Note

Thin-layer chromatographic studies of anils
I. Separation and infrared correlation

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Large numbers of organic compounds have been studied by thin-layer chromatography (TLC) and much work has been carried out on primary aromatic amines[1–3] and carbonyl compounds[4–6]. However, no TLC studies have yet been made on anils[7], the condensation products of ketones and aldehydes with primary aromatic amines. The chromatographic separation[8] of disubstituted derivatives of benzene, particularly *meta*- and *para*-isomers, has been difficult and even paper chromatography yields few results. The successful separation of all three isomers of chloronitrobenzene[9], even in neutral medium, encouraged us to undertake this work. Our investigations of the separation of many anils (isomers) have shown that the TLC method is successful.

The relationship between the stretching frequencies of the azomethine group ($>C=N$) of isomeric anils with their R_F values in different solvents has also been studied.

EXPERIMENTAL

For coating the glass plates, silica gel (N.C.L., Poona, India) was used, having been freed from iron and chloride ions before use, and mixed with starch (E. Merck, Darmstadt, G.F.R.) as binder (19:1, w/w). An aqueous slurry was used to prepare layers of 0.10 cm thickness with a home-built apparatus[10]. The coated plates were dried at 100° for 4 h in an oven. Sample solutions were prepared in chloroform and applied with fine capillaries. The R_F values were determined on 18×3 cm glass strips, and the results were checked using 18×10 cm glass plates. The R_F values were found to be essentially independent of plate size.

The plates were developed in glass chambers with ground-in lids by the ascending technique. The time of development given in Table I is for a distance of 10–11 cm travelled by the solvent front. The developed plates were air dried and the spots were clearly discernible in daylight.

Synthesis of anils
All the anils (except *p*-dimethylaminoanil) were synthesized by condensing the

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appropriate weights of the corresponding amine and 3-phenanthrylglyoxal at room or water-bath (100°) temperature in acetic acid. In most instances, the products were precipitated by adding a small amount of water to the reaction mixture; the products were washed with 50–60% (v/v) acetic acid and finally with diethyl ether.

p-Dimethylaminoanil was prepared at room temperature in alcoholic medium and washed successively with benzene and diethyl ether. The anils were recrystallized from chloroform.

Glyoxal was obtained by oxidizing 3-acetylphenanthrene with an equimolar amount of selenium dioxide in 20% aqueous acetic acid with boiling (m.p. 104°).

RESULTS AND DISCUSSION

The R_F values of the compounds chromatographed using different solvents with silica gel as adsorbent are given in Table I.

The highest R_F values were obtained for benzene–methanol (1:1, v/v) although the resolution was poor; only a binary mixture of any anil with the anil from p-dimethylaminoaniline or p-phenylenediamine is separable. Abnormally high R_F values in a mixture, greater than that of methanol or benzene, may be attributed[11] to the interaction of the carbonyl group of the anils with methanol in the presence of benzene (inert solvent); further disruption of the association among alcohol molecules as a consequence of increased protonation or pH led to the formation of hemiacetals or ketals. A high resolving capability was shown by benzene, in which the separation of ten compounds was promising. These anils are derived from p-dimethylaminoaniline, 1-amino-2-naphthol-4-sulphonic acid, p-anisidine, o- and m-chloroanilines, m- and p-toluidines, p-phenylenediamine and α- and β-naphthylamines. In methanol eight anils are separated, and in diethyl ether, acetone and acetic acid only six are separated.

Chromatographic studies of various ternary and binary mixtures of isomers gave interesting results, each mixture giving a particular order of R_F values, although the solvent plays the dominant role.

Anils from α- and β-naphthylamines

Maximum separation was achieved with diethyl ether. For oxygen-containing solvents, the R_F values increased in the order β-, α-, while for benzene and benzene–methanol (1:1) the order of increase was reversed (α-, β-). Acetic acid behaved in a similar manner to benzene in establishing the R_F order.
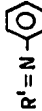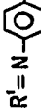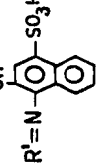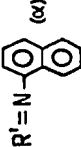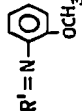
Anils from o- and p-anisidines
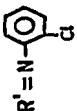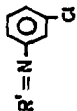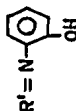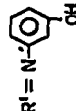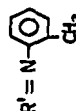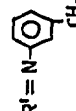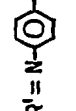
The mixture of components was resolved best in acetone. The R_F values increased in the order *ortho*-, *para*-, independent of the developing solvent.

Anils from o- and m-chloroanilines

The R_F values increased in the order *ortho*-, *meta*-, except for diethyl ether, which gave maximum separation. Some interactions between the solvent and components of the mixture are possibly responsible for the change in the order of R_F values.

