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GAS CHROMATOGRAPHIC AND MASS SPECTROMETRIC PROPERTIES OF PHENANTHRENEMETHYL ESTERS OF ORGANIC ACIDS

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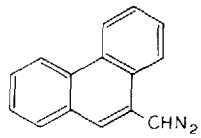
SUMMARY

The preparation of the esterifying reagent, phenanthryldiazomethane is described. The reagent has been used to prepare esters of various types of carboxylic acids. Data are presented for the gas chromatographic retention times of the esters on OV-1 and also for their mass spectral fragmentation patterns.

INTRODUCTION

Esters prepared by esterification with naphthyl and other analogues of diazomethane have been investigated extensively in our laboratory[1,2] and elsewhere[3,4] by gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS). In this paper we describe the preparation of a further reagent, 9-phenanthryldiazomethane (PHDM), and outline some of the GC and GC–MS properties of the phenanthrenemethyl (PHM) esters of carboxylic acids selected from those studied previously[1,2], as other esters, in this series.



9-phenanthryldiazomethane, PHDM
(9-diazomethylphenanthrene)

EXPERIMENTAL

Materials

Lithium aluminium hydride ($LiAlH_4$) and 9-cyanophenanthrene were purchased from Aldrich (Gillingham, U.K.), methyl behenate from Sigma (Poole, U.K.) and octacosanoic acid from Fluka (Fluorochem, Glossop, U.K.). The methyl ester of octacosanoic acid was prepared using diazomethane. Other reagents, carboxylic acids and solvents were as described previously[1].

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Synthesis of the diazo precursor N-phenanthrenemethyl-N-nitrosotoluene-4-sulphonamide

The amine starting-material for the toluene sulphonation (tosylation) sequence was prepared by reduction of 9-cyanophenanthrene with $LiAlH_4$ by modification of procedures[5,6] for the reduction of other aromatic nitriles with $LiAlH_4$. The remaining reactions were adapted from the synthesis[1] of the naphthalenemethyl derivative. GC analyses of the intermediates were performed on OV-1 (see GC and GC–MS below) at the temperatures noted in the text.

9-Phenanthrenemethylamine. A solution of 4 g 9-cyanophenanthrene in 30 ml tetrahydrofuran (THF) was added over a 4-h period to a suspension of 1.4 g $LiAlH_4$ in 120 ml THF under gentle reflux. The mixture was refluxed for a further 12 h. Progress of the reduction and extraction procedure was minitored by GC. Aliquots (20 μl) were diluted 1:4 in THF and chromatographed at 240°C (injector 280°C) when t_R 9-cyanophenanthrene = 2.6 min, and 9-phenanthrenemethylamine = 3.3 min. On completion of the reduction, excess reducing agent was destroyed by the careful addition of THF–water (3:1). After cooling, the mixture was acidified (< pH 2) with conc. hydrochloric acid. Diethyl ether, 100 ml, was added and the mixture extracted with 50 ml of water. The organic phase was further extracted with 2 × 50 ml 5 *N* hydrochloric acid, and the pooled aqueous extracts were rendered alkaline (pH 10) by careful addition of saturated sodium hydroxide solution. After cooling, the solution was extracted with 3 × 50 ml diethyl ether–THF (5:1) and the pooled organic extracts were dried over potassium hydroxide. Due to the possible instability[1] in air of the amine, the solution of amine was evaporated under reduced pressure to yield a light yellow oil which was immediately redissolved in dimethylformamide (30 ml) under nitrogen. The amine was quantified by GC (240°C) by comparison with a standard solution of the nitrile, characterised by GC MS and the tosylation reaction performed without further isolation of the amine. Yield 2.8 g, mass spectrum (GC at 250°C) M^+ at 207 (93% base), and *m/z* 206 (100%), 190 (36%), 188 (13%), 178 (26%), 177 (42%) and 175 (22%).

