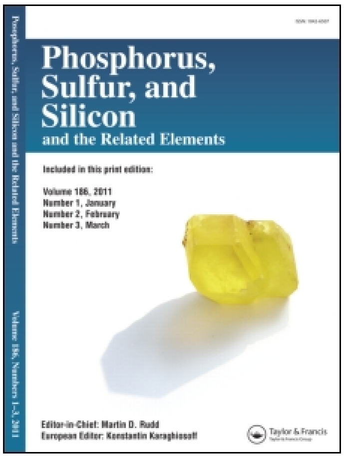

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SYNTHESIS, SPECTRAL STUDIES AND C-S BOND FISSION OF SOME NOVEL ALKYL [(SUBSTITUTED PHENYLSULFONYL)-METHYL]-3-NITROBENZOATES AND THEIR SULFINYL DERIVATIVES

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SYNTHESIS, SPECTRAL STUDIES AND C—S BOND FISSION OF SOME NOVEL ALKYL [(SUBSTITUTED PHENYLSULFONYL)-METHYL]-3-NITROBENZOATES AND THEIR SULFINYL DERIVATIVES

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Methyl and ethyl-4-[(4′-substituted phenylsulfonyl)methyl]-3-nitrobenzoates and the corresponding sulfinyl derivatives have been synthesized. The structure of these esters were proved by IR, NMR and mass spectra.

A linear relationship between δ-ppm values of the benzylic protons and σ-Hammett values of the 4′-substituents has been found.

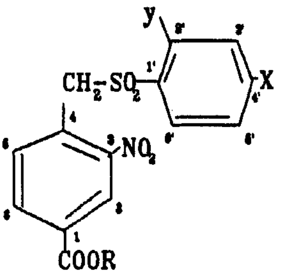
The carbon-sulfur bond fission with 5% sodium hydroxide solution in addition to the alkaline ester hydrolysis is discussed.

Key words: Arylsulfonyl; arylsulfinyl nitrobenzoate; NMR; mass spectra; C—S bond fission.

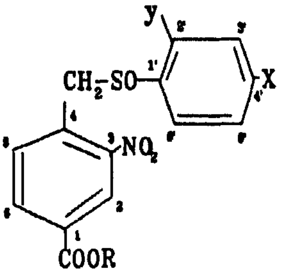
Previously we have described the synthesis of substituted diaryl, aryl benzyl sulfides, sulfones and sulfoxides,[1–6] phenylthioacetate and propionate.[7] 4[(4′-Substituted phenylthio)methyl]-3-nitrobenzoic acids and their sulfonyl and sulfinyl derivatives[1,2] showed a toxicity towards the Mosquito larvae of Culex pipiens molestus Forskal and Aedes caspius (pallas) (collected from the outdoor breeding places in Burg El-Arab district, about 50 km. to the west of Alexandria, Egypt), some of them were found to be effective against bacteria as well as being nontoxic to the tested crops, including wheat, besides the chemotherapeutic and herbicide activities recorded for analogous compounds.[8–10] This has generated our interest in synthesizing other derivatives of the basic structure with ester group for chemical and biological studies. A new series of methyl and ethyl-4-[(4′-substituted phenylsulfonyl)methyl]-3-nitrobenzoates **1a–h**, **2a–h** and their corresponding sulfinyl derivatives **3a–h**, **4a–h** has been synthesized.

In this respect, the synthetic routes are the same as cited in literature.[1–7,11] The esters were prepared by the esterification of the sulfonyl or the sulfinyl nitrobenzoic acid derivatives. The physical properties, sulfur analysis and ^{1}H NMR data of the products are listed in Tables I–IV.

Plots of the ^{1}H NMR δ chemical shift of the benzylic protons for the sulfones **1a–g**, **2a–g** and the sulfoxides **3a–g**, **4a–g** against σ-Hammett constants gave good straight lines, Figs. 1 and 2. It is noticed that the chemical shifts of the benzylic protons do not change when a methyl or ethyl ester group is introduced. Therefore, the 4′-substituents have the greatest effect on the chemical shifts of the benzylic protons.[1,2] Also, it is observed that the chemical shift values of the benzylic protons for the sulfone esters resonate at lower field (δ 5.04–5.45 ppm) with respect to those of the sulfoxide esters (δ 4.52–4.92 ppm). This can be attributed to the strong electron withdrawing nature of the sulfonyl group. On the other hand, the sulfoxides



(1,2)



(3,4)

Cpd. 1, 3, R = CH_3 ; 2, 4, R = C_2H_5

	x	y		x	y
a	H	H	e	Cl	H
b	CH_3	H	f	Br	H
c	OCH_3	H	g	NO_2	H
d	NH_2	H	h	H	COOR

TABLE I

Yield, melting points, found S% and ^{1}H NMR spectra of methyl-[(phenylsulfonyl) methyl]-3-nitrobenzoate **1a** and its derivatives **1b–h**

