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Note

Gas-liquid and thin-layer chromatography of some 3- and 3,X-substituted pyrenes

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The chemistry of pyrene and its derivatives has been extensively studied by various investigators over many years. However, mainly because of the stereoelectronic characteristics of these molecules, there still exist considerable difficulties in the synthesis, separation and identification of many of these compounds¹. In the present work, we have extended our previous work on 9- and 9,10-disubstituted anthracenes², and we now report on the use of gas-liquid chromatography (GLC) and thin-layer chromatography (TLC) for the qualitative and quantitative determination of pyrene and some of its derivatives.

EXPERIMENTAL

The pyrenes used are identified in Fig. 1. They were obtained as already described³.

After synthesis, all of these compounds were purified by column chromatography (Spence alumina, Grade H) using, according to the particular substance, one of a series of solvents, *viz.*, light petroleum (boiling range 60-80°), benzene and carbon tetrachloride, and were recrystallized from the appropriate solvent until a constant melting-point and a single gas-liquid chromatographic (GLC) peak were obtained. Elemental analysis and TLC of these compounds were also performed. When necessary, further identification was made by UV and IR spectroscopy as well as by nuclear magnetic resonance and mass spectroscopic techniques.

A Perkin-Elmer Model 801 gas-liquid chromatograph with a flame ionization detector was used, with an injector block temperature of 270° and a detector temperature of 240°. The column was maintained at 220°. The column packing and other conditions were similar to those previously reported². Thin layers were prepared as previously described². The gas chromatographic response factor was calculated for each of the compounds listed in Table I. The values obtained were similar for all

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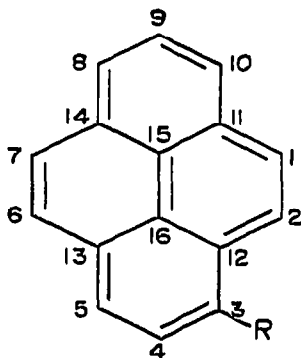


Fig. 1. Structures of pyrenes used.

- | | |
|---|---|
| (1) R = CHO- | (7) R = CH ₃ - |
| (2) R = CH ₃ -CO- | (8) R = CH ₃ -CH ₂ - |
| (3) R = CH ₃ -CH ₂ -CO- | (9) R = CH ₃ -CH ₂ -CH ₂ - |
| (4) R = C ₆ H ₅ -CO- | (10) R = C ₆ H ₅ -CH ₂ - |
| (5) R = <i>p</i> -Cl-C ₆ H ₄ -CO- | (11) R = Cl- |
| (6) R = <i>o</i> -Cl-C ₆ H ₄ -CO- | (12) R = Br- |

the compounds studied, and they did not vary to a significant extent when these compounds were in mixtures. Pyrene was used as the internal standard.

RESULTS AND DISCUSSION

Considerable difficulties in the synthesis, purification and identification of many mono-, di- and polysubstituted pyrenes¹ arise mainly from the high degree of symmetry presented by the pyrene molecule, *viz.*, positions 3, 5, 8 and 10 have the same electronic density, the same applying to carbon atoms 1, 2, 6 and 7 as well as to positions 4 and 9, and to positions 11, 12, 13 and 14 and to 15 and 16 (Fig. 1). Thus, as in studies on anthracene derivatives, UV and IR spectrophotometric techniques lack the necessary specificity for the analysis of mixtures of the compounds listed in Table I, *i.e.*, for purity assays, competitive halogenation rate studies¹, etc.

We have found that GLC is a very useful analytical technique for the qualitative and quantitative resolution of a relatively large number of 3,X- and 3,X'-disubstituted pyrenes (Table I), when they were either in pure samples or in mixtures. Thus, 3-alkyl- or 3-benzylpyrenes are easily distinguishable from their corresponding 3-acyl analogues, as well as from their monochloro- or monobromo-ring-substituted derivatives. Moreover, our results indicate that this technique can also, within certain limitations, resolve structures belonging to the same chemical series, *viz.*, 3-methyl- from 3-ethyl- or 3-propylpyrene, 3-formyl- from the other 3-acyl compounds listed, and 3-chloro- from 3-bromopyrene.