N-9-Phenanthrenemethyltoluene-4-sulphonamide. 9-Phenanthrenemethylamine, 2 g in 20 ml dimethylformamide (DMF), was tosylated[1] with 2.2 g toluenesulphonyl chloride at 70°C and the mixture left a further 2 h at 70°C. For chromatography, 5-μl aliquots were diluted 1:3 in DMF and analysed by GC through a temperature programme 3 min at 280°C, 45°C/min to 350°C, when t_R 9-phenanthrenemethylamine = 1.4 min, N-9-phenanthrenemethyltoluene 4-sulphonamide = 6.6 min (isothermal at 340°C, t_R tosyl derivative = 2.5 min). On completion of the reaction, the cooled mixture was added to 100 ml of water and extracted with 2 × 30 ml portions of diethyl ether THF (5:1). The organic extracts were dried (sodium sulphate) and crystals of crude material obtained by precipitation with light petroleum (b.p. 40–60°C). After recrystallisation from boiling ethanol–propanol (1:1) the tosyl derivative (2.9 g) had m.p. 153–154°C and mass spectrum (direct probe, 160°C) M^+ at 361 (17%) and *m/z* 267 (1.2%), 228 (3.2%), 205 (76%), 204 (100%), 191 (21%), 178 (35%), 176 (21%), 151 (10%) and 91 (58%).

N-(9-Phenanthrenemethyl)-N-nitrosotoluene-4-sulphonamide. The nitrosation was conducted as described previously[1], commencing with 2 g N-(9-phenanthrenemethyl)-toluene-4-sulphonamide in 15 ml glacial acetic acid and 50 ml acetic anhydride, with a total of 2.5 g solid sodium nitrite added. Progress of the reaction and

purity of the product were assessed by thin-layer chromatography on silica gel (F-1500) with solvent *n*-hexane–dichloromethane–methanol (30:19:1) when R_F product = 0.60, R_F tosyl intermediate = 0.27. After isolation[1] the product was recrystallised from boiling ether–THF (3:1) to yield 1.6 g cream crystals of N-(9-phenanthrenemethyl)-N-nitrosotoluene-4-sulphonamide, m.p. 133–134°C (decomp.) and mass spectrum (direct probe 200°C) M^+ at 390 (8.8%) and *m/z* 356 (5.8%), 218 (6.5%), 206 (9.6%), 205 (21%), 204 (41%), 192 (75%), 191 (100%), 178 (11%), 165 (10%), 155 (8.7%) and 91 (29%). The product was stored at 5°C in a dark bottle.

Generation of phenanthryldiazomethane and preparation of esters

The procedures described previously[1] were followed with minor modifications, using the equivalent phenanthrenemethyl compounds. Generation of PHDM was carried out in the solvent mixture methanol–water (5:1) and the mixture was reheated to gentle boiling for 1 min after completion of addition of the nitroso precursor. The final brick-red solution of PHDM was stored at +5°C. Acids were dissolved in 20–30 μl THF–methanol (1:1) prior to esterification and the esterification reactions were left for up to 24 h at room temperature before dilution and analysis.

GC and combined GC–MS

All GC separations were carried out on a packing of 3% OV-1 on Diatomite CQ, 100–120 mesh. Table I gives conditions for retention data chromatography; the reference compounds were co-injected with the samples. Synthesis intermediates were chromatographed on a 2.1 m × 4 mm I.D. glass column, nitrogen flow-rate 40 ml/min, and GC–MS on 2.1 m × 4 mm I.D. glass column, helium flow-rate 40 ml/min. For GC–MS the esters were chromatographed through a temperature programme, which for group 1 esters was 260°C for 3 min, 25°C/min to 360°C for 6 min, and for group 2 esters was 290°C for 2 min, 20°C/min to 360° for 6 min, injector (both programmes) 300°C. Other mass spectrometric parameters were as described previously[1]. Direct-probe spectra were taken at 70 eV, temperatures as noted in Table II.

RESULTS AND DISCUSSION

Relative retention data for the GC of PHM esters are listed in Table I. Esters were arranged into two temperature groups and allocated a "parent acid number" for reference in the mass spectral data.

Many of the esters of high-molecular-weight acids showed extensive decomposition during gas chromatography and it was difficult to obtain GC peaks which were clearly attributable to intact esters. GC–MS analysis of these samples showed that these esters were accompanied by, or the sample to consist solely of, slowly eluting broad GC peaks. The only components detected during the GC–MS analysis of PHM anthracene 9-carboxylic and PHM indole 2-carboxylic had the highest mass ions at [M^+ ester −44 a.m.u.], with the mass spectra showing molecular ions and fragmentations which were more characteristic of aromatic hydrocarbons. The appearance of molecules with [M^+ ester −44] as apparent molecular ions led to the conclusions that thermal rearrangement, accompanied by decarboxylation, was occurring during chromatography. Hence GC retention times could not be measured for all the esters prepared.