Cpd. 1	Yield %	Colour	m.P °C	Found S%	^{1}H NMR(δppm, d_6-acetone)						
					methyl ester gp.	CH_2	H_2	H_5	H_6	$H_{2',6'}$	$H_{3',5'}$
a	88	white	117-8	9.57	3.95 (s,3H)	5.16 (s,2H)	8.52 (s,1H)	7.60 (d,1H)	8.20 (d,1H)	7.70 (d,2H)	7.55,H4' (t,3H)
b[i]	85	white	141-3	9.13	3.94 (s,3H)	5.14 (s,2H)	8.51 (s,1H)	7.41 (d,1H)	8.18 (d,1H)	7.57 (d,2H)	7.31 (d,2H)
c[ii]	78	white	148-9	8.75	3.94 (s,3H)	5.10 (s,2H)	8.51 (s,1H)	7.56 (d,1H)	8.19 (d,1H)	7.60 (d,2H)	7.18 (d,2H)
d[iii]	67	yellow	165-7	9.12	3.93 (s,3H)	5.02 (s,2H)	8.50 (s,1H)	7.62 (d,1H)	8.12 (d,1H)	7.56 (d,2H)	7.21 (d,2H)
e	94	white	162-3	8.67	3.95 (s,3H)	5.22 (s,2H)	8.54 (s,1H)	7.58 (d,1H)	8.23 (d,1H)	7.71 (d,2H)	7.68 (d,2H)
f	91	white	187-8	7.72	3.95 (s,3H)	5.23 (s,2H)	8.55 (s,1H)	7.59 (d,1H)	8.22 (d,1H)	7.64 (d,2H)	7.83 (d,2H)
g	89	yellow	133-5	8.43	3.95 (s,3H)	5.34 (s,2H)	8.56 (s,1H)	7.63 (d,1H)	8.25 (d,1H)	7.99 (d,2H)	8.43 (d,2H)
h	90	yellow	225-7	8.14	3.97, 4.14 (2s,6H)	5.42 (s,2H)	8.53 (s,1H)	7.58 (d,1H)	8.21 (d,1H)	H6' 7.82 (d,2H)	H3' H4',5' 8.45, 7.64 (d,2H) (t,2H)

i 4'-CH_3 appears at δ2.43 ppm (s,3H)·

ii 4'-OCH_3 appears at δ 3.88 ppm (s,3H)·

iii 4'-NH_2 appears at δ 4.21 ppm (s,2H), disappears in D2O.

TABLE II

Yield, melting points, found S% and ^1H NMR spectra of ethyl-[(phenylsulfonyl)methyl]3-nitrobenzoate **2a** and its derivatives **2b–h**

Cpd. 2	Yield %	Colour	m.P °C	Found S%	^1H NMR(δppm,d_6-acetone)							
					methyl ester gp.	methylene ester gp.	CH_2	H_2	H_5	H_6	$H_{2',6'}$	$H_{3',5'}$
a	89	white	115-6	9.52	1.38 (t,3H)	4.42 (q,2H)	5.18 (s,2H)	8.53 (s,1H)	7.64 (d,1H)	8.22 (d,1H)	7.76 (d,2H)	7.57,H'4 (t,3H)
b[i]	83	white	138-9	8.80	1.38 (t,3H)	4.45 (q,2H)	5.15 (s,2H)	8.52 (s,1H)	7.54 (d,1H)	8.19 (d,1H)	7.59 (d,2H)	7.39 (d,2H)
c[ii]	79	white	123-5	8.45	1.37 (t,3H)	4.44 (q,2H)	5.12 (s,2H)	8.51 (s,1H)	7.56 (d,1H)	8.23 (d,1H)	7.61 (d,2H)	7.11 (d,2H)
d[iii]	68	yellow	196-7	8.81	1.36 (t,3H)	4.42 (q,2H)	5.04 (s,2H)	8.48 (s,1H)	7.52 (d,1H)	8.17 (d,1H)	7.58 (d,2H)	7.21 (d,2H)
e	95	white	135-6	8.34	1.37 (t,3H)	4.40 (q,2H)	5.21 (s,2H)	8.55 (s,1H)	7.67 (d,1H)	8.22 (d,1H)	7.73 (d,2H)	7.59 (d,2H)
f	93	white	160-1	7.46	1.38 (t,3H)	4.45 (q,2H)	5.22 (s,2H)	8.55 (s,1H)	7.65 (d,1H)	8.25 (d,1H)	7.76 (d,2H)	7.89 (d,2H)
g	91	yellow	164-5	8.14	1.39 (t,3H)	4.45 (q,2H)	5.32 (s,2H)	8.57 (s,1H)	7.63 (d,1H)	8.26 (d,1H)	8.00 (d,2H)	8.44 (d,2H)
h	96	white	92-3	7.61	1.37, 1.39 (2t,6H)	4.38, 4.44 (2q,4H)	5.45 (s,2H)	8.52 (s,1H)	7.52 (d,1H)	8.20 (d,1H)	H6' 7.85 (d,1H)	H3' 8.28 (d,1H) H4',5' 7.62 (t,2H)

i 4'-CH_3 appears at δ2.43 ppm (s,3H).

ii 4'-OCH_3 appears at δ 3.90 ppm (s,3H).

iii 4'-NH_2 appears at δ 4.23 ppm (s,2H), disappears in D2O.

