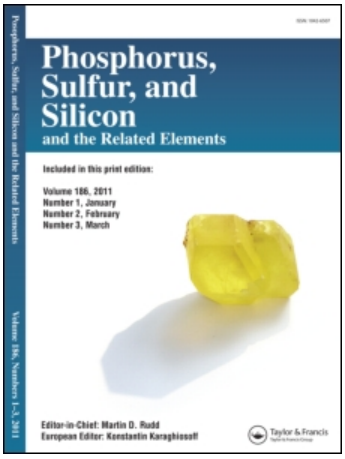

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SYNTHESIS AND SPECTRAL STUDIES OF SOME NOVEL ETHYL (SUBSTITUTED PHENYLTHIO) ACETATE AND PROPIONATE DERIVATIVES

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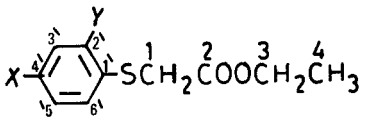
Ethyl (substituted phenylthio) acetate and propionate derivatives have been synthesised, their structures were proved by IR, NMR and mass spectra.

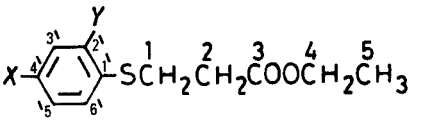
Key words: Arylthioacetates; arylthiopropionates; NMR- and mass spectra.

In continuation of our interest in substituted diaryl and aryl benzyl sulfides, sulfoxides and sulfones,[1–5] a new series of ethyl (substituted phenylthio) acetate I_{a-g} and propionate $II_{a-e,g}$ have been synthesized.

In this respect, the synthetic route is the same as cited in literature.[1–7] The sulfide esters were synthesised by the reaction of ethyl bromoacetate and ethyl β-bromopropionate with substituted thiophenoxide sodium salts. The NMR data and physical properties of the obtained products are listed in Tables I–III.



(*I*)



(*II*)

	X	Y
a	H	H
b	CH_3	H
c	OCH_3	H
d	Cl	H
e	Br	H
f	NO_2	H
g	H	COOH

Th mass spectra[1,2,4,5,8,9] of ethyl(phenylthio)acetate I_a is studied as shown in Scheme I and the relative intensities of the most prominent peaks in their fragmentation are given in Table IV.

The IR spectra[10,11] of all compounds I_{a-g} and $II_{a-e,g}$ showed a sharp band at 1735–1750 cm^{-1} (5.71–5.76 μ) (C=O) and a characteristic stretching band at 635–650 cm^{-1} (14.30–16.70 μ) due to C—S bond.

TABLE I

Yield, melting points, refractive index and ^{1}H-NMR spectra of ethyl phenylthio acetate derivatives I_{a-g}

Cpd	Yield%	colour	m. p°C / n^{20}_D	^{1}H-NMR, (δ ppm, $CDCl_3$) H_1	H_3	H_4	$H_{2',6'}$	$H_{3',5'}$
Ia	78	Colourless	1.551	3.60 (s, 2H)	4.13 (q, 2H)	1.20 (t, 3H)	7.41 (m, 2H)	7.15, H4' (m, 3H)
b[i]	89	White	31	3.52 (s, 2H)	4.17 (q, 2H)	1.20 (t, 3H)	7.37 (d, , 2H)	7.07 (d, 2H)
c[ii]	74	Colourless	1.552	3.50 (s, 2H)	4.13 (q, 2H)	1.21 (t, 3H)	7.44 (d, 2H)	7.62 (d, 2H)
d	82	Colourless	1.557	3.61 (s, 2H)	4.16 (q, 2H)	1.23 (t, 3H)	7.25 (d, 2H)	7.38 (d, 2H)
e	93	White	71	3.61 (s, 2H)	4.16 (q, 2H)	1.23 (t, 3H)	7.26 (d, 2H)	7.43 (d, 2H)
f	86	Deep yellow	34	3.79 (s, 2H)	4.22 (q, 2H)	1.27 (t, 3H)	7.42 (d, 2H)	8.16 (d, 2H)
g[iii]	94	White	131	3.90 (s, 2H)	4.12 (q, 2H)	1.17 (t, 3H)	7.21-8.04 ($H_{3',4',5',6'}$ (m, 4H))	

[i] 4'-CH_3 appears at δ 2.30 ppm (s, 3H).
[ii] 4'-OCH_3 appears at δ 3.78 ppm (s, 3H).
[iii] DMSO-d_6.

TABLE II

^{13}C-NMR chemical shifts (δ ppm, $CDCl_3$) of ethyl phenylthio acetate derivatives I_{a-g}

Cpd.	C_1	C_2	C_3	C_4	$C_{1'}$	$C_{4'}$	$C_{2'},C_{6'}$	$C_{3'},C_{5'}$
Ia	36.61	169.65	61.5	14.11	135.08	126.91	129.04	129.89
b[i]	37.40	169.83	61.45	14.16	131.28	137.28	129.84	130.95
c[ii]	38.62	169.93	61.33	14.12	129.93	159.65	134.21	114.62
d	36.76	169.41	61.63	14.08	133.45	133.07	130.40	129.13
e	36.54	169.29	61.60	14.04	133.38	120.93	131.45	132.01
f	34.58	168.62	62.14	14.10	141.81	145.54	124.04	168.62
g[iii]	33.62	167.28	60.92	13.87	139.79	124.31	$C_{2'}$, 127.79, $C_{5'}$, 132.39,	$C_{3'}$, 130.92 $C_{6'}$, 125.47

[i] 4'-CH_3 appears at δ 21.10 ppm.
[ii] 4'-OCH_3 appears at δ 55.30 ppm.
[iii] COOH appears at δ 169.25 ppm in DMSO-d_6.