TABLE I

RETENTION DATA FOR PHENANTHRENEMETHYL ESTERS OF CARBOXYLIC ACIDS

Column: 2.1 m × 2 mm I.D. glass, 3% OV-1 on Diatomite CQ, 100–120 mesh. Temperatures as indicated.

Group	*Parent acid number*	*Parent acid*	*Relative retention*
Group 1	1	Acetic	0.57
Column 245°C	2	Propionic	0.70
Injector 270°C	3	Pivalic	0.75
Reference:	4	Vinylacetic	0.85
Methyl behenate	5	Glycolic	1.00
Retention time 4.4 min	6	Crotonic	1.15
	7	Monochloroacetic	1.30
	8	Monobromoacetic	1.35
	9	4-Hydroxybutyric	1.38
	10	Cyclopentylcarboxylic	2.70
Group 2	11	Furan 2-carboxylic	0.55
Column 280°C	12	Octanoic	0.61
Injector 300°C	13	Phenylacetic	0.78
Reference:	14	Cyclohexaneacetic	0.78
methyl octacosanoate	15	Benzoic	0.80
Retention time 4.5 min	16	Nicotinic	0.88
	17	2,6-Dimethylbenzoic	0.89
	18	3-Methoxybenzoic	1.24
	19	Cinnamic	1.58
	20	3,4,5-Trimethoxybenzoic	2.62
	21	Naphthalene 2-carboxylic	3.74
	22	Mandelic	4.95

In order to complete the MS data for these esters, their mass spectra therefore were obtained by direct probe with careful control of the probe temperature. Parent acid numbers for these esters are listed in Table II.

The above decomposition probably occurs to a lesser extent in Group 2 esters, where clean elution of samples on GC and GC–MS was achieved only when the injection temperature was maintained just above that of the column (Table I). As might be expected for the bulky PHM group, differences in retention between indi-

TABLE II

PHENANTHRENEMETHYL ESTERS FOR WHICH MASS SPECTRA WERE OBTAINED BY DIRECT PROBE

	Parent acid number	*Parent acid*	*Probe temperature (°C)*
Group 3	23	Quinaldic	165
	24	Indole-2-carboxylic	170
	25	Naphthalene-2-acetic	150
	26	Anthracene-9-carboxylic	180
	27	Phenylcinnamic	165

vidual PHM esters was less than that observed[1,7,8] for previous derivatives.

Principal ions and other structurally relevant ions are listed in Table III, with identification and possible formal structures given in Table IV; all ion intensities have been corrected for background. To maintain comparison with previous tabulations[1], equivalent ion structures from the previous derivatives are denoted by the same letter in this paper. Ion c, RCOOH (Table V, ref. 1) was observed in only four PHM esters and therefore is omitted from Table III as a separate entry.

Most fragments from the PHM group appeared as ion clusters due to hydrogen rearrangements, thus predictable fragmentations gave rise to the major ions of the PHM moiety appearing as groups centred at *m/z* 165 (ion d), *m/z* 179 (ion e), *m/z* 191 (ion f, normally base peak) and *m/z* 208 (ion g). These ions are commonly observed[9] in other phenanthrene derivatives. Some esters gave no major ions other than M^+ and ion groups a to g, hence their abbreviated listings in Table III. Migration of hydrogen occurred predominantly to ions e and g, whereas a loss of two hydrogens was normally observed for ions f and d, giving a second ion at *m/z* 163 and *m/z* 189 respectively. In a few esters, a contribution to *m/z* 192 (f+H) was observed (Table III) above that due to the isotope contribution of 16.5% at *m/z* 192 from *m/z* 191.

Fragments from the acid group, ions a and b, were also of high abundance and in many esters were of higher intensity than PHM fragment ions. Thus, ions a or b were the base peak in the esters 6 PHM, 10 PHM, 15 PHM, 16 PHM, 18 PHM, 19 PHM and 23 PHM. The "free acid" ions, RCOOH, were observed in only four esters, 18 PHM (*m/z* 152, 4.4%), 19 PHM (*m/z* 147, 1.8%), 20 PHM (*m/z* 212, 11%) and 27 PHM (*m/z* 224, 2.9%). Phenylcinnamate, 27 PHM, was the only ester to show further rearrangement ions in its spectrum, mirroring similar behaviour in its other esters[1,2]. The overall fragmentation patterns of PHM esters thus resemble other arylmethyl esters[1,2] but with enhanced relative intensities of M^+ and ions a and b.