TABLE I

R_F VALUES, SPOT COLOURS AND FREQUENCY OF AZOMETHINE GROUP IN THE COMPOUNDS EXAMINED

| Compound*	Azomethine group frequency (cm^{-1})	Spot colour	Solvent							
			Diethyl ether	Acetone	Methanol	Benzene	Benzene–methanol (1:1)	Acetic acid	Chloroform	Benzene–chloroform (4:1)
R'=N—⟨benzene⟩	1625	Dirty yellow	0.87	0.89	0.72	0.46	0.93	0.87	–	–
R'=N—⟨C₆H₄⟩—N(CH₃)₂	1613	Brown	0.85	0.87	0.64	0.05	0.87	0.94	–	–
R'=N—⟨C₆H₄⟩—⟨C₆H₄⟩—N=R'	1613	Yellow	0.97	0.93	0.74	0.03	0.95	0.93	–	–
R'=N—⟨C₆H₄⟩—N=R'	1613	Pink	0.96	0.48	0.55	0.00	0.88	0.84	–	–
R'=N—⟨OH / SO₃H naphthalene⟩	1626	Light brown	0.88	0.77	0.76	0.56	0.96	0.95	–	–
R'=N—⟨naphthalene (α)⟩	1587	Light brown	0.92	0.95	0.87	0.12	0.95	0.92	–	–
⟨naphthalene (β)⟩	1626	Yellow	0.72	0.92	0.69	0.17	0.97	0.94	–	–
R'=N—⟨OCH₃ / OCH₃⟩	1587	Dirty yellow	0.91	0.56	0.55	0.10	0.92	0.74	–	–
R'=N—⟨C₆H₄⟩—OCH₃	1613	Light brown	0.93	0.90	0.73	0.19	0.95	0.94	–	–

$R'=N$	IR	Color	1	1.5	1.5	2	1.5	4	3	3.5
⬡–Cl (ortho)	1587	Light yellow	0.97	0.88	0.69	0.77	0.92	0.90	—	—
⬡–Cl	1603	Brown	0.83	0.93	0.71	0.86		0.91	—	—
⬡–OH	1613	Orange	0.90	0.90	0.77	0.02	0.95	0.92	—	—
⬡–OH	1626	Brown	0.97	0.95	0.83	0.00	0.98	0.87	—	—
⬡–CH₃	1603	Light brown	0.92	0.88	0.67	0.47	0.92	0.96	0.45	0.06
⬡–CH₃	1603	Light brown	0.89	0.87	0.63	0.48	0.94	0.82	0.65	0.20
⬡–CH₃	1613	Brown	0.95	0.92	0.70	0.62	0.95	0.67	0.92	0.40
Developing time (h)			1	1.5	1.5	2	1.5	4	3	3.5

$R' =$ CO·CH (anthracene structure)
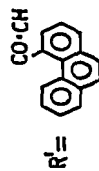
Anils from o- and m- aminophenols

Diethyl ether was the best solvent for separation. The R_F values increased in the order *ortho-*, *meta-* with oxygen-containing solvents, but acetic acid and benzene gave the opposite results. Methanol was found to be more effective than benzene and in admixture with benzene (1:1) the same order of R_F values was obtained as when methanol was used alone.

Anils from o-, m- and p-toluidines

This mixture was resolved best in chloroform. The resolving capability of chloroform mixed with various proportions of benzene was tested. Even 20% of chloroform in benzene was found to be sufficient to give good separations. However, smaller proportions of chloroform were effective only for the separation of *m-* and *p-* isomers. For oxygen-containing solvents, the R_F values increased in the order *meta-*, *ortho-*, *para-*, while for non-oxygen-containing solvents the order of increase in R_F values changed to *ortho-*, *meta-*, *para-*. The latter order occurred even if 50% of methanol was mixed with benzene, but a different order, *para-*, *meta-*, *ortho-*, occurred in acetic acid. In each instance, the order of R_F increase was independent of the degree of saturation of the chamber with developing solvent,

The effect of substitution on R_F values was studied using *para*-substituted anils, their R_F values being compared with that of the anil of aniline (non-substituted). It was observed that the presence of $-N(CH_3)_2$ and $-N=R'$ lowered the R_F values, whereas $-OCH_3$, p-C_6H_4-$N=R'$ and $-CH_3$ substituents increased the R_F values. The effects were observed for almost all of the solvents examined.

An interesting feature of the studies was the correlation between R_F and infrared results. The stretching frequencies of the azomethine group of the isomers increased in the same order as the R_F values: *ortho-* $<$ *meta*; *ortho-* $<$ *para-*; and *ortho-* $\leqslant$ *meta-* $<$ *para-*.

ACKNOWLEDGEMENTS

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