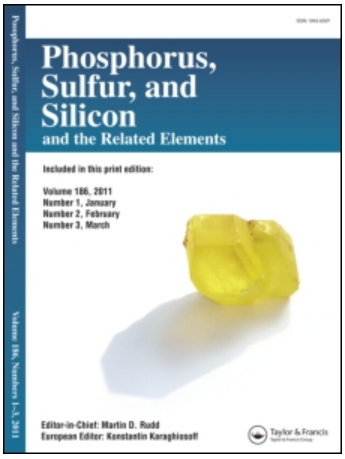

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ALKALINE C-S BOND CLEAVAGE OF SOME ARYLTHIOMETHYL BENZOATES

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ALKALINE C—S BOND CLEAVAGE OF SOME ARYLTHIOMETHYL BENZOATES

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Methyl and ethyl-[(substituted phenylthio)methyl]-3-nitrobenzoates and the corresponding non-nitro derivatives have been synthesized and their structures proven. The action of 5% sodium hydroxide solution on these esters gave the corresponding diaryl disulfides besides 3-nitro-4-methylbenzoic acid or 4-methylbenzoic acid.

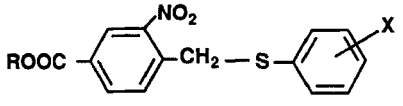
Key words: Arylthiomethyl benzoates; C—S bond fission and mass spectra.

INTRODUCTION

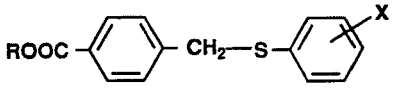
We have previously reported the synthesis of substituted diaryl, arylbenzyl sulfides, sulfones and sulfoxides.[1–8] Some of these compounds showed a toxicity toward the mosquito larvae of cluex pipiens molestus Forskal and Aedes caspius (pallas),[9] while others were found to be effective against bacteria as well as being nontoxic to the tested crops including wheat.[10] Both chemotherapeutic and herbicide activities have been recorded for analogous compounds.[11,12]

The action of 5% NaOH on α-(4-nitrobenzyl) acetic and propionic acids and 4-nitrobenzyl aryl sulfide derivatives were reported.[13–15] The alkaline hydrolysis of the former compounds gave 4,4′-diformylazobenzene or the corresponding azoxy derivatives whereas the latter gave 4,4′-diformylazoxybenzene as the main product and 4,4′-dicarboxyazoxybenzene beside a mercaptan or its disulfide.[16]

In connection with our previous work on phenylthio, sulfinyl and sulfonyl derivatives,[1–8] our initial effort was directed toward the synthesis and study of the spectral behavior of methyl and ethyl 4-[(substituted phenylthio) methyl]-3-nitrobenzoates (**1a–i**), (**2a–h,j**) and the corresponding non-nitro derivatives (**3a–i**), (**4a–h,j**). An ester group was introduced in an effort to gain understanding of the alkaline hydrolysis mechanism involving C—S fission in these structures.



1a-i, 2a-h,J



3a-i, 4a-h,J

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

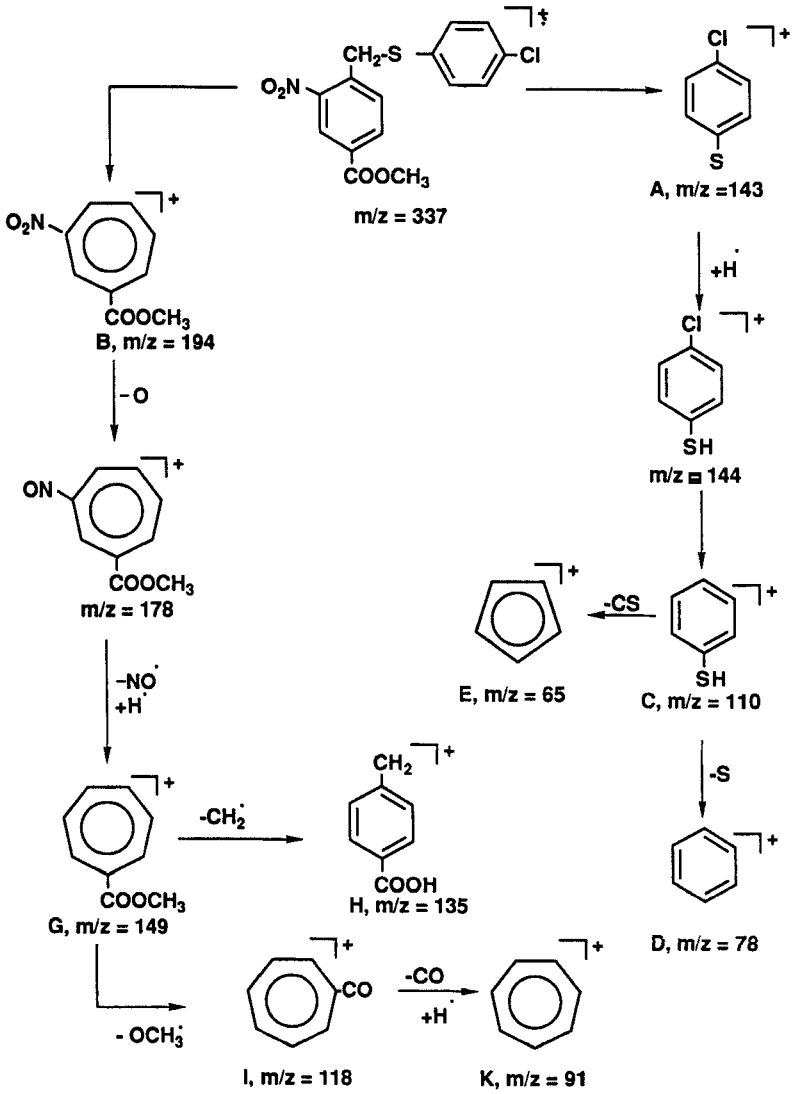
a, X = H; b, X = 4-CH_3; c, X = 4-OCH_3
d, X = 4-NH_2; e, X = 4-Cl; f, X = 4-Br;
g, X = 4-NO_2; h, X = 2-CO_2H ; i, X = 2-CO_2CH_3 ;
j, X = 2-$CO_2C_2H_5$;

†Author to whom correspondence should be addressed.