The possibility of benzyl-benzoate type rearrangements[10] occurring in the PHM esters used in this study was considered unlikely (for discussion of possible criteria see refs. 1 and 2). However, small peaks due to the loss of 45 or 46 a.m.u. were observed for 6 PHM (*m/z* 231, 2.0%), 11 PHM (*m/z* 258, 1.0%), 16 PHM (*m/z* 268, 0.68%), 19 PHM (*m/z* 292, 2.0% and *m/z* 293, 2.8%), 21 PHM (*m/z* 317, 1.5% and *m/z* 318, 1.9%), 23 PHM (*m/z* 318, 0.67%) and 27 PHM (*m/z* 368, 1.9% and *m/z* 369, 1.4%), which may, however, represent a very weak tendency towards such a rearrangement (under the conditions used for recording these spectra it was assumed that these ions were not due to thermal decomposition). These acids belong to the group which showed similar fragmentation behaviour to their benzyl[2] and naphthalenemethyl[1] esters.

Ion structures suggested in Table IV are based on general considerations of other arylmethyl esters[1–4] and other phenanthrene derivatives[9,11]. There is considerable debate about the exact structures of ions formed from aromatic systems, and consequently various equivalent structures have been suggested and discussed for ions from phenanthrene derivatives[11,12]. Thus, ion f, *m/z* 191, may be methanophenanthrene, diphenyltropylium or part open-chain. Steric considerations lead to the suggestion that unless considerable rearrangement takes place, *m/z* 189 from 9-positional PHM esters is unlikely to have the same structure as that suggested[11] for *m/z* 189 in the spectrum of 2-methyl phenanthrene. The relative intensities of *m/z* 191 and *m/z* 189 in PHM esters also indicate less tendency towards the formation of

TABLE III

MASSES AND RELATIVE INTENSITIES OF IONS IN THE MASS SPECTRA OF PHENANTHRENE-METHYL ESTERS OF CARBOXYLIC ACIDS

Ester	M^+		*Ion a*		*Ion b*		*Ion d*		*Ion e*		*Ion f*	
	m/z	*I*	*m/z*	*I*	*m/z*	*I*	*m/z*	*I*	*m/z*	*I*	*m/z*	*I*
1 PHM	250	100	–	–	43	21	165	15	179	43	191	95
2 PHM	264	48	29	19	57	25	165	16	179	30	191	100
3 PHM	292	24	57	44	85	4.3	165	8.9	179	5.5	191	100
4 PHM	276	28	41	14	69	8.5	165	14	179	10	191	100
5 PHM	266	15	31	38	–	–	165	16	179	11	191	100
6 PHM	276	27	41	64	69	100	165	13	179	20	191	67
7 PHM	284	26	49	9.0	77	2.2	165	15	179	15	191	100
8 PHM	329	16	–	–	–	–	165	17	179	25	191	100
9 PHM	294	22	–	–	–	–	165	20	179	28	191	100
10 PHM	304	19	69	100	97	22	165	12	179	8.2	191	98
11 PHM	302	26	–	–	95	59	165	12	179	10	191	100
12 PHM	334	20	–	–	127	2.3	165	8.7	179	12	191	100
13 PHM	326	36	91	47	–	–	165	26	178	9.7	191	100
14 PHM	332	15	97	17	125	4.5	165	11	179	9.4	191	100
15 PHM	312	16	77	16	105	100	165	5.8	179	4.1	191	33
16 PHM	313	44	78	24	106	100	165	19	179	22	191	92
17 PHM	340	10	105	13	133	48	165	7.6	178	2.6	191	100
18 PHM	342	15	107	10	135	100	165	16	179	11	191	86
19 PHM	338	17	103	22	131	100	165	14	178	10	191	76
20 PHM	402	16	–	–	195	47	165	24	179	11	191	100
21 PHM	362	11	127	17	155	43	165	15	178	15	191	100
22 PHM	342	11	107	47	–	–	165	14	178	8.9	191	100
23 PHM	363	3.8	128	100	157	17	165	13	178	21	191	35
24 PHM	351	10	116	6.9	145	6.3	165	13	178	8.3	191	100
25 PHM	376	10	141	26	–	–	165	14	178	16	191	100
26 PHM	412	14	–	–*	–	–	165	26	177	46	191	100
27 PHM	414	12	–	–*	–	–*	165	17	178	44	191	100

* Ions common to acid and ester groups.

m/z 189 in 9-positional derivatives of phenanthrene compared to other positional derivatives[11]. The absolute and relative intensities of *m/z* 207 and *m/z* 208 also resemble previous[1,2] esters in that esters of non-aromatic acids generally show migration of hydrogen to form *m/z* 208 as a major ion, whereas in aromatic acid esters this hydrogen migration is suppressed and both ions have much reduced intensities.