3a–h and **4a–h** showed an *AB* spectrum centered at $(\delta A + \delta B)/2 = 4.52–4.92$ due to the presence of two diastereotropic benzylic protons.[12]

The mass spectra[1,2,4,6,13–15] of methyl-4-[(phenylsulfonyl)methyl]-3-nitrobenzoate (**1a**) and ethyl-4-[(-4′-toulylsulfinyl)methyl]-3-nitrobenzoate (**4b**) were studied as shown in Schemes I and II and the relative intensities of the most prominent peaks in their fragmentation are recorded in Table V.

Scheme I and Table V illustrate the mode of fragmentation of methyl-4-[(phenylsulfonyl)methyl]-3-nitrobenzoate (**1a**). The compound gave molecular ion peak at *m/z* 336. Scission of the sulfonylmethyl bond gave 3-nitro troplium ester ion, at *m/z* 194, as a base peak and a peak corresponding to Ar SO_2 ion at *m/z* 141. This fragmentation pattern has not been detected in the mass spectra of diarylsulfones.[4] The loss of $\dot{O}$ and $N\dot{O}$ radicals from the base peak led to troplium ester ion, at *m/z* 149. This ion fragments further with loss of $\dot{O}CH_3$ radical and CO to give the troplium ion, at *m/z* 91. On the other hand, the 3-nitro troplium ester ion produced

TABLE III

Yield, melting points, refractive index, found S% and ^1H NMR spectra of methyl-[(phenylsulfinyl)methyl]-3-nitrobenzoate **3a** and its derivatives **3b–h**

Cpd. 3	Yield %	Colour	m.P °C / n^{25}_{D}	Found S%	^1H NMR(δppm, d_6-acetone) methyl ester gp.	CH_2 (δA+δB)/2	H_2	H_5	H_6	$H_{2',6'}$	$H_{3',5'}$
a	89	white	115-6	9.99	3.93 (s,3H)	4.68 (2d,2H)	8.52 (s,1H)	7.29 (d,1H)	8.10 (d,1H)	7.51 (d,2H)	7.45,H4' (t,3H)
b[i]	87	yellow	120-2	9.60	3.94 (s,3H)	4.66 (2d,2H)	8.51 (s,1H)	7.27 (d,1H)	8.08 (d,1H)	7.31 (s,2H)	7.31 (s,2H)
c[ii]	72	colourless	1.589	9.14	3.93 (s,3H)	4.64 (2d,2H)	8.50 (s,1H)	7.04 (d,1H)	8.07 (d,1H)	7.39 (d,2H)	6.89 (d,2H)
d[iii]	66	brown	]1.70	9.60	3.92 (s,3H)	4.52 (2d,2H)	8.47 (s,1H)	7.12 (d,1H)	8.06 (d,1H)	7.35 (d,2H)	6.74 (d,2H)
e	92	white	118-9	9.08	3.94 (s,3H)	4.72 (2d,2H)	8.52 (s,1H)	7.31 (d,1H)	8.15 (d,1H)	7.42 (d,2H)	7.76 (d,2H)
f	91	yellow	130-2	9.05	3.93 (s,3H)	4.74 (2d,2H)	8.52 (s,1H)	7.30 (d,1H)	8.14 (d,1H)	7.40 (d,2H)	7.68 (d,2H)
g	89	yellow	143-4	8.80	3.94 (s,3H)	4.85 (2d,2H)	8.54 (s,1H)	7.31 (d,1H)	8.15 (d,1H)	7.74 (d,2H)	8.33 (d,2H)
h	85	while	121-3	8.50	3.92, 3.98 (2s,6H)	4.92 (2d,2H)	8.52 (s,1H)	7.18 (d,1H)	8.10 (d,1H)	H6' 7.65 (d,1H)	H3' 8.18 (d,1H) H4'5' 7.30 (t,2H)

i 4'-CH_3 appears at δ2.37 ppm (s,3H).

ii 4'-OCH_3 appears at δ 3.36 ppm (s,3H).

iii 4'-NH_2 appears at δ 4.20 ppm (s,2H), disappears in D2O.

the nitro troplium ion, at *m/z* 135, through the loss of $\dot{O}CH_3$ radical and elimination of carbon monoxide. The loss of $N\dot{O}$ radical from this ion led to the troplium-1-one ion, at *m/z* 105, which underwent successive loss of CO giving the benzonium ioin, at *m/z* 77.