It can also be seen (Table I) that the compounds studied in the 3-alkylpyrene series have similar retention times. This result was expected, as these compounds do not have appreciable differences in molecular weights and volume, general stereo-

TABLE I
GLC RETENTION TIMES OF VARIOUS PYRENE DERIVATIVES

Compound (R in 3-R-pyrene)	Retention time (sec)	Relative retention time*	Compound (3-R-X- or -X'-R ₁ -pyrene**)		Retention time (sec)	Relative retention time*
			R	R ₁		
H	16.2	1.00	Chloro	Chloro	45.0	2.77
Chloro	28.2	1.74	Chloro	Chloro	46.4	2.81
Bromo	36.2	2.23	Bromo	Bromo	58.0	3.59
Methyl	22.3	1.38	Bromo	Bromo	61.0	3.75
Ethyl	28.4	1.75	Methyl	Chloro	42.2	2.60
Propyl	30.8	1.90	Methyl	Bromo	57.4	3.54
Benzyl	160.7	9.96	Ethyl	Chloro	48.0	2.96
Formyl	26.4	1.62	Ethyl	Bromo	63.0	3.88
Acetyl	44.2	2.73	Propyl	Chloro	51.0	3.14
Propionyl	58.6	3.62	Propyl	Bromo	67.0	4.13
Benzoyl	214.7	13.25	Benzyl	Chloro	243.0	15.00
3- <i>o</i> -Chlorobenzoyl	236.5	14.58	Benzyl	Bromo	315.0	19.44
3- <i>p</i> -Chlorobenzoyl	274.3	16.98	Benzyl	Bromo	397.0	21.46

* The relative retention time refers in every instance to pyrene as the internal standard.

** Satisfactory elemental analysis, after TLC purification, was obtained for these compounds.

TABLE II
TLC *R_F* VALUES OF SOME 3-R-PYRENES

Three developments on Silica Gel G. Solvent systems: I, cyclohexane-hexane (50:50); II, benzene-ether (90:10). Development for 2 h at room temperature. A Mineralight short-wavelength UV lamp was used to locate the samples.

Compound	<i>R_F</i> value	
	Solvent I	Solvent II
Pyrene	0.54	0.93
3-Chloropyrene	0.77	0.96
3-Bromopyrene	0.70	0.98
3-Methylpyrene	0.61	0.96
3-Ethylpyrene	0.72	0.97
3-Propylpyrene	0.64	0.82
3-Benzylpyrene	0.50	0.91
3-Formylpyrene	0.45	0.71
3-Acetylpyrene	0.34	0.76
3-Propionylpyrene	0.32	0.58
3-Benzoylpyrene	0.21	0.77
3- <i>o</i> -Chlorobenzoylpyrene	0.16	0.63
3- <i>p</i> -Chlorobenzoylpyrene	0.11	0.70

electronic properties or melting-points. Also, with some reservations, similar considerations could account for the retention times of the corresponding acyl analogues. 3-Benzyl-, 3-benzoyl- and 3-substituted-benzoylpyrenes have considerably higher retention times than those of 3-alkyl or 3-acyl compounds. It is clear that the introduction of substituents into the phenyl ring of 3-benzoylpyrene generally increases its retention time significantly, the extent of this increase being related mainly to the stereoelectronic characteristics of the new compound, *i.e.*, 3-*o*- and 3-*p*-chlorobenzoylpyrene, as well as to its new molecular weight, volume and melting-point. The above reasoning can also be used to account for the higher retention times obtained in all instances for 3-halogeno- or 3-alkyl-X- or -X'-halogenopyrenes with respect to their non-halogenated parent compounds. Table II shows the R_F values obtained for the 3-substituted pyrenes listed in Table I. It can be seen that with either of the two solvent systems used, pyrene, 3-halogenopyrenes and 3-alkylpyrenes can be easily separated from the compounds of the 3-acylpyrene series. As expected, more difficulty was found in obtaining satisfactory separations of compounds belonging to the same chemical series.

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