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Gas–liquid and thin-layer chromatographic determination of some 9- and 9,10-substituted anthracenes

In a series of previous papers[1–6], we reported on the mechanisms involved in the halogenation reaction of anthracene and anthracene derivatives with anhydrous cupric halides under heterogeneous conditions in non-polar solvents. In this communication, we discuss some aspects of the use of gas–liquid (GLC) and thin-layer chromatographic (TLC) techniques for the qualitative and quantitative determination of the compounds listed in Table I, either as pure substances or in mixtures.

TABLE I

GAS–LIQUID CHROMATOGRAPHIC RETENTION TIME AND MELTING-POINT DATA FOR VARIOUS ANTHRACENE DERIVATIVES

Compound, 9-R-anthracene	*RT (sec)*	*RRT*[a]	*m.p. (°C)*	*Compound, 9-R-10-X-anthracene*		*RT (sec)*	*RRT*[a]	*m.p. (°C)*
R				*R*	*X*			
H	22	1.00	216	H	H	22	1.00	216
Methyl	48	2.18	80	Methyl	Cl	77	3.50	180–181
Methyl	48	2.18	80	Methyl	Br	105	4.77	171–173
Ethyl	53	2.41	59	Ethyl	Cl	96	4.36	111
Propyl	53	2.41	69–70	Propyl	Cl	106	4.78	93–94
Isopropyl	53	2.41	76	Isopropyl	Cl	96	4.36	65–66
tert.-Butyl	58	2.63	103.5–105	*tert.*-Butyl	Cl	34	1.50	98–100
Allyl	43	1.95	49–51	Allyl	Cl	77	3.50	94
Cyclohexyl	158	7.18	135–136	Cyclohexyl	Cl	274	12.45	138–139
Phenyl	130	5.91	154–155	Phenyl	Cl	226	10.03	174.5–175
Phenyl	130	5.91	154–155	Phenyl	Br	264	12.00	154–155
o-Methylphenyl	144	6.55	125–126	*o*-Methylphenyl	Cl	226	10.03	96
p-Methylphenyl	168	7.64	145	*p*-Methylphenyl	Cl	293	13.32	199
p-Chlorophenyl	250	11.36	179–180	*p*-Chlorophenyl	Cl	441	20.05	208–209
p-Methoxyphenyl	240	10.98	168–170	*p*-Methoxyphenyl	Cl	413	18.77	199–201
Benzyl	194	8.82	136	Benzyl	Cl	331	15.05	128–129
Phenyl	130	5.91	154–155	Phenyl	CH_2Cl	146	6.56	171–173
Phenyl	130	5.91	154–155	Phenyl	CH_2Br	134	5.93	177
p-Methylphenyl	168	7.64	145	*p*-Methylphenyl	CH_2Br	228	10.05	163 (charr
Benzyl	194	8.82	136	Benzyl	CH_2Cl	163	7.41	—
Benzyl	194	8.82	136	Benzyl	CH_2Br	154	7.00	157–162
Ethyl	53	2.41	59	Ethyl	CH_3	58	2.63	143–144
Phenyl	130	5.91	154–155	Phenyl	CH_3	161	7.32	112–113
Benzyl	194	8.82	136	Benzyl	CH_3	230	10.45	168

[a] The RRT (relative retention time) refers in every case to anthracene as the internal standard.

Experimental

Materials and methods. 9-Alkyl- and 9-arylanthracenes were synthesized by a Grignard reaction between 9-anthrone and the appropiate alkyl- or aryl halide[2]. Cupric halide halogenation of these compounds afforded in every case the corresponding 10-halogeno derivative[2]. Halogenomethylation of the 9-alkyl- or arylanthracenes gave the corresponding 10-bromo- or 10-chloromethyl derivative. 10-Methylation of 9-alkyl- and 9-arylanthracenes was accomplished by Huang Minlon reduction of the previously formylated parent hydrocarbon[3]. After synthesis, all of these compounds were purified by column chromatography (alumina Spence, 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 GLC peak were obtained. Elemental analysis and TLC of these compounds were also performed (Table II). When necessary, further identification by UV and IR spectroscopy as well as by nuclear magnetic resonance and mass spectroscopic techniques was accomplished[7].

GLC analyses were carried out by using a Perkin-Elmer Model F-11 gas–liquid chromatograph equipped with a flame ionization detector. Samples, in carbon disulphide solution, were analyzed on a 12 ft. × 1/4 in. twin column system packed with Silicone Gum Rubber E-301 on AW-DMCS 80–100 mesh Chromosorb G, 2.5:97.5. The temperature of the injection block was 290° and the detector temperature was 310°. The column was maintained at 245°. Nitrogen was used as the carrier gas at a flow rate of approximately 60 ml/min.

Preparation of thin layers. TLC plates, 0.2 mm thick, were prepared from 1 part of Silica Gel G (E. Merck) and 2.1 parts of water suspension. The plates were heated at 110° for 1 h and allowed to cool to room temperature before use. A Mineralight short wavelength UV lamp was used to locate the samples.