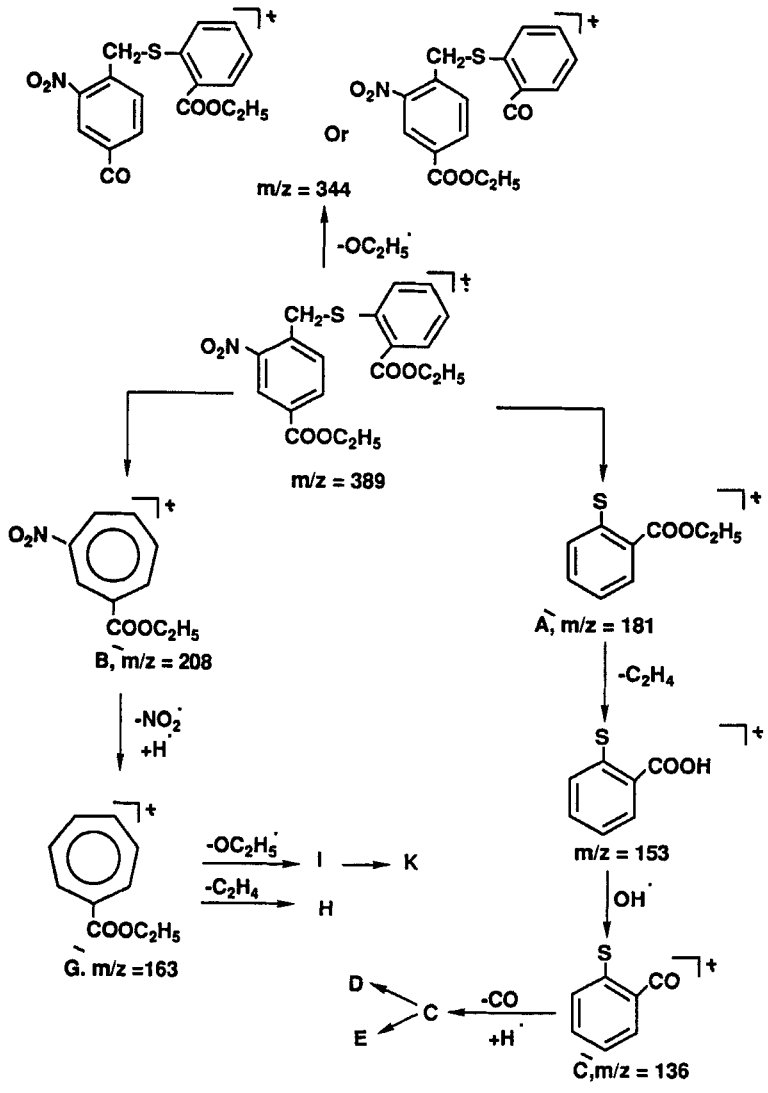
RESULTS AND DISCUSSION

Esters (**1–4**) were synthesized by the treatment of methyl or ethyl 4-chloromethyl-3-nitrobenzoate (**5**) and 4-chloromethylbenzoate (**6**) with a substituted phenylthiol in the presence of a catalytic amount of sodium metal in alcohol. The physical properties, elemental analyses, and spectral data of the products are given in the experimental.

The proposed mass spectra fragmentation patterns of (**1e**) (R = CH_3, Y = H, X = Cl) and (**2j**) (R = $CO_2C_2H_5$, Y = $CO_2C_2H_5$, X = H) are in accordance with the ions produced under electron impact (Schemes 1 and 2). The relative intensities of the most prominent peaks in the fragmentation pattern are given in Table I.



SCHEME 1



SCHEME 2

Scheme 1 shows that the parent ion methyl 4-[(4′-chlorophenylthio)methyl]-3-nitrobenzoate (**1e**) underwent cleavage through the thiomethyl bond giving 4-chlorothiophenyl ion A and tropylium nitro methyl ester B differing from that reported in literature[17,18] and similar to that observed for the non-nitro derivative.[6] The base peak at m/z 144 underwent a routine fragmentation pattern[19,20] to give ion C at m/z 110. Subsequent loss of a chlorine atom followed by elimination of S atom or CS group to give D and E at m/z 78 and 65, respectively. The tropylium nitromethyl ester ion B underwent successive loss of nitrogen dioxide[21] to give tropylium ester ion G which loses CH_2 radical to give the tropylium carboxylic acid H. Ion I arises by loss of a OCH_3 radical from G which in turn loses carbon monoxide giving tropylium ion K.

