in various shades<sup>1-4</sup>. The need for a simpler synthesis for these dyestuffs, giving a good yield and minimal formation of troublesome byproducts, has led to the synthesis of some new dianilino quinones.

Although a number of references<sup>5-8</sup> deal with the thin-layer chromatographic separation and identification of quinones, there is no report in the literature with regard to the TLC of dianilino quinones. In the present investigation we successfully applied this technique to the separation and identification of these compounds in submicrogram quantities on thin layers of silica gel using nonaqueous developing solvent systems.

#### Experimental

*Apparatus and reagents.* Standard TLC equipment (plates (20 × 20 cm), atomizers, fixed thickness applicator, and developing tanks) was obtained from Adair Dutt and Co., New Delhi. All reagents used were of reagent grade.

*Chromatographic procedure.* A slurry was obtained by adding 60 ml of distilled water to 30 g of Kieselgel G and mixing them thoroughly. This was immediately used to coat the plates with a 250–300  $\mu$  thick layer of Kieselgel G. The plates were dried for 30 min at room temperature and then heated for 30–45 min at 105–110° in an oven. The plates were then cooled and stored in a desiccator for at least 2 h before use.

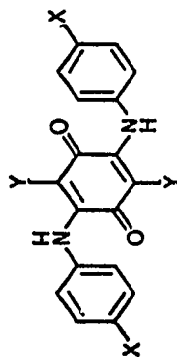
The plates were spotted with a micropipette 1 cm from one end with 1–2  $\mu$ l of a pyridine solution containing 1–5  $\mu$ g/ml test solution. After drying the spots in an oven at 120° for 30 min, the plates were placed in a chamber saturated with the solvent, and developed by the ascending method until the solvent front had travelled 10–15 cm beyond the original spots. The plates were removed from the tanks and, after marking the solvent front, allowed to air dry. The spots were visible and could be detected very easily with white light. Finally, the plates were sprayed with concentrated sulphuric acid until uniformly wet, but without making them so wet that the spray solution runs. Suitable colour development on the plate is usually achieved within 30–45 sec after completion of spraying. Ordinary  $R_F$  data for dianilino quinones were obtained using this procedure for all solvent systems. Relative  $R_F$  values were also calculated using 2,5-dianilino-3,6-dichloro-*p*-benzoquinone as a standard.

#### Results and discussion

Many solvent combinations were examined for developing the chromatograms on silica gel: the best of these were found to be:

- (A) Benzene-pyridine (9:1);
- (B) *n*-Hexane-pyridine (6:4);
- (C) Nitrobenzene-benzene (6:4);
- (D) Benzene-1-butanol-nitrobenzene (8:1:1).

TABLE I  
R<sub>F</sub> AND RELATIVE R<sub>F</sub> VALUES OF SOME DIANILINO QUINONES



System A: benzene-pyridine (9:1); system B: *n*-hexane-pyridine (6:4); system C: nitrobenzene-benzene (6:4); system D: benzene-*i*-butanol-nitrobenzene (8:1:1).

No.	Compound	M.p. (°C) <sup>a</sup>	System A		System B		System C		System D		Colour before spray	Colour after spray
			R <sub>F</sub> × 100	Rel. R <sub>F</sub>	R <sub>F</sub> × 100	Rel. R <sub>F</sub>	R <sub>F</sub> × 100	Rel. R <sub>F</sub>	R <sub>F</sub> × 100	Rel. R <sub>F</sub>		
1	X=H, Y=Cl	315 (dec)	91	1.00	85	1.00	56	1.00	58	1.00	yellow	violet
2	X=H, Y=Br	285	89	0.97	71	0.83	46	0.82	47	0.81	yellow	violet
3	X=Y=Cl	350	75	0.82	55	0.64	41	0.73	59	1.01	yellow	blue
4	X=Cl, Y=Br	320	55	0.60	53	0.62	29	0.51	39	0.67	yellow	blue
5	X=Br, Y=Cl	325	59	0.64	69	0.81	64	1.14	64	1.10	yellow	blue
6	X=Y=Br	324-327	56	0.61	50	0.58	44	0.78	41	0.70	yellow	blue
7	X=I, Y=Cl	335	84	0.92	87	1.02	77	1.37	79	1.36	brown	blue
8	X=I, Y=Br	303	78	0.85	77	0.90	60	1.07	70	1.20	brown	blue
9	X=F, Y=Cl	>360	47	0.51	75	0.88	52	0.92	58	1.00	yellow	blue
10	X=F, Y=Br	>360	43	0.47	70	0.82	50	0.89	55	0.94	yellow	blue
11	X=CH <sub>3</sub> , Y=Cl	310	65	0.60	39	0.45	38	0.67	43	0.74	yellow	blue
12	X=CH <sub>3</sub> , Y=Br	>360	48	0.52	25	0.29	23	0.41	33	0.56	yellow	blue
13	X=OCH <sub>3</sub> , Y=Cl	298	61	0.67	52	0.61	66	1.17	49	0.84	yellow	blue
14	X=OCH <sub>3</sub> , Y=Br	267	49	0.53	50	0.58	50	0.89	36	0.62	yellow	blue
15	X=OC <sub>2</sub> H <sub>5</sub> , Y=Cl	291	79	0.86	81	0.95	49	0.87	38	0.65	yellow	blue
16	X=OC <sub>2</sub> H <sub>5</sub> , Y=Br	265	75	0.82	79	0.92	30	0.53	23	0.39	yellow	blue

<sup>a</sup> dec = decomposition

It was found that benzene-acetone, benzene-methanol, acetone and various systems of pyridine with or without water did not yield good separations. This was due either to tailing of the spots or to the lowering of the  $R_F$  values obtained thus resulting in poor separation. It was found that silica gel washed with chloroform prior to development gave much better and reproducible  $R_F$  values than when used unwashed.

It is essential that the plates are allowed to cool to room temperature before development; if warm plates are dipped into the cooler solvent solution, spots of inferior quality are obtained. As can be concluded from Table I, the 3,6-dichloro derivative has a higher  $R_F$  value than the corresponding 3,6-dibromo derivative in all the solvent systems studied.

The authors wish to express their sincere thanks to Prof. R. C. MEHROTRA, Head of the Chemistry Department, for providing laboratory facilities, and to the Council of Scientific and Industrial Research, New Delhi, for a Junior Research Fellowship to one of us (S.K.J.).

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Received January 5th, 1970

*J. Chromatog.*, 48 (1970) 572-574