The ratio of the molar concentration to area, *i.e.* the relationship between the molar concentration of a tested standard sample of each of the compounds studied and the area under its GLC peak, was calculated. The results showed that this ratio was fairly constant for both pure samples and mixtures. In each case, the retention time is also expressed relative to anthracene, which was used as the internal standard.

Results and discussion

As could be anticipated from an analysis of the chemical structure of the compounds listed in Table I, UV and IR spectrophotometric techniques, although providing an accurate and reliable method for the qualitative and quantitative determination of these compounds as pure samples, lack the necessary specificity for the analysis of mixtures of these same compounds, *i.e.*, for competitive halogenation-rate studies[2]. Moreover, IR spectrophotometry needs relatively large amounts of samples.

GLC proved itself to be very useful in resolving both qualitatively and quantitatively 9-alkyl- from 9-arylanthracenes and also from their 10-halogeno derivatives. The same can be said of 9-arylanthracenes. It can be also seen (Table I) that the compounds studied in the 9-alkylanthracene series, except for 9-*tert.*-butylanthracene, have very similar retention times. This was expected, as these compounds do not

have appreciable differences in molecular weight and volume, general stereo-electronic properties or melting points. The bulky *tert.*-butyl group of 9-*tert.*-butylanthracene is responsible for the relatively large molecular volume and high melting point of this compound, which in turn results in a larger retention time. It is worthwhile to note the smaller retention time of 9-allylanthracene and the significative increase of the 9-cyclohexyl- and 9-benzylanthracene values.

TABLE II

TLC R_F VALUES AND FLUORESCENCE OF SOME 9-R-ANTHRACENES

Three developments on Silica Gel G. Solvent systems: I, cyclohexane–hexane (90:10); II, benzene–light petroleum (boiling range 60–80°) (90:10). Development for 2 h at room temperature. A Mineralight short wavelength UV lamp was used to locate the samples.

Compound	*Solvent*	*TLC R_F value*	*Fluorescence*
9-Methylanthracene	I	0.42	Yellow
9-Propylanthracene	I	0.31	Yellow
9-Cyclohexylanthracene	I	0.55	Green
9-Phenylanthracene	I	0.24	Yellow–greenish
9-*p*-Methylphenylanthracene	I	0.38	Green
9-Benzylanthracene	I	0.20	Yellow
9-Methylanthracene	II	0.74	Orange–yellow
9-Propylanthracene	II	0.88	Yellow
9-Cyclohexylanthracene	II	0.81	Green
9-Phenylanthracene	II	0.94	Green
9-*p*-Methylphenylanthracene	II	0.96	Green–yellowish
9-Benzylanthracene	II	0.94	Green–yellowish

9-Phenyl- and 9-substituted phenylanthracenes have a considerably larger retention time than 9-alkylanthracenes. It is clear that the introduction of substituents in the phenyl ring of 9-phenylanthracene generally increases significantly its retention time, the extent of this increase being mainly related to the stereo-electronic characteristics of the new compound, *i.e.*, 9-*o*- and 9-*p*-methylphenylanthracene, as well as to its new molecular weight, volume, and melting point. The above reasoning can also be used to account for the larger retention times obtained in all cases for 9-alkyl- and 9-aryl-10-halogenoanthracenes, except for 9-*tert.*-butyl-10-chloroanthracene, with respect to their non-halogenated parent compounds. It is noteworthy that in most cases the 10-halogenated compound has a lower melting point than its parent compound.

Within the limitations arising from the reduced number of compounds analysed, it can be said that 10-halogenomethylation of 9-alkyl- or 9-arylanthracenes varies the retention time of these compounds in a rather unpredictable way. This could be explained, in part, by the fact that under the conditions used, 9-halogenomethylanthracenes decompose, giving rise to a number of peaks[4]. 10-Methylation of these compounds yielded, as expected, products with higher retention times.

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1 A. D. MOSNAIM AND D. C. NONHEBEL, *Tetrahedron*, 25 (1969) 1595.
2 A. D. MOSNAIM, D. C. NONHEBEL AND J. RUSSELL, *Tetrahedron*, 25 (1969) 3485.
3 J. GIBSON, A. D. MOSNAIM, D. C. NONHEBEL AND J. RUSSELL, *Tetrahedron*, 25 (1969) 5047.
4 A. D. MOSNAIM AND D. C. NONHEBEL, *J. Chem. Soc., C*, (1970) 942.
5 A. D. MOSNAIM, D. C. NONHEBEL AND J. RUSSELL, *Tetrahedron*, 26 (1970) 1123.
6 J. FLOOD, A. D. MOSNAIM AND D. C. NONHEBEL, *Chem. Commun.*, (1970) 12.
7 A. D. MOSNAIM, *Ph. D. Thesis*, University of Strathclyde, 1969.

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