TABLE I

Relative intensities of the most prominent peaks in the mass spectra of (**1e**) (R = CH_3, Y = H, X = Cl) and (**2j**) (R = Y = $CO_2C_2H_5$, X = H)

(1e)		(2j)	
m/z	Rel. intens, %	m/z	Rel. intens, %
337	5.5	389	2.10
194	12.7	344	6.10
178	49.3	208	4.10
149	32.2	192	16.80
144/146	100.0	181	44.00
143	71.2	163	15.80
135	40.0	153	74.00
118	26.7	135	5.50
110	30.0	136	100.00
108	54.8	118	14.40
91	15.8	108	32.00
78	13.0	91	10.30
65	13.0	78	18.50
		65	21.20

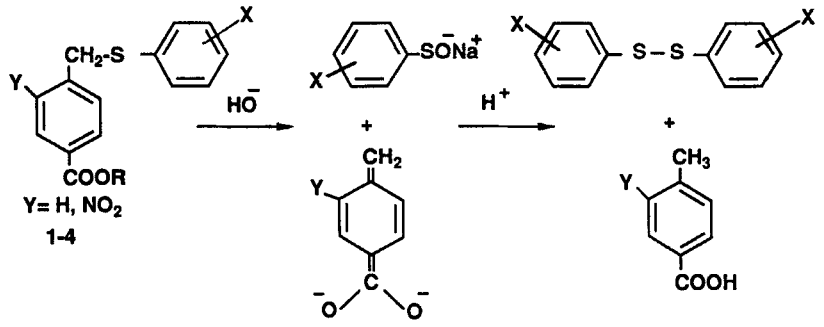
The diester (**2j**) shows approximately the same fragmentation processes as (**1e**) with little differences due to the type and position of the substituent in the thioaryl moiety (Scheme 2). The parent ion undergoes cleavage either through the thiomethyl bond to give *o*-carboethoxy thiophenate A′ and tropylium nitroethyl ester B′ or loses OC_2H_5 radical giving the corresponding carbonyl derivative at m/z 344. Ion A′ loses C_2H_4 to give *o*-carboxythiophenate ion at m/z 153, which in turn loses OH to give C′ at m/z 136. This undergoes several cleavages similar to those observed in the case of (**1e**) giving D and E.

The tropylium nitroethyl ester B′ underwent loss of nitrogen dioxide giving tropylium ethyl ester G′ which in turn loses C_2H_4 to give tropylium carboxylic acid ion H. Ions I and K wer obtained by the same manner as in (**1e**).

The IR spectra of (**1a–i**), (**2a–h,j**), (**3a–i**) and (**4a–h,j**), showed characteristic peaks at 1735–1750 and 635–650 cm^{-1} due to C=O and C—S stretching, respectively.

The action of 5% sodium hydroxide solution on the sulfide esters (**1a–i**) and (**3a–i**) in dioxane, followed by acidification, gave 4-methyl-3-nitrobenzoic acid and 4-methylbenzoic acid, respectively, in addition to diphenyl disulfide derivatives (Scheme 3). The structures of 4-methyl-3-nitrobenzoic acid,[22] 4-methylbenzoic acid and 4,4′-disubstituted diphenyl disulfides were identified by comparison of their TLC, IR and ^1H NMR spectra with those of authentic specimens.

As mentioned before, the alkaline hydrolysis of α-4-(nitrobenzylthio) acids[13–15] and 4-nitrobenzyl aryl sulfides,[16] underwent prior benzylic proton abstraction to give 4,4′-diformylazobenzene and 4,4′-diformylazoxybenzene, respectively. The title compounds proceeded via direct C—S bond fission to give 4-toluic acid and diaryl disulfide rather than through a benzylic proton abstraction. This behavior is presumably due to the electrostatic repulsion between the OH^- and the negatively charged oxygen atom of the nitro group and the carboxylate anion if present.[23] The C—S bond fission could be rationalized by the attack of OH^- on the S atom



SCHEME 3

to give sodium aryl sulfene while the remaining moiety gives 4-toluic acid derivatives after acidification.

However, the diaryl disulfide was formed by acidification of sodium aryl sulfene to aryl sulfene, which in turn underwent several reactions[24] to give the disulfide and the aryl sulfinic acid, Equations (1) and (2).

$$2\ \mathrm{Ar\,SOH} \rightarrow \mathrm{Ar{-}\overset{\overset{\uparrow}{O}}{S}{-}S{-}Ar} + \mathrm{H_2O} \qquad (1)$$

$$\mathrm{Ar{-}\overset{\overset{\uparrow}{O}}{S}{-}S{-}Ar} \rightarrow \mathrm{Ar{-}SO_2H} + \mathrm{Ar{-}S{-}S{-}Ar} \qquad (2)$$

Experimentally, when **(1a)** (X = H) was heated with 5% aqueous NaOH in dioxane and the reaction mixture was acidified, both disulfide and nitrotoluic acid were precipitated and filtered. Their separation took place by fractional crystallization and the aryl sulfinic acid was detected in the filtrate by formation of an orange yellow precipitate with $FeCl_3$.[25]

EXPERIMENTAL

The melting and boiling points are uncorrected. Refractive indices were measured on a PZO RL 1AAB instrument. ^{1}H NMR spectra was measured on a Bruker AM 300L spectrometer. IR (KBr pellets or nujol) and UV spectra were measured on a Perkin-Elmer 1430 ratio recording infrared and UV-VIS Shimadzu 160-A spectrometers, respectively. The mass spectra was carried out at 70 ev on a Varian VXR-300. Elemental analyses were done in the Faculty of Science, Cairo University, Egypt.

1-Synthesis of Chloromethyl Benzoate Ester Derivatives: A mixture of 4-chloromethyl-3-nitrobenzoic acid or 4-chloromethyl benzoic acid[4,22] [0.1 mole] and few drops of concentrated sulfuric acid in absolute methanol or ethanol was refluxed for 10 h under dry conditions. The cooled reaction mixture was diluted with water and extracted with ether, and the ether layer was washed with sodium bicarbonate solution. Evaporation of the dried ether layer gave an oil which was purified by vacuum distillation.

Methyl 4-chloromethyl-3-nitrobenzoate (**5**). Colorless liquid; Yield 78%; n_D^{20} 1.5418; b.p. 186°/2 mm Hg; UV (MeOH) λ_{max} = 226 nm (ε = 19100); ^{1}H NMR (acetone-d_6): δ 3.98 (s, 3 H, CH_3 ester), 5.10 (s, 2 H, CH_2 benzylic), 7.92 and 8.22 (dd, 2 H, $H_{5,6}$) and 8.48 (s, 1 H, H_2). Anal. Calcd. for $C_9H_8ClNO_4$: C, 47.05; H, 3.48; N, 6.10; Cl, 15.46. Found: C, 47.30; H, 3.60; N, 6.30; Cl, 15.10.