Scheme II and Table V show the most probable structure of the peaks obtained from ethyl-4-[(4′-toulylsulfinyl)methyl]-3-nitro benzoate (**4b**). The parent ion of (**4b**), *m/z* 347, underwent cleavage through the sulfinyl methyl bond[4] to give 4′-methylphenylsulfinyl ion, at *m/z* 139 and 3-nitro troplium ester ion, at *m/z* 208 as a base peak. As shown in Scheme I, the 3-nitro troplium ester ion gave several major peaks at *m/z* 163 (troplium ester ion), 118 (carbonyl troplium ion) and at 91 (troplium ion). In accordance with the other route, it fragments to the various ions at *m/z* 135 (nitro troplium ion), 105 (troplium-1-one ion) and 77 (benzonium ion).

The IR spectra[16,17] of all compounds showed a sharp band at 1720–1750 cm^{-1}

TABLE IV

Yield, melting points, refractive index, found S% and ^{1}H NMR spectra of ethyl-[(phenylsulfinyl)methyl]-3-nitrobenzoate **4a** and its derivatives **4a–h**

Cpd. 4	Yield %	Colour	m.P °C / n^{20}_D	Found S%	^{1}H NMR(δppm,d_6-acetone)							
					methyl ester gp.	methylene ester gp.	CH_2 (δA+δB)/2	H_2	H_5	H_6	$H_{2',6'}$	$H_{3',5'}$
a	91	yellow	58-9	9.62	1.37 (t,3H)	4.38 (q,2H)	4.69 (2d,2H)	8.52 (d,1H)	7.29 (d,1H)	8.11 (d,1H)	7.54 (d,2H)	7.42,H4' (t,3H)
b[i]	78	colourless	1.572	9.21	1.37 (t,3H)	4.39 (q,2H)	4.66 (2d,2H)	8.51 (d,1H)	7.22 (d,1H)	8.12 (d,1H)	7.32 (s,2H)	7.32 (s,2H)
c[ii]	81	yellow	70-1	8.81	1.37 (t,3H)	4.38 (q,2H)	4.63 (2d,2H)	8.50 (d,1H)	7.15 (d,1H)	8.12 (d,1H)	7.37 (d,2H)	6.93 (d,2H)
d[iii]	69	brown	162-3	9.20	1.37 (t,3H)	4.37 (q,2H)	4.53 (2d,2H)	8.51 (d,1H)	7.11 (d,1H)	8.11 (d,1H)	7.33 (d,2H)	6.70 (d,2H)
e	93	white	130-1	8.73	1.37 (t,3H)	4.38 (q,2H)	4.73 (2d,2H)	8.52 (d,1H)	7.39 (d,1H)	8.12 (d,1H)	7.52 (d,2H)	7.70 (d,2H)
f	92	yellow	141-2	7.75	1.37 (t,3H)	4.38 (q,2H)	4.75 (2d,2H)	8.53 (d,1H)	7.32 (d,1H)	8.14 (d,1H)	7.47 (d,2H)	7.67 (d,2H)
g	88	yellow	117-9	8.48	1.37 (t,3H)	4.38 (q,2H)	4.85 (2d,2H)	8.55 (d,1H)	7.35 (d,1H)	8.11 (d,1H)	7.74 (d,2H)	8.37 (d,2H)
h	86	white	133-5	7.88	1.36, 1.38 (2t,6H)	4.37, 4.39 (2q,4H)	4.91 (2d,2H)	8.52 (d,1H)	7.20 (d,1H)	8.12 (d,1H)	H6' 7.68 (d,1H)	H3' H4',5' 8.21 7.32 (d,1H)(t,2H)

i 4'-CH_3 appears at δ2.37 ppm (s,3H).

ii 4'-OCH_3 appears at δ 3.78 ppm (s,3H).

iii 4'-NH_2 appears at δ 4.22 ppm (s,2H), disappears in D2O.

(C=O), the sulfones showed strong absorption bands at 1350–1300 cm^{-1} and at 1150 cm^{-1} for the asymmetric and symmetric stretching (SO_2), respectively. The sulfoxides showed, beside others, an absorption band at 1010–1035 cm^{-1} (SO).

The action of 5% sodium hydroxide solution on the sulfones **2a,b,e,f,g** and the sulfoxides **4a,b,e,f,g** in dioxane gave 4-methyl-3-nitrobenzoic acid[18] in all cases, in addition to benzene sulfonic and sulfinic acid derivatives, respectively. These products were obtained through the alkaline hydrolysis of the ester group and the carbon-sulfur bond fission, (Schemes III and IV).

The structure of 4-methyl-3-nitrobenzoic acid was established by comparison of its IR and ^{1}H-NMR spectrum with that of an authentic specimen.

