

THIN-LAYER CHROMATOGRAPHY OF 2-SUBSTITUTED FLUORENES

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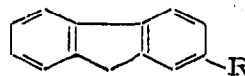
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(Received October 20th, 1964)

The separation of aromatic hydrocarbons by thin-layer chromatography on silica gel¹, alumina^{1,2} and acetylated cellulose³⁻⁵ has been reported many times. In the present investigation, the influence of 2-substituents on the migration of fluorene in thin layers was studied. Four types of adsorbents and six developing solvents have been used. In addition, the five isomeric monomethylfluorenes were compared, and as expected, it was practically impossible to distinguish between them by thin-layer chromatography.

Table I shows that acetylated cellulose is much less effective than silica gel or alumina in distinguishing between the variously substituted fluorenes. One has the impression that cellulose acetate "senses" only the aromatic ring system; indeed, it has been useful in separating various polycyclic aromatic hydrocarbons⁶. On alumina and silica, on the other hand, it is the functional groups which determine the adsorbability of the compound. The sequence of elution of the substituents obtained from our results is practically identical with that established by BROCKMANN AND VOLPERS⁷ in other cases; the nitrile group is similar to the carbomethoxy radical, and

TABLE I

 R_F VALUES OBTAINED BY TLC OF 2-SUBSTITUTED FLUORENES

R^*	Silica gel G						Alumina G	Acetylated cellulose	MN 300G/Ac.
	1*	2	3	4	5	6			
-H	0.61	0.78	0.95	0.98	0.95	0.97	0.58	0.74	0.85
-OH	—	0.02	0.14	0.15	0.12	0.32	—	0.68	0.84
-NH ₂	0.02	0.04	0.16	0.23	0.14	0.31	0.02	0.30	0.70
-OOCCH ₃	0.02	0.04	0.34	0.45	0.28	0.48	0.02	0.54	0.81
-COOCH ₃	0.03	0.09	0.48	0.60	0.39	0.65	0.03	0.60	0.85
-CN	0.04	0.10	0.61	0.74	0.53	0.73	0.04	0.56	0.78
-NO ₂	0.15	0.22	0.71	0.85	0.59	0.90	0.10	0.50	0.75
-OCH ₃	0.16	0.36	0.80	0.91	0.84	0.92	0.20	0.64	0.82
-F	0.60	0.80	0.91	0.93	0.92	0.94	0.56	0.72	0.84
-Cl	0.64	0.84	0.93	0.95	0.94	0.96	0.57	0.74	0.85
-Br	0.65	0.84	0.93	0.95	0.95	0.97	0.58	0.76	0.86
-I	0.65	0.85	0.94	0.94	0.95	0.97	0.58	0.76	0.86
-CH ₃	0.62	0.81	0.96	0.95	0.96	0.97	0.61	0.76	0.87

* The numbers refer to the solvent systems used (see p. 528).

the various halogens behave practically identically, the fluorine atom perhaps occupying a somewhat separate position.

EXPERIMENTAL

Chromatography was carried out on glass plates (20 × 20 cm) coated with a layer of 0.25 mm thickness of silica gel G, alumina G or acetylated cellulose.

Preparation of silica gel G and alumina G plates

The suspension required for five plates was prepared by vigorously shaking 30 g of silica gel G and 60 ml of water, or 50 g of alumina G and 100 ml of water, in a stoppered conical flask for 30 sec; it was then immediately transferred to a Desaga thin-layer applicator which was drawn across the plates to give a uniform layer. The plates were allowed to dry at room temperature for 30 min and then heated for 30 min at 120°. After cooling, they were kept in a vacuum desiccator.

Preparation of acetylated cellulose plates

Whatman's cellulose chromatography powder was acetylated by SPOTSWOOD'S method⁸.

The suspension required for 5 plates was prepared by shaking 35 g of acetylated cellulose and 60 ml of methanol. It was then spread on the plates with a Desaga thin-layer applicator to give a 0.5 mm layer. The plates were dried in air.

Preparation of MN300G/Ac. plates (Macherey and Nagel Co., Düren, Rhineland, Germany)

A mixture of 20 g MN300G/Ac. (acetylated cellulose containing plaster of Paris) with 100 ml of methanol and 10 ml of distilled water was vigorously shaken for 1 min. The suspension was then spread on the plates with a Desaga applicator (thickness 0.5 mm) and the plates were dried for 10 min at 60°.

Materials

Fluorene, m.p. 116° (from ethanol)*, and 2-hydroxyfluorene, m.p. 170° (from aqueous alcohol) were commercial samples. The following fluorenes were available from the collection in the Department: 1-methyl- (from methanol), m.p. 85°; 2-methyl- (from ethanol), m.p. 104°; 3-methyl- (from ethanol), m.p. 88°; 9-methyl- (from petroleum ether), m.p. 46°; 2-fluoro- (from ethanol), m.p. 100°; 2-methoxy- (from aqueous ethanol), m.p. 113°, and 2-acetoxy- (from ethanol), m.p. 132°.