Ethyl 4-chloromethyl-3-nitrobenzoate (**6**). Yellow crystals, Yield 82%; m.p. 40°C; UV (EtOH): λ_{max} = 225 nm (ε = 18105), ^{1}H NMR (acetone-d_6): δ 1.36 (t, 3 H, CH_3 ester), 4.38 (q, 2 H, CH_2 ester),

5.02 (s, 2H, CH_2 benzylic), 7.48 and 8.20 (dd, 2 H, $H_{5,6}$) and 8.60 (s, 1 H, H_2). Anal. Calcd. for $C_{10}H_{10}ClNO_4$: C, 49.28; H, 4.10; N, 5.75; Cl, 14.58. Found: C, 49.40; H, 4.00; N, 5.90; Cl, 14.80.

Methyl 4-chloromethyl benzoate (**7**). Colorless oil; Yield 85% n_D^{20} 1.5221; b.p. 138°/2 mm Hg; m.p. 33°C; UV (MeOH) λ_{max} = 237 nm (ε = 15000); ^{1}H NMR (acetone-d_6): δ 3.85 (s, 3 H, CH_3 ester), 4.52 (s, 2 H, CH_2 benzylic), 7.91 (dd, 2 H, $H_{2,6}$) and 7.48. (dd, 2 H, $H_{3,5}$). Anal. Calcd. for $C_9H_9ClO_2$: C, 58.53; H, 4.87; Cl, 19.24. Found: C, 58.70; H, 4.60; Cl, 19.40.

Ethyl 4-chloromethyl benzoate (**8**). Colorless oil; Yield 80%; n_D^{20} 1.5018; b.p. 158°/2 mm Hg; UV (EtOH): λ_{max} = 236 nm (ε = 16950); ^{1}H NMR (acetone-d_6): δ 1.38 (t, 3 H, CH_3 ester), 4.42 (q, 2 H, CH_2 ester), 4.02 (s, 2 H, CH_2 benzylic), 8.04 (dd, 2 H, $H_{2,6}$) and 7.46 (dd, 2 H, $H_{3,5}$). Anal. Calcd. for $C_{10}H_{11}ClO_2$: C, 60.45; H, 5.54; Cl, 17.88. Found: C, 60.30; H, 5.40; Cl, 17.50.

2-Synthesis of Alkyl 4-[(Substituted Phenylthio)Methyl]-3-Nitro Benzoates (**1a–i**), (**2a–h,j**) *and the Corresponding Non-Nitro Derivatives* (**3a–i**) and (**4a–h,j**).

General procedure. A mixture of the appropriate esters **5–8** (0.1 mole), arylthiol (0.15 mole) and a catalytic amount of sodium in methanol (or ethanol) was refluxed on a steam bath for 2 hours. The reaction mixture was cooled, diluted with 2% sodium hydroxide solution, and extracted with ether. Evaporation of ether layer gave a residue which was purified either by crystallization from ethanol or column chomatography (9:1 petroleum ether:ethyl acetate, respectively).

Methyl 4-[(phenylthio)methyl]-3-nitrobenzoate (**1a**). Colorless oil, yield 82%, n_D^{20} 1.570; UV (MeOH): λ_{max} = 226 nm (ε = 34000), ^{1}H NMR (acetone-d_6): δ 3.98 (s, 3 H, CH_3 ester), 4.45 (s, 2 H, CH_2 benzylic), 7.25 (m, 5 H, $H_{2',3',4',5',6'}$), 7.92 (d, 1 H, H_5), 8.18 (d, 1 H, H_6), 8.58 (s, 1 H, H_2). Anal. Calcd. for $C_{15}H_{13}NO_4S$: C, 59.40; H, 4.29; S, 10.56. Found: C, 59.0; H, 4.41; S, 10.72.

Methyl 4-[(4'-methylphenylthio)methyl]-3-nitrobenzoate (**1b**). Colorless oil, yield 86%, n_D^{20} 1.568; UV (MeOH): λ_{max} = 225 nm (ε = 38000); ^{1}H NMR (acetone-d_6): δ 2.25 (s, 3 H, 4'—CH_3), 4.00 (s, 3 H, CH_3 ester), 4.39 (s, 2 H, CH_2 benzylic), 7.12 (d, 2 H, $H_{3',5'}$), 7.45 (d, 2 H, $H_{2',6'}$), 7.90 (d, 1 H, H_5), 8.15 (d, 1 H, H_6), 8.60 (s, 1 H, H_2). Anal. Calcd. for $C_{16}H_{15}NO_4S$: C, 60.56; H, 4.73; S, 10.09. Found: C, 60.70; H, 4.60; S, 9.90.

Methyl 4-[(4'-methoxyphenylthio)methyl]-3-nitrobenzoate (**1c**). Colorless oil, yield 73%, n_D^{20} 1.69; UV (MeOH) λ_{max} = 226 nm (ε = 46600); ^{1}H NMR (acetone-d_6): δ 3.75 (s, 3 H, 4'—OCH_3), 3.90 (s, 3 H, CH_3 ester), 4.35 (s, 2 H, CH_2 benzylic), 6.80 (d, 2 H, $H_{3',5'}$), 7.40 (d, 2 H, $H_{2',6'}$), 7.88 (d, 1 H, H_5), 8.13 (d, 1 H, H_6), 8.55 (s, 1 H, H_2). Anal. Calcd. for $C_{16}H_{15}NO_5S$: C, 57.65; H, 4.50; S, 9.60. Found: C, 57.70; H, 4.40; S, 9.80.