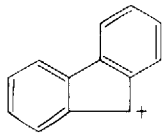
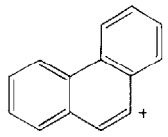
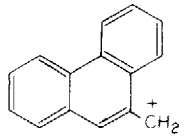
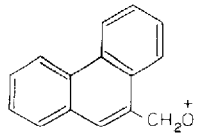
The potential usefulness of higher aryl esters in GC and GC–MS has been

Ion g		*Other ions*											
m/z	*I*	*m/z*	*I*	*m/z*	*I*	*m/z*	*I*	*m/z*	*I*	*m/z*	*I*	*m/z*	*I*
208	89	176	13	178	20	189	59	190	38	207	8.1	–	–
208	76	176	9.5	178	15	189	48	190	31	207	14	–	–
208	12	176	4.0	178	4.8	189	17	190	7.9	207	1.3	–	–
208	23	176	6.5	178	8.3	189	26	190	14	207	2.0	–	–
208	7.1	178	9.5	189	24	190	12	192	24	207	3.1	–	–
209	22	178	12	189	38	190	22	207	4.9	231	2.0	–	–
208	14	82	22	176	9.0	178	11	189	29	190	21	207	4.1
207	24	178	17	189	37	190	17	192	24	208	21	249	3.7
208	44	45	38	189	36	192	26	207	11	250	3.3	276	1.5
208	43	41	57	176	5.0	178	7.5	189	24	190	13	207	2.7
207	5.0	178	6.4	189	27	190	17	208	1.0	229	0.91	258	1.0
208	42	57	11	178	6.5	189	22	190	16	207	4.4	–	–
208	23	176	8.4	179	9.1	189	39	190	22	192	45	207	3.5
208	45	55	42	178	6.5	189	21	190	13	192	26	207	2.7
207	2.6	176	2.3	178	4.0	189	19	190	12	208	0.68	–	–
207	5.1	176	7.8	178	13	189	46	190	19	192	25	208	2.7
207	0.76	103	3.0	176	2.4	189	12	190	7.1	208	0.29	–	–
206	3.1	92	19	177	8.2	189	30	190	15	192	21	208	1.8
206	4.5	147	1.8	179	7.7	189	28	190	14	208	2.2	292	3.0
206	4.9	109	11	152	8.0	177	11	189	33	207	2.9	212	11
208	6.3	128	11	189	22	190	12	192	39	317	1.5	318	1.9
208	4.4	77	22	79	18	105	22	189	20	190	11	192	54
206	4.8	127	18	176	12	189	17	192	13	202	8.3	318	0.67
206	1.7	64	10	90	32	117	5.8	144	5.2	176	6.0	189	14
208	4.6	115	12	176	9.4	179	15	189	19	192	29	207	2.9
205	8.4	150	9.4	151	17	176	44	178	30	189	26	367	3.4
207	5.3	176	13	179	30	189	18	192	29	224	2.9	368	1.9

discussed briefly elsewhere[1]. As this and previous work[1] has shown, there is a limitation governed by thermal stability and volatility (*ca.* 400 mol.wt.) in the GC of such derivatives. In high-performance liquid chromatography (HPLC), however, no such limitations apply, and the analogous 9-anthracenemethyl esters have recently found favour for HPLC[13] and synthetic[14] work.

TABLE IV

PRINCIPAL IONS IN THE MASS SPECTRA OF PHENANTHRENEMETHYL ESTERS OF CARBOXYLIC ACIDS

Ion	*Formal structure*	*Formula*
a	R^+	From acid moiety
b	$RCO(H)^+$	
d		$C_{13}H_9^+$ *m/z* 165 group
e		$C_{14}H_9^+$ *m/z* 177 group
f		$C_{15}H_{11}^+$ *m/z* 191 group
g		$C_{15}H_{11}O^+$ *m/z* 207 group

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