Benzene sulfonic acid derivatives formed from **2a,b,e,f,g** were stable in alkaline dioxane medium as sodium salt. A proof for this step is that the acidification of the reaction mixture did not liberate any gas, either H_2S or SO_2, and did not form Na_2S or $NaHSO_3$. The benzene sulfinic acid derivatives formed from **4a,b,e,f,g**

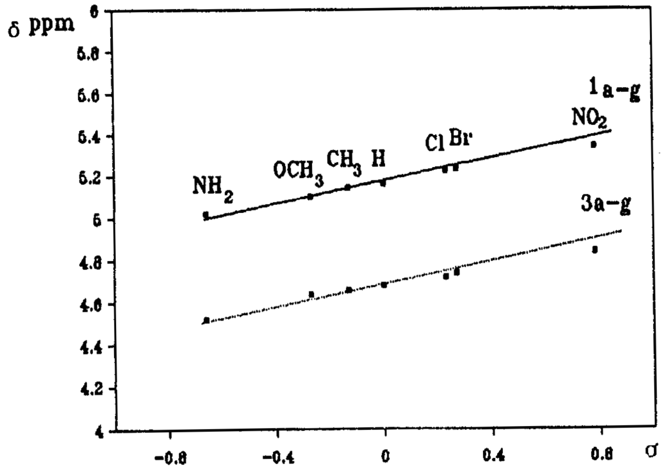


FIGURE 1 δ-ppm values of the benzylic protons of methyl-4-[(4′-substituted phenylsulfonyl)methyl]-3-nitrobenzoate **1a–g** and its corresponding sulfoxides **3a–g** against the σ-Hammett values of the 4′-substituents (*X*).

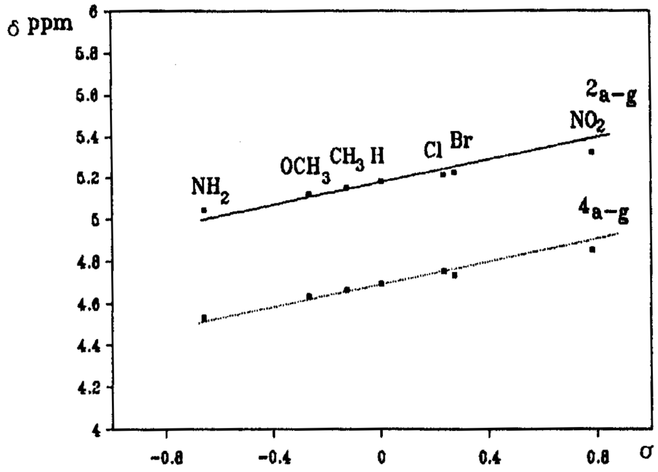
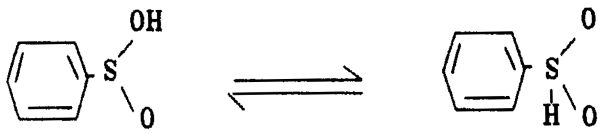
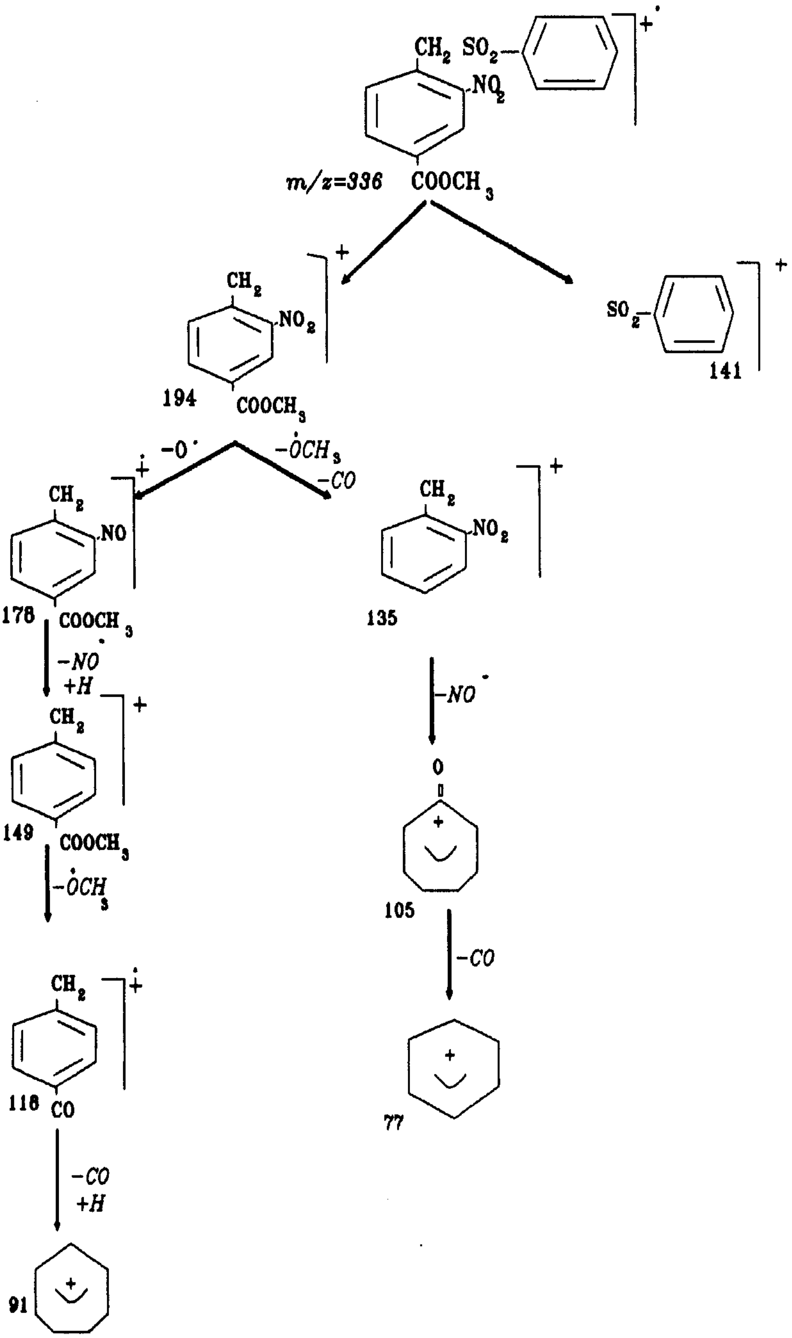