Methyl 4-[(4'-aminophenylthio)methyl]-3-nitrobenzoate (**1d**). Pale yellow oil, yield 65%, n_D^{20} 1.579; UV (MeOH): λ_{max} = 224 nm (ε = 32500); ^{1}H NMR (acetone-d_6): δ 3.15 (s, 2 H, 4'—NH_2), 3.95 (s, 3 H, CH_3 ester); 4.20 (s, 2 H, CH_2 benzylic), 6.72 (d, 2 H, $H_{3',5'}$), 7.25 (d, 2 H, $H_{2',6'}$), 7.82 (d, 1 H, H_5), 8.00 (d, 1 H, H_6), 8.50. (s, 1 H, H_2). Anal. Calcd. for $C_{15}H_{14}N_2O_4S$: C, 56.60; H, 4.40; S, 10.06. Found: C, 56.30; H, 4.50; S, 10.10.

Methyl 4-[(4'-chlorophenylthio)methyl]-3-nitrobenzoate (**1e**). Yellow needles, yield 91%, m.p. 83°C; UV (MeOH): λ_{max} = 227 nm (ε = 34200); ^{1}H NMR (acetone-d_6): δ 3.98 (s, 3 H, CH_3 ester), 4.55 (s, 2 H, CH_2 benzylic), 7.35 (m, 4 H, $H_{2',3',5',6'}$), 7.77 (d, 1 H, H_5), 8.10 (d, 1 H, H_6), 8.54 (s, 1 H, H_2). Anal. Calcd. for $C_{15}H_{12}ClNO_4S$: C, 53.33; H, 3.56; S, 9.49. Found: C, 53.64; H, 3.44; S, 9.45.

Methyl 4-[(4'-bromophenylthio)methyl]-3-nitrobenzoate (**1f**). Yellow crystals, yield 96%, m.p. 78°C; UV (MeOH): λ_{max} = 226 nm (ε = 35300); ^{1}H NMR (acetone-d_6): δ 3.92 (s, 3 H, CH_3 ester), 4.58 (s, 2 H, CH_2 benzylic), 7.12 (d, 2 H, $H_{2',6'}$), 7.38 (d, 2 H, $H_{3',5'}$), 7.68 (d, 1 H, H_5), 8.12 (d, 1 H, H_6), 8.60. (s, 1 H, H_2). Anal. Calcd. for $C_{15}H_{12}BrNO_4S$: C, 47.12; H, 3.14; S, 8.37. Found: C, 47.30; H, 3.20; S, 8.30.

Methyl 4-[(4'-nitrophenylthio)methyl]-3-nitrobenzoate (**1g**). Yellow crystals, yield 80%, m.p. 90°C; UV (MeOH): λ_{max} = 230 nm (ε = 36000); ^{1}H NMR (acetone-d_6): δ 4.05 (s, 3 H, CH_3 ester), 4.81 (s, 2 H, CH_2 benzylic), 7.22 (d, 1 H, H_5), 7.35 (d, 2 H, $H_{2',6'}$) 8.00 (d, 1 H, H_6), 8.18 (d, 2 H, $H_{3',5'}$), 8.64. (s, 1 H, H_2). Anal. Calcd. for $C_{15}H_{12}N_2O_6S$: C, 51.72; H, 3.44; S, 9.19. Found: C, 50.90; H, 3.50; S, 9.20.

Methyl 4-[(2'-carboxyphenylthio)methyl]-3-nitrobenzoate (**1h**). Colorless plates, yield 92%, m.p. 268°C; UV (MeOH): λ_{max} = 227 nm (ε = 18500); ^{1}H NMR (acetone-d_6): δ 4.00 (s, 3 H, CH_3 ester), 4.56 (s, 2 H, CH_2 benzylic), 7.78 (d, 1 H, $H_{3'}$), 7.80 (t, 2 H, $H_{4',5'}$), 7.90 (d, 1 H, $H_{6'}$), 7.96 (d, 1 H, H_5), 8.12 (d, 1 H, H_6), 8.58. (s, 1 H, H_2). Anal. Calcd. for $C_{16}H_{13}NO_6S$: C, 55.33; H, 3.74; S, 9.22. Found: C, 55.60; H, 3.60; S, 9.00.

Methyl 4-[(2'-carbomethoxyphenylthio)methyl]-3-nitrobenzoate (**1i**). Pale yellow crystals, yield 92%, m.p. 68°C; UV (MeOH): λ_{max} = 228 nm (ε = 24500); ^{1}H NMR (acetone-d_6): δ 4.00 (s, 6 H, CH_3 ester), 4.62 (s, 2 H, CH_2 benzylic), 7.80 (d, 1 H, $H_{3'}$), 7.88 (t, 2 H, $H_{4',5'}$), 7.92 (d, 1 H, $H_{6'}$), 8.00 (d, 1 H, H_5), 8.10 (d, 1 H, H_6), 8.62. (s, 1 H, H_2). Anal. Calcd. for $C_{17}H_{15}NO_6S$: C, 56.50; H, 4.15; S, 8.86. Found: C, 56.30; H, 4.30; S, 8.60.

Ethyl 4-[(Phenylthio)methyl]-3-nitrobenzoate (**2a**). Colorless oil; yield 85%, n_D^{20} 1.550; UV (EtOH): λ_{max} = 226 nm (ε = 36400); ^{1}H NMR (acetone-d_6); δ 1.35 (t, 3 H, CH_3 ester), 4.38 (q, 2 H, CH_2 ester), 4.43 (s, 2 H, CH_2 benzylic), 7.28 (m, 4 H, $H_{2',3',4',5',6'}$), 8.05 (d, 1 H, H_5), 8.15 (d, 1 H, H_6), 8.58. (s, 1 H, H_2). Anal. Calcd. for $C_{16}H_{15}NO_4S$: C, 60.56; H, 4.73; S, 10.09. Found: C, 60.10; H, 4.70; S, 9.80.

