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Separation of isomeric thioureas, thiazoles and thiazolines by thin-layer chromatography

During investigations of the condensation of unsaturated[1] and saturated[2] ketones on monoaryl and *sym.*-diaryl thioureas[3] in the presence of bromine or iodine, it was necessary to study the separation and identification of the final products and the optimum conditions for their maximum yield. Thin-layer chromatography (TLC), which has shown wide applicability in recent years, has advantages in simplicity and unsophisticated instrumentation and in particular in its quickness and better separation compared with paper chromatography, and suggests itself as a suitable technique for this purpose. During the investigations, it was evident that it is not only possible to separate thiazoles from the corresponding thioureas, but also to separate isomeric thioureas, thiazoles and thiazolines from one another. A large number of solvent systems[4] were tried, out of which six solvent systems as in Table I gave promising results.

An equimolecular mixture of: (a) *o*- and *p*-carboxyphenylthiourea, (b) *sym.*-di-*o*-carboxyphenylthiourea and *sym.*-di-*p*-carboxyphenylthiourea, (c) 2-*o*-carboxyphenylamino-4-methylthiazole and 2-*p*-carboxyphenylamino-4-methylthiazole, and (d) 2-*m*-chlorophenylimino-3-*m*-chlorophenyl-4-methyl-Δ^4-thiazoline and 2-*p*-chlorophenylimino-3-*p*-chlorophenyl-4-methyl-Δ^4-thiazoline, were successfully separated from one another on TLC plates in each of the six solvent systems.

Experimental

The TLC applicator used is an adjustable applicator Model S II and the adsorbent used for this technique was Silica Gel G for TLC with binding material. The well cleansed glass plates were coated with the adsorbent to a thickness of 250 μ

TABLE I

R_F VALUES OF THE VARIOUS COMPOUNDS IN VARIOUS SOLVENT SYSTEMS

Solvents: A = benzene–methanol (50:50); B = benzene–absolute ethanol (50:50); C = benzene–*n*-propanol (50:50) D = benzene–isopropanol (50:50); E = benzene–*n*-butanol (50:50); F = *n*-butanol–isopropanol (50:50).

Compound	*R_F values in solvent systems*					
	A	*B*	*C*	*D*	*E*	*F*
o-Carboxyphenylthiourea	0.85	0.75	0.87	0.72	0.85	0.77
p-Carboxyphenylthiourea	0.40	0.234	0.14	0.128	0.36	0.41
sym.-Di-*o*-carboxyphenylthiourea	0.88	0.87	0.85	0.82	0.81	0.78
sym.-Di-*p*-carboxyphenylthiourea	0.39	0.36	0.34	0.32	0.39	0.38
2-*o*-Carboxyphenylamino-4-methylthiazole	0.79	0.73	0.78	0.76	0.75	0.73
2-*p*-Carboxyphenylamino-4-methylthiazole	0.48	0.46	0.42	0.48	0.51	0.55
2-*m*-Chlorophenylimino-3-*m*-chlorophenyl-4-methyl-Δ^4-thiazoline	0.62	0.58	0.61	0.56	0.60	0.59
2-*p*-Chlorophenylimino-3-*p*-chlorophenyl-4-methyl-Δ^4-thiazoline	0.94	0.91	0.95	0.85	0.92	0.88
Time of development (min)	35	45	40	42	45	40

and the developing time was 35–45 min, differing from solvent to solvent. After the development was over, in the case of the monoaryl thioureas, the spots were visualised by spraying the plates with Feigl's reagent[5] (0.05 *N* iodine in 50 % ethanol containing 1.5 % sodium azide) followed by a starch solution spray, when colourless spots on a bluish background were obtained. In the case of the *sym.*-diaryl thioureas, the visualising agent used was Tollens' reagent when grey spots against a colourless background were observed. In the case of thiazoles, 5 % Na_2CO_3 solution followed by freshly prepared diazotised sulphanilic acid solution was used as the visualising agent when orange-red coloured spots on a whitish background were obtained. In the case of the thiazolines, a 0.5 % solution of acidified $KMnO_4$ was used as the visualising agent when white spots against a pink background were obtained. In all the above cases the spots were compact, and well separated from one another.

The details of the R_F values in the various solvent systems and the times of development are given in the Table I.

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1 H. TRIPATHY, B. C. DASH AND G. N. MAHAPATRA, *Indian J. Chem.*, 8 (1970) 586.
2 B. C. DASH AND G. N. MAHAPATRA, *Indian J. Chem.*, 5 (1967) 40.
3 G. N. MAHAPATRA AND B. C. DASH, *J. Proc. Inst. Chem.*, 39 (1967) 178.
4 G. GURU, *Thesis*, Utkal University, Bhubaneswar, India, 1970.
5 B. K. PATNAIK, B. C. DASH, D. P. DAS AND G. N. MAHAPATRA, *Curr. Sci.*, 23 (1966) 595.

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