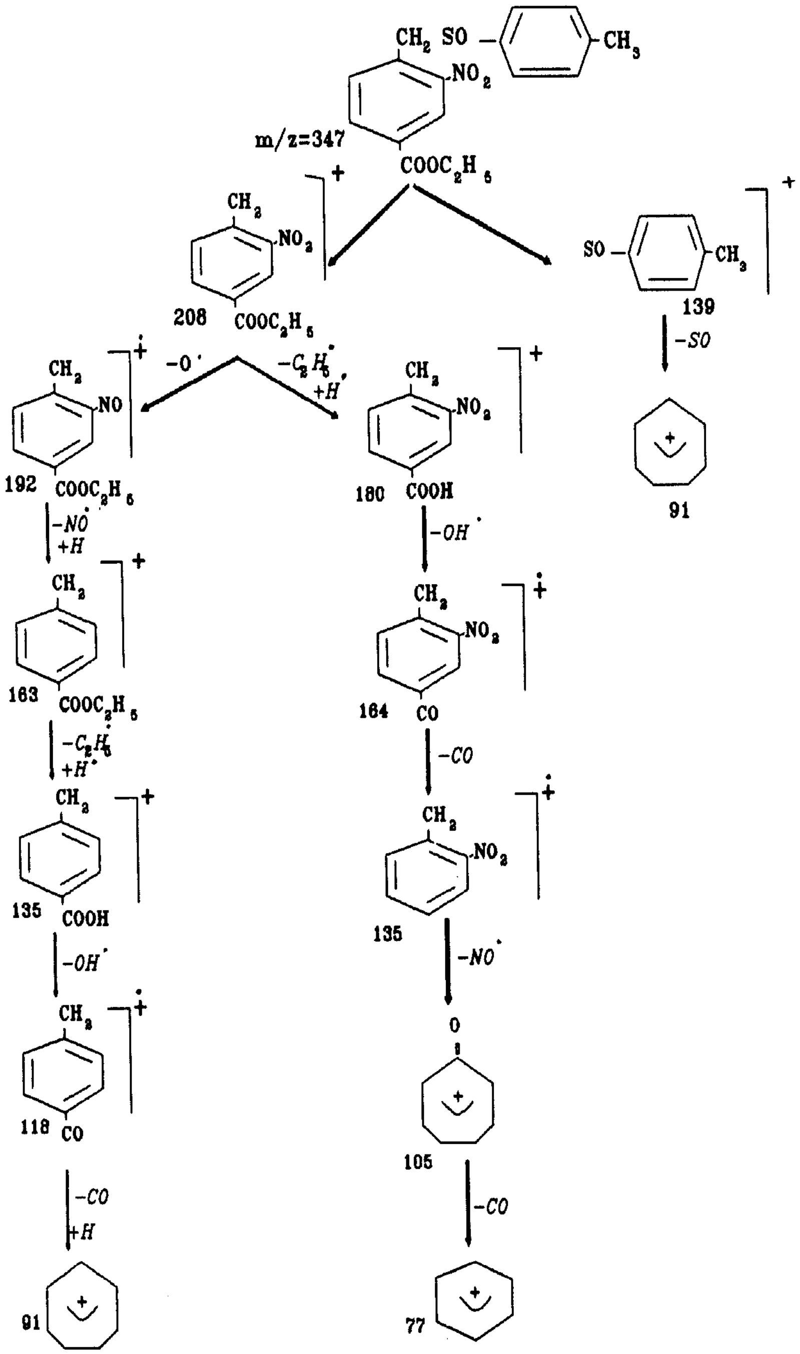
FIGURE 2 δ-ppm values of the benzylic protons of ethyl-4-[(4′-substituted phenylsulfonyl)methyl]-3-nitrobenzoate **2a–g** and its corresponding sulfoxides **4a–g** against the σ-Hammett values of the 4′-substituents (*X*).