Ethyl 4-[(4'-methylphenylthio)methyl]-3-nitrobenzoate (**2b**). Colorless oil; yield 74%, $n_D^{20} > 1.70$; UV (EtOH): λ_{max} = 226 nm (ε = 57300); ^{1}H NMR (acetone-d_6): δ 1.32 (t, 3 H, CH_3 ester), 2.28 (s, 3 H, 4'—CH_3), 4.35 (q, 2 H, CH_2 ester), 4.37 (s, 2 H, CH_2 benzylic), 7.14 (d, 2 H, $H_{3',5'}$), 7.32 (d, 2 H, $H_{2',6'}$), 8.00 (d, 1 H, H_5), 8.21 (d, 1 H, H_6), 8.56 (s, 1 H, H_2). Anal. Calcd. for $C_{17}H_{17}NO_4S$: C, 61.63; H, 5.13; S, 9.66. Found: C, 61.20; H, 5.40; S, 10.00.

Ethyl 4-[(4'-methoxyphenylthio)methyl]-3-nitrobenzoate (**2c**). Colorless oil; yield 68%, $n_D^{20} > 1.70$; UV (EtOH): λ_{max} = 227 nm (ε = 47800); ^{1}H NMR (acetone-d_6): δ 1.30 (t, 3 H, CH_3 ester), 3.75 (s, 3 H, 4'—OCH_3), 4.35 (q, 2 H, CH_2 ester), 4.37 (s, 2 H, CH_2 benzylic), 7.22 (d, 2 H, $H_{3',5'}$), 7.45 (d, 2 H, $H_{2',6'}$), 7.95 (d, 1 H, H_5), 8.18 (d, 1 H, H_6), 8.53. (s, 1 H, H_2). Anal. Calcd. for $C_{17}H_{17}NO_5S$: C, 58.78; H, 4.89; S, 9.22. Found: C, 58.40; H, 4.60; S, 8.90.

Ethyl 4-[(4'-aminophenylthio)methyl]-3-nitrobenzoate (**2d**). Yellow oil; yield 62%, $n_D^{20} > 1.70$; UV (EtOH): λ_{max} = 225 nm (ε = 33300); ^{1}H NMR (acetone-d_6): δ 1.32 (t, 3H, CH_3 ester), 3.35 (s, 2 H, 4'—NH_2), 4.28 (q, 2 H, CH_2 ester), 4.31 (s, 2 H, CH_2 benzylic), 7.06 (d, 2 H, $H_{3',5'}$), 7.28 (d, 2 H, $H_{2',6'}$), 7.68 (d, 1 H, H_5), 7.82 (d, 1 H, H_6), 8.43. (s, 1 H, H_2). Anal. Calcd. for $C_{16}H_{16}N_2O_4S$: C, 57.83; H, 4.81; S, 9.63. Found: C, 57.60; H, 4.40; S, 9.30.

Ethyl 4-[(4'-chlorophenylthio)methyl]-3-nitrobenzoate (**2e**). Colorless crystals, yield 92%, m.p. 59°C; UV (EtOH): λ_{max} = 226 nm (ε = 33300); ^{1}H NMR (acetone-d_6); δ 1.39 (t, 3 H, CH_3 ester), 4.38 (q, 2 H, CH_2 ester), 4.51 (s, 2 H, CH_2 benzylic), 7.15 (m, 4 H, $H_{2',3',5',6'}$), 7.65 (d, 1 H, H_5), 8.16 (d, 1 H, H_6), 8.58. (s, 1 H, H_2). Anal. Calcd. for $C_{16}H_{14}ClNO_4S$: C, 54.62; H, 3.98; S, 9.11. Found: C, 55.10; H, 3.90; S, 8.80.

Ethyl 4-[(4'-bromophenylthio)methyl]-3-nitrobenzoate (**2f**). Pale yellow crystals, yield 95%, m.p. 68°C; UV (EtOH): λ_{max} = 228 nm (ε = 34900); ^{1}H NMR (acetone-d_6): δ 1.40 (t, 3 H, CH_3 ester), 4.40 (q, 2 H, CH_2 ester), 4.45 (s, 2 H, CH_2 benzylic), 7.30 (d, 2 H, $H_{2',6'}$), 7.60 (d, 1 H, H_5), 7.76 (d, 2 H, $H_{3',5'}$), 8.10 (d, 1 H, H_6), 8.59. (s, 1 H, H_2). Anal. Calcd. for $C_{16}H_{14}BrNO_4S$: C, 48.48; H, 3.53; S, 8.08. Found: C, 48.50; H, 3.00; S, 7.70.

Ethyl 4-[(4'-nitrophenylthio)methyl]-3-nitrobenzoate (**2g**). Yellow crystals, yield 90%, m.p. 82°C; UV (EtOH): λ_{max} = 229 nm (ε = 34900); ^{1}H NMR (acetone-d_6): δ 1.45 (t, 3 H, CH_3 ester), 4.42 (q, 2 H, CH_2 ester), 4.72 (s, 2 H, CH_2 benzylic), 7.28 (d, 1 H, H_5), 7.38 (d, 2 H, $H_{2',6'}$), 7.93 (d, 2 H, H_6), 8.16 (d, 2 H, $H_{3',5'}$), 8.65. (s, 1 H, H_2). Anal. Calcd. for $C_{16}H_{14}N_2O_6S$: C, 53.03; H, 3.86; S, 8.83. Found C, 53.20; H, 3.90; S, 8.60.

