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Note

Thin-layer chromatography of 1,1′-azulenylmethyleneazulenium perchlorates

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1,1′-Azulenylmethyleneazulenium perchlorates are intensely coloured, fairly stable compounds, and are readily accessible from azulenes[1–6]. In some circumstances[5,7], however, the formation of such salts is ambiguous, and a simple chromatographic method for distinguishing salts derived from different azulenes would be useful. We have found that thin-layer chromatography (TLC) on alumina allows some of these compounds to be separated.

Table I shows the behavior of the ten possible 1,1′-azulenylmethyleneazulenium perchlorates derived from four azulenes (azulene, 1-methylazulene, guaiazulene and 4,6,8-trimethylazulene). Of these, only the symmetrical salt derived from guaiazulene has a unique R_F value. The others form three groups, whose members do not separate easily. However, this method can often provide useful information, for of the six possible pairs of azulenes considered here, a mixture of the three derivable perchlorates can be resolved in four cases: for guaiazulene and 4,6,8-trimethylazulene each with azulene and 1-methylazulene.

EXPERIMENTAL AND RESULTS

The perchlorates shown in Table I were freshly prepared by described methods[4]. Test solutions were prepared in acetone and were about 10^{-4} *M* with respect to each salt.

Glass plates, 7.5 × 2.5 cm, spread with a 0.254-mm layer of aluminium oxide S (Hopkin & Williams, Chadwell Heath, Great Britain) were used, and these were activated by oven drying at 100–120° for 1 h or more before use. The distance travelled by the solvent front was best kept below 5–6 cm, otherwise the spots of lower R_F value (Groups C and D, Table I) became too faint. Development was carried out with an ambient temperature range of 6–12°, in tanks lined with filter paper. No detecting agent was necessary.

Some of the salts, particularly the ones of lower R_F value, react appreciably with the adsorbent, for the spots get smaller as development proceeds, and after standing the plates often show other streaks and diffuse spots of high R_F value. Some of the salts also showed faint accompanying spots at about 10% higher R_F value. In practice these factors do not interfere with the method, for when the plates are first developed the sharp spots of the original salts have a much more intense colour than anything else.

TABLE I

TYPICAL $R_F \times 100$ VALUES FOR 1,1'-AZULENYLMETHYLENEAZULENIUM PERCHLORATES

Thin layer, Aluminium Oxide S (Hopkin & Williams); solvent, acetone (May & Baker, Dagenham, Great Britain; R grade); solvent run, 63 mm; detecting agent, none*.

Group	*Compound* $[R_1\text{–}CH\text{–}R_2]^+ClO_4^-$		$R_F \times 100$
	R_1	R_2	
A	5-Isopropyl-3,8-dimethylazulen-1-yl (Guaiazulen-3-yl)	5-Isopropyl-3,8-dimethylazulen-1-yl (Guaiazulen-3-yl)	60
B	5-Isopropyl-3,8-dimethylazulen-1-yl	4,6,8-Trimethylazulen-1-yl	
	5-Isopropyl-3,8-dimethylazulen-1-yl	3-Methylazulen-1-yl	
	5-Isopropyl-3,8-dimethylazulen-1-yl	Azulen-1-yl	53
	4,6,8-Trimethylazulen-1-yl	4,6,8-Trimethylazulen-1-yl	
C	4,6,8-Trimethylazulen-1-yl	3-Methylazulen-1-yl	
	4,6,8-Trimethylazulen-1-yl	Azulen-1-yl	43
D	3-Methylazulen-1-yl	3-Methylazulen-1-yl	
	3-Methylazulen-1-yl	Azulen-1-yl	
	Azulen-1-yl	Azulen-1-yl	24

* The spot colours are best viewed in transmitted light and range through various shades of blue.

It does, however, show that the conditions used are not suitable for quantitative measurements.

Acidic or basic grades of alumina (Woehlm, Eschwege, G.F.R.) gave less satisfactory results. The former gave a poorer separation, while with basic alumina the salts react and fade too rapidly. Silica gel gives a slight resolution if acid solvents such as formic acid are used, but the separations were small, and the spots tended to tail badly.

Acetone was the simplest and most effective solvent. Others tested which gave similar results were cyclohexanone, acetonitrile, and, less good, pyridine.

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