exhibited a characteristic thiol odor on acidification. This is because sulfinic acid could be associated in nonpolar solvent such as dioxane, so that the proton is placed pretty close to the sulfur to behave like an S—H bond.[19] Dipole moments[20] and spectroscopic measurements[21] show the presence of the sulfinic acid molecule in two tautomeric equilibrium structures.




m/z=336
194
141
178
135
149
105
118
77
91
-O•
-OCH₃
-CO
-NO
+H
-NO•
-OCH₃
-CO
-CO
+H

SCHEME I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NO2
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NO2
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CH2
NO
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CH2
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COOH
-NO· +H
-OH·
CH2
163
COOC2H5
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NO2
164
CO
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-CO
CH2
135
COOH
CH2
NO2
135
-OH·
-NO·
CH2
118
CO
O
105
-CO +H
-CO
91
77

SCHEME II

TABLE V

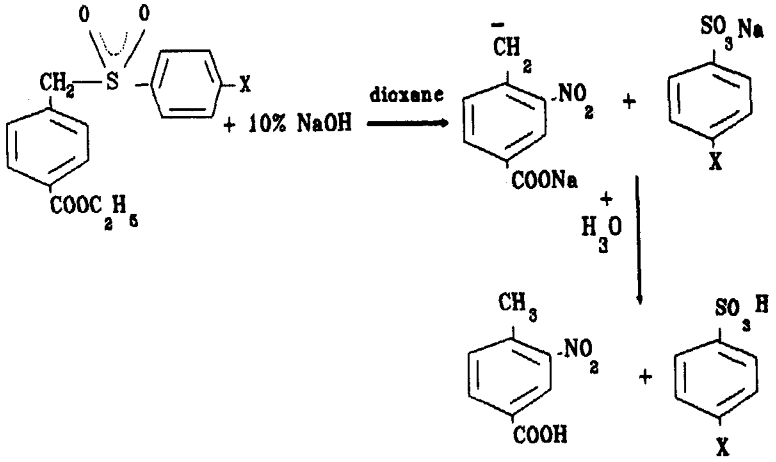
Relative intensity of prominent peaks in the mass spectra of methyl-4-[(phenylsulfonyl)methyl-3-nitrobenzoate (**1a**) and ethyl-4-[(4′-tolylsufinyl)methyl]-3-nitrobenzoate (**4b**)

1_a		4_b	
m/Z	rel.intens,%	m/Z	rel.intens,%
336	1.08	347	0.89
195	9.70	252	7.71
194	100.00	224	6.38
177	12.00	209	9.70
165	3.79	208	100.00
149	2.76	192	4.22
141	6.94	180	7.42
136	9.77	164	5.35
117	5.17	149	3.85
105	30.65	140	9.30
97	3.67	139	89.83
89	9.04	123	11.61
77	47.37	122	10.62
59	7.94	105	16.73
		91	27.66
		77	20.37
		65	14.87

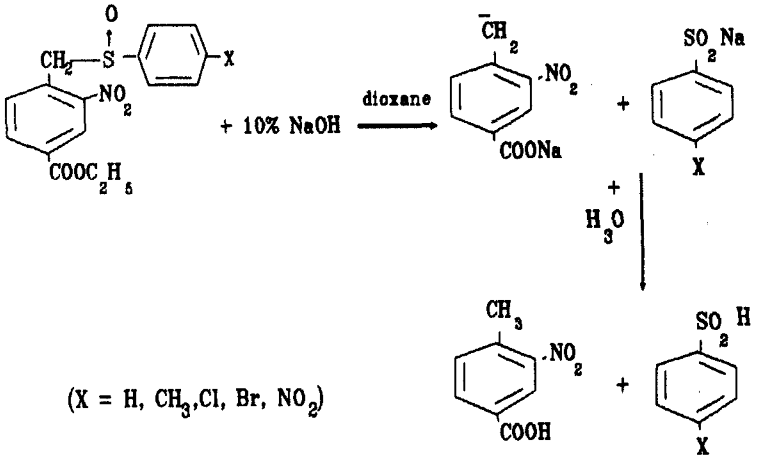
The structures of 4-methyl and 4-chlorobenzene sulfinic acids were proved by ^{1}H NMR in dioxane, which showed a singlet for the SO_2—H group at δ 8.40 and 8.60, respectively, as previously reported.[22]

The formation of 4-methyl-3-nitrobenzoic acid, benzene sulfonic and sulfinic acid derivatives can be explained on the basis that the methylene protons α to the sulfonyl or sulfinyl group are acidic in nature; thus α-sulfonyl or sulfinyl carbanion can readily be formed upon treatment with a strong base.[23] The presence of a carbanion was proved by the immediate appearance of a deep violet color in cold 5% sodium hydroxide, which on warming changed to pale brown.