TABLE III

Yield, melting points, refractive index and ^{1}H-NMR spectra of ethyl phenylthio propionate derivatives $II_{a-c,g}$

Cpd	Yield%	colour	m. p°C / n^{20}_D	^{1}H-NMR, (δ ppm, acetone-d_6) H_1	H_2	H_4	H_5	$H_{2',6'}$	$H_{3',5'}$
Ia	72	Colourless	1.552	2.58 (t, 2H)	3.15 (t, 2H)	4.05 (q, 2H)	1.15 (t, 3H)	7.24 (d, 2H)	7.16, $H_{4'}$ (m, 3H)
b[i]	74	White	58	2.52 (t, 2H)	3.10 (t, 2H)	4.02 (q, 2H)	1.18 (t, 3H)	7.18 (d, 2H)	7.03 (d, 2H)
c[ii]	70	Colourless	1.530	2.48 (t, 2H)	3.05 (t, 2H)	4.03 (q, 2H)	1.15 (t, 3H)	7.28 (d, 2H)	6.85 (d, 2H)
d	78	white	82	2.60 (t, 2H)	3.10 (t, 2H)	4.00 (q, 2H)	1.18 (t, 3H)	7.22 (d, 2H)	7.22 (d, 2H)
e	86	White	78	2.64 (t, 2H)	3.18 (t, 2H)	4.06 (q, 2H)	1.20 (t, 3H)	7.28 (d, 2H)	7.36 (d, 2H)
g	92	White	84	2.62 (t, 2H)	3.16 (t, 2H)	4.00 (q, 2H)	1.18 (t, 3H)	7.82 (d, $H_{3'}$, 1H) 7.28 (t, $H_{4'}$, 1H)	7.38 (d, $H_{6'}$, 1H) 7.18 (t, $H_{5'}$, 1H)

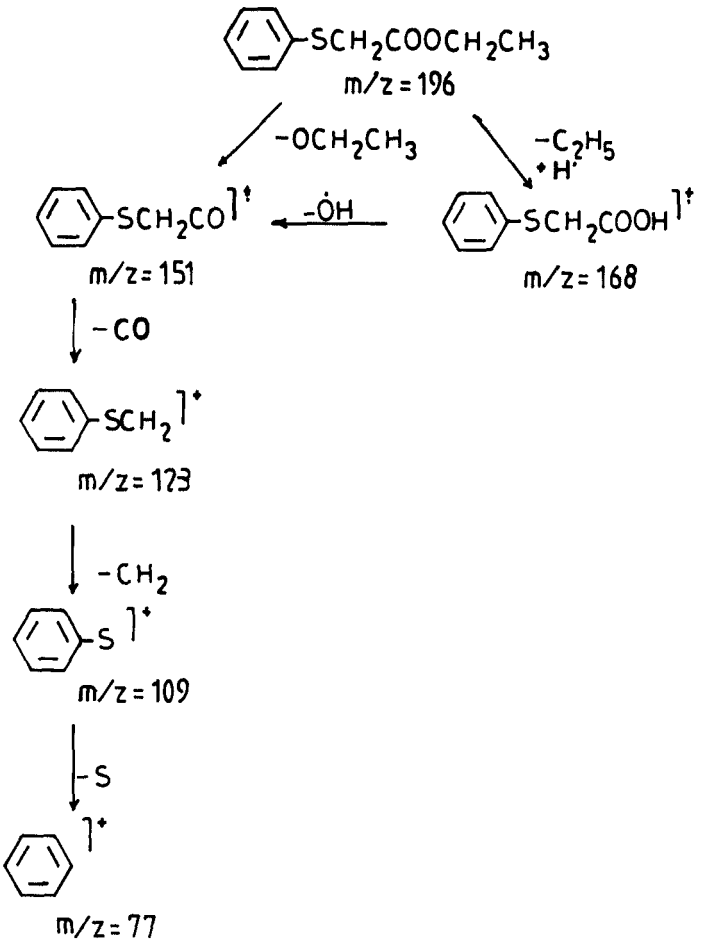
[i] 4'-CH_3 appears at δ 2.26 ppm (s, 3H).
[ii] 4'-OCH_3 appears at δ 3.65 ppm (s, 3H).

TABLE IV

Relative intensities of the most prominent peaks in the mass spectra of ethyl phenylthioacetate I_a

m/z	Rel. Intens, %
196	100.0
168	3.5
151	5.6
123	71.3
109	6.4
77	4.2

Scheme (1)



EXPERIMENTAL

Melting points are uncorrected. Refractive index were measured on PZ0, RL1 AAB, NMR were obtained in $CDCl_3$, acetone-d_6 or DMSO-d_6 using a BRUKER AM 300L spectrometer with Me_4Si as internal standard. IR spectra were measured on a Pye Unicam Cambridge SP^3 200 instrument and the mass spectra on MAT 212 MS, 70 eV.

Analytical thin-layer chromatography (TLC) were carried out on silica gel using (9:1) petroleum ether:ethyl acetate, respectively.

Elemental analysis were carried out in the Faculty of Science, Cairo University, Egypt.

General Procedure. Ethyl bromoacetate or ethyl β-bromopropionate (0.1 mol) in ethanol and sodium salt of thiol (Aldrich Chemical Co. Inc.) (0.1 mole) were refluxed for 1–2 h. Cooling, dilution and acidification with aqueous hydrochloric acid gave a solid, which was purified by crystallization from aqueous ethanol, or a liquid which was extracted with ether and purified by flash column chromatography using (9:1) petroleum ether:ethyl acetate respectively as eluent.

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