Ethyl 4-[(2'-carboxyphenylthio)methyl]-3-nitrobenzoate (**2h**). Colorless plates, yield 95%, m.p. > 300°C; UV (EtOH): λ_{max} = 217 nm (ε = 42930); ^{1}H NMR (acetone-d_6): δ 1.36 (t, 3 H, CH_3 ester), 4.36 (q, 2 H, CH_2 ester), 4.65 (s, 2 H, CH_2 benzylic), 7.30 (m, 2 H, $H_{4',5'}$), 7.50 (d, 1 H, $H_{6'}$), 7.72 (d, 1 H, H_5), 7.85 (d, 1 H, $H_{3'}$), 8.15. (d, 1 H, H_6), 8.70 (s, 1 H, H_2). Anal. Calcd. for $C_{17}H_{15}NO_6S$: C, 56.50; H, 4.15; S, 8.86. Found: C, 56.60; H, 4.40; S, 8.90.

Ethyl 4-[(2'-carboethoxyphenylthio)methyl]-3-nitrobenzoate (**2i**). Yellow crystals, yield 95%, m.p. 78°C; UV (EtOH): λ_{max} = 223 nm (ε = 13660); ^{1}H NMR (acetone-d_6): δ 1.33, 1.38 (tt, 6 H, $2CH_3$ ester),

4.30, 4.35 (qq, 4 H, $2CH_2$ ester), 4.72 (s, 2 H, CH_2 benzylic), 7.32 (t, 2 H, $H_{4',5'}$), 7.51 (d, 1 H, $H_{6'}$), 7.78 (d, 1H, H_5),7.88 (d, 1 H, $H_{3'}$), 8.12 (d, 1 H, H_6), 8.78. (s, 1 H, H_2). Anal. Calcd. for $C_{19}H_{19}NO_6S$: C, 58.61; H, 4.88; S, 8.22. Found: C, 58.80; H, 4.50; S, 8.60.

Methyl 4-[(phenylthio)methyl] benzoate (**3a**). Colorless plates, yield 90%, m.p. 72°C; UV (MeOH): λ_{max} = 239 nm (ε = 23200); ^{1}H NMR (acetone-d_6): δ 3.82 (s, 3 H, CH_3 ester), 4.21 (s, 2 H, CH_2 benzylic), 7.37 (m, 3 H, $H_{3',4',5'}$) 7.50 (d, 2 H, $H_{3,5}$), 7.58 (d, 2 H, $H_{2',6'}$), 7.95. (d, 2 H, $H_{2,6}$). Anal. Calcd. for $C_{15}H_{14}O_2S$: C, 69.77; H, 5.43; S, 12.40. Found: C, 69.80; H, 4.90; S, 12.40.

Methyl 4-[(4'-methylphenylthio)methyl] benzoate (**3b**). Colorless oil, yield 75%, n_D^{20} 1.558; UV (MeOH): λ_{max} = 240 nm (ε = 22300); ^{1}H NMR (acetone-d_6): δ 2.34 (s, 3 H, 4' —CH_3), 3.88 (s, 3 H, CH_3), 4.14 (s, 2 H, CH_2 benzylic), 7.00 (d, 2 H, $H_{3',5'}$), 7.28 (d, 2 H, $H_{2',6'}$), 7.42 (d, 2 H, $H_{3,5}$), 7.98 (d, 2 H, $H_{2,6}$). Anal. Calcd. for $C_{16}H_{16}O_2S$: C, 70.58; H, 5.88; S, 11.76. Found: C, 70.50; H, 5.70; S, 11.70.

Methyl 4-[(4'-methoxyphenylthio)methyl] benzoate (**3c**): Colorless oil, yield 72%, n_D^{20} 1.587; UV (MeOH): λ_{max} = 242 nm (ε = 23300); ^{1}H NMR (acetone-d_6): δ 3.62 (s, 3 H, 4'—OCH_3 ester), 3.80 (s, 3 H, CH_3 ester), 4.08 (s, 2 H, CH_2 benzylic), 6.92 (d, 2 H, $H_{3',5'}$), 7.18 (d, 2 H, $H_{2',6'}$), 7.26 (d, 2 H, $H_{3,5}$), 7.93. (d, 2 H, $H_{2,6}$). Anal. Calcd. for $C_{16}H_{16}O_3S$: C, 66.67; H, 5.56; S, 11.14. Found: C, 66.80; H, 5.30; S, 11.00.

Methyl 4-[(4'-aminophenylthio)methyl] benzoate (**3d**). Pale brown crystals, yield 66%, m.p. 53°C, UV (MeOH): λ_{max} = 209 nm (ε = 8300); ^{1}H NMR (acetone-d_6): δ 3.32 (s, 2 H, 4'—NH_2), 3.78 (s, 3 H, CH_3 ester), 3.94 (s, 2 H, CH_2 benzylic), 6.78 (d, 2 H, $H_{3',5'}$), 7.32 (d, 2 H, $H_{2',6'}$), 7.26 (d, 2 H, $H_{3,5}$), 8.02. (d, 2 H, $H_{2,6}$). Anal. Calcd. for $C_{15}H_{15}NO_2S$: C, 65.93; H, 5.49; S, 11.72. Found: C, 50.40; H, 5.30; S, 11.70.

Methyl 4-[(4'-chlorophenylthio)methyl] benzoate (**3e**). Colorless needles, yield 90%, m.p. 75°C, UV (MeOH): λ_{max} = 247 nm (ε = 22700); ^{1}H NMR (acetone-d_6): δ 3.88 (s, 3 H, CH_3 ester), 4.92 (s, 2 H, CH_2 benzylic), 7.33 (m, 4 H, $H_{2',3',5',6'}$) 7.42 (d, 2 H, $H_{3,5}$), 7.98. (d, 2 H, $H_{2,6}$). Anal. Calcd. for $C_{15}H_{13}ClO_2S$: C, 61.53; H, 4.44; S, 10.94. Found: C, 61.50; H, 4.00; S, 10.95.