Due to the presence of the nitro group in the ortho position, there is no direct conjugation between it and the α-carbon, i.e., the mesomeric effect of the nitro group is not operating, because this group is not planar with the ring. This shields the benzylic hydrogens from being easily attacked by the alkali, and the formed carbanion has no chance for reasonance stabilization with the nitro group, once it formed, and returns back to the reactant. This gives a chance for the formation of 4-methyl-3-nitrobenzoic acid[18] via the attack of the $\overline{O}H$ ion on the positively



SCHEME III



SCHEME IV

charged sulfur atom, leading to a carbon-sulfur bond fission and liberating 4-carboxy-2-nitrobenzyl anion which in turn gives 4-methyl-3-nitrobenzoic acid on acidification (Schemes III and IV).

EXPERIMENTAL

The melting points are determined on a Thomes-Hoover capillary apparatus and are uncorrected. Refractive index were measured on PZO RL 1 AAB, ^{1}H NMR in d_6-acetone using a BRUKER AM 300 L spectrometer with Me_4Si as internal standard, IR spectra (KBr pellets or Nujol) were measured on a Beckman Acculab T.M.4 infrared spectrophotometer and the mass spectra on a Varian VXR-300, 70 ev. Analytical thin-layer chromatography (TLC) were carried out on silica gel using (9.5:0.5) petroleum ether:ethyl acetate, respectively. Elemental analysis were carried out in the Faculty of Science, Cairo University, Egypt. The found analysis for carbon, hydrogen and sulfur were in excellent agreement with those calculated.

General Procedure

Synthesis of methyl and ethyl sulfone and sulfoxide esters. The sulfides, sulfones and sulfoxides were prepared as previously reported.[1,2]

The sulfone **1a–h**, **2a–h** and the sulfoxide **3a–h**, **4a–h** esters were synthesized by refluxing the corresponding acids in a mixture of absolute methyl or ethyl alcohol and a few drops of concentrated sulfuric acid for 10 h. On washing the reaction mixture with 10% sodium bicarbonate solution either a solid or oil was obtained. The solids were purified by recrystallization from aqueous ethanol. The oils were extracted with ether and purified by flash column chromatography using petroleum ether:ethyl acetate (9:1), respectively.

Action of 5% sodium hydroxide solution. Ethyl sulfone **2a,b,e,f,g** or sulfoxide **4a,b,e,f,g** esters (**1g**) dissolved in dioxane were treated with 5% sodium hydroxide solution (10 ml). A deep violet color developed immediately which, on warming the mixture turned pale brown. The reaction mixture was refluxed for 1 hour. On cooling and acidifying with dilute hydrochloric acid no gas evolved but a characteristic thiol odor was detected in the case of the sulfoxide esters **4a,b,e,f,g**.

TLC of the ether extracts indicates the presence of two compounds in each case which were separated by column chromatography using silica gel (particle size 0.063–0.20 mm, 70–230 mesh ASTM) and (9:1) petroleum ether:ethanol, respectively. The first compound, separated from the sulfone or the sulfoxide esters, was identified as 4-methyl-3-nitrobenzoic acid[18] (m.p. 189–90°C).

The second compound in the mixture was identified as a benzene sulfonic or sulfinic acid derivative, respectively. Benzene sulfonic acid, m.p. 45°C (lit., 43–44°C)[24]; 4-methylbenzene sulfonic acid, m.p. 106°C (lit., 104°C)[25] 4-chlorobenzene sulfonic acid, m.p. 66°C (lit., 68°C)[26]; 4-bromobenzene sulfonic acid, m.p. 102°C (lit., 102°C)[26]; 4-nitrobenzene sulfonic acid, m.p. 95°C (lit., 95°C)[27]; benzene sulfinic acid, m.p. 82°C (lit., 83–84°C)[28]; 4-methylbenzene sulfinic acid, m.p. 87°C (lit., 85°C)[29]; 4-chlorobenzene sulfinic acid, m.p. 98°C; 4-bromobenzene sulfinic acid, m.p. 114°C; 4-nitrobenzene sulfinic acid, m.p. 158°C (lit., 159°C).[30] All these products were compared with a commercial specimen (melting points and some ^{1}H NMR).

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