The other substances were prepared by known methods: 4-methylfluorene¹² (from methanol), m.p. 70°; 2-chlorofluorene¹³ (from ethanol), m.p. 98°; 2-bromofluorene¹⁴ (from ethanol), m.p. 110°; 2-iodofluorene¹⁵ (from ethanol), m.p. 128°; 2-cyanofluorene¹⁶ (from petroleum ether), m.p. 105°; 2-aminofluorene¹⁷ (from aqueous ethanol), m.p. 127°; 2-nitrofluorene¹⁷ (from acetic acid), m.p. 158°.

For the preparation of 2-carbomethoxyfluorene (from ethanol), m.p. 120°, fluorenone-2-carboxylic acid¹⁸ was reduced by means of sodium amalgam to fluorene-2-carboxylic acid by a similar procedure to that used by BERGMANN AND IKAN¹⁹ for the 1-isomer. The acid was then esterified by Fischer's method.

* The solvents in parentheses were those used for crystallization.

Development

The samples were dissolved in chloroform for the silica gel and the alumina plates, and in methanol for the acetylated cellulose plates and then spotted on the plates with micropipettes along a line 2 cm from the edge of the plate.

The following solvent systems were used for silica gel:

- (1) *n*-Heptane
- (2) Carbon tetrachloride
- (3) Carbon tetrachloride-ethyl acetate, 19:1
- (4) Carbon tetrachloride-ethyl alcohol, 19.8:0.2
- (5) Benzene
- (6) Benzene-ethyl acetate, 19:1.

For alumina G the solvent *n*-heptane was used, a mixture of methanol-ether-water (4:4:1) was used for the acetylated cellulose plates^{3,4} and a mixture of ethanol-toluene-water (17:4:4) for MN 300G/Ac⁵.

The solvents were allowed to travel up the plate to a height of 15 cm. The plates were then taken out of the tanks, and dried in air.

Detection

The dried plates were observed under U.V. light and also sprayed with the following reagents:

- (a) 1,3,5-Trinitrobenzene (T.N.B.), 10% in acetone.
- (b) Tetracyanoethylene (T.C.E.), 10% in benzene^{9,10}.
- (c) Antimony pentachloride, 10% in chloroform.
- (d) Formaldehyde, 2 ml (37%) in 100 ml of conc. sulfuric acid¹¹.

TABLE II

DETECTION OF 2-SUBSTITUTED FLUORENES ON THIN LAYERS*

<i>2-R-Fluorene</i>	U.V.		Reagents**			
	Acetylated cellulose	Silica gel G	T.N.B.	T.C.E.	SbCl ₅	HCHO/H ₂ SO ₄
-H	W	V	Y	DV	LG	BGr
-OH	V	V	O	BGr	Br	G
-NH ₂	V	V	Br	Y	DG	LV
-OOCCH ₃	GY	LGGr	LY	P	DY	Y
-COOCH ₃	V	V	Y	Br	LP	Gr
-CN	Y	V	—	LP	DY	Y
-NO ₂	LY	Y	Y	LY	Y	LY
-OCH ₃	P	V	LO	BGr	LGGr	B
-F	Y	V	LY	P	DY	BGr
-Cl	Y	V	Y	G	DY	BGr
-Br	LG	V	Y	G	DY	BGr
-I	LG	Br	Y	G	DY	BGr
-CH ₃	Y	V	Y	V	B	BGr

* B = blue, Br = brown, D = dark, G = grey, Gr = green, L = light, O = orange, P = pink, V = violet, W = white, Y = yellow.

** On silica gel G layers.

RESULTS

The R_F values for the 2-substituted fluorenes are summarized in Table I, and the colors observed in Table II. It will be seen from Table I that the following mixtures are easily separated: (a) 2-nitro- and 2-amino-fluorene, (b) 2-hydroxy- and 2-acetoxy-fluorene, and (c) 2-hydroxy- and 2-methoxy-fluorene.

The results obtained for the monomethyl isomers are shown in Table III.

TABLE III

R_F VALUES OBTAINED BY TLC OF METHYLFLUORENES

Methyl- fluorenes (substituted position)	Silica gel G						Alumina G	Acetylated cellulose	MN 300G/Ac.
	1*	2	3	4	5	6			
1-	0.60	0.80	0.98	0.96	0.97	0.97	0.60	0.76	0.86
2-	0.62	0.81	0.96	0.95	0.96	0.97	0.61	0.76	0.87
3-	0.62	0.81	0.98	0.96	0.96	0.98	0.60	0.77	0.87
4-	0.60	0.82	0.95	0.94	0.95	0.97	0.61	0.73	0.86
9-	0.62	0.81	0.95	0.94	0.95	0.98	0.62	0.72	0.84

* The numbers refer to the solvent systems used (see p. 528).

SUMMARY

The possibility of separating 2-substituted fluorenes by thin-layer chromatography has been studied, using silica gel G, alumina G and acetylated cellulose plates. The isomeric monomethylfluorenes cannot be separated by this method.

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