Methyl 4-[(4'-bromophenylthio)methyl] benzoate (**3f**). Colorless crystals, yield 90%, m.p. 95°C, UV (MeOH): λ_{max} = 248 nm (ε = 31200); ^{1}H NMR (acetone-d_6): δ 3.94 (s, 3 H, CH_3 ester), 4.33 (s, 2 H, CH_2 benzylic), 7.38 (d, 2 H, $H_{2',6'}$), 7.45 (d, 2 H, $H_{3,5}$), 7.78 (d, 2 H, $H_{3',5'}$), 8.02. (d, 2 H, $H_{2,6}$). Anal. Calcd. for $C_{15}H_{13}BrO_2S$: C, 53.41; H, 3.86; S, 9.49. Found: C, 53.20; H, 3.60; S, 9.50.

Methyl 4-[(4'-nitrophenylthio)methyl] benzoate (**3g**). Yellow crystals, yield 82%, m.p. 114°C, UV (MeOH): λ_{max} = 253 nm (ε = 33300); ^{1}H NMR (acetone-d_6): δ 4.02 (s, 3 H, CH_3 ester), 4.53 (s, 2 H, CH_2 benzylic), 7.28 (d, 2 H, $H_{3,5}$), 7.62 (d, 2 H, $H_{2',6'}$), 8.00 (d, 2 H, $H_{2,6}$), 8.18. (d, 2 H, $H_{3',5'}$). Anal. Calcd. for $C_{15}H_{13}NO_4S$: C, 59.41; H, 4.29; S, 10.56. Found: C, 59.70; H, 3.80; S, 10.50.

Methyl 4-[(2'-carboxyphenylthio)methyl] benzoate (**3h**). Colorless crystals, yield 80%, m.p. 211°C, UV (MeOH): λ_{max} = 277 nm (ε = 15510); ^{1}H NMR (acetone-d_6): δ 3.95 (s, 3 H, CH_3 ester), 4.37 (s, 2 H, CH_2 benzylic), 7.28 (t, 2 H, $H_{4',5'}$), 7.50 (d, 1 H, $H_{6'}$), 7.82 (d, 2 H, $H_{3,5}$), 7.88 (d, 1 H, H_3), 7.95 (d, 2 H, $H_{2,6}$). Anal. Calcd. for $C_{16}H_{14}O_4S$: C, 63.58; H, 4.64; S, 10.60. Found: C, 63.50; H, 4.20; S, 10.80.

Methyl 4-[(2'-carbomethoxyphenylthio)methyl] benzoate (**3i**). Yellow crystals, yield 80%, m.p. 131°C, UV (MeOH): λ_{max} = 277 nm (ε = 20450); ^{1}H NMR (acetone-d_6): δ 3.92 (s, 6 H, $2CH_3$ ester), 4.32 (s, 2 H, CH_2 benzylic), 7.25 (t, 2 H, $H_{4',5'}$), 7.48 (d, 1 H, $H_{6'}$), 7.75 (d, 2 H, $H_{3,5}$), 7.84 (d, 1 H, $H_{3'}$), 7.90. (d, 2 H, $H_{2,6}$). Anal. Calcd. for $C_{17}H_{16}O_4S$: C, 64.55; H, 5.04; S, 10.13. Found: C, 64.60; H, 4.80; S, 10.20.

Ethyl 4-[(phenylthio)methyl] benzoate (**4a**). Colorless oil, yield 69%, n_D^{20} 1.575; UV (EtOH): λ_{max} = 238 nm (ε = 22850); ^{1}H NMR (acetone-d_6): δ 1.38 (t, 3 H, CH_3 ester), 4.12 (s, 2 H, CH_2 benzylic), 4.36 (q, 2 H, CH_2 ester), 7.19 (m, 5H, $H_{2',3',4',5',6'}$), 7.48 (d, 2 H, $H_{3,5}$), 7.96 (d, 2 H, $H_{2,6}$). Anal. Calcd. for $C_{16}H_{16}O_2S$: C, 70.58; H, 5.88; S, 11.76. Found: C, 70.90; H, 5.70; S, 11.70.

Ethyl 4-[(4'-methylphenylthio)methyl] benzoate (**4b**). Colorless oil, yield 67%, n_D^{20} 1.574; UV (EtOH): λ_{max} = 243 nm (ε = 21500); ^{1}H NMR (acetone-d_6): δ 1.41 (t, 3 H, CH_3 ester), 2.42 (s, 3 H, 4'—CH_3), 4.08 (s, 2 H, CH_2 benzylic), 4.39 (q, 2 H, CH_2 ester), 7.20 (d, 2 H, $H_{3',5'}$), 7.32 (d, 2 H, $H_{2',6'}$), 7.45 (d, 2 H, $H_{3,5}$), 8.04. (d, 2 H, $H_{2,6}$). Anal. Calcd. for $C_{17}H_{18}O_2S$: C, 71.32; H, 6.29; S, 11.18. Found: C, 71.10; H, 6.20; S, 11.2.

Ethyl 4-[(4'-methoxyphenylthio)methyl] benzoate (**4c**). Colorless oil, yield 62%, n_D^{20} 1.585; UV (EtOH): λ_{max} = 242 nm (ε = 23300); ^{1}H NMR (acetone-d_6): δ 1.47 (t, 3 H, CH_3 ester), 3.82 (s, 3 H, 4'—OCH_3), 4.05 (s, 2 H, CH_2 benzylic), 4.41 (q, 2 H, CH_2 ester), 6.98 (d, 2 H, $H_{3',5'}$), 7.29 (d, 2 H, $H_{2',6'}$), 7.41 (d, 2 H, $H_{3,5}$), 8.02. (d, 2 H, $H_{2,6}$). Anal. Calcd. for $C_{17}H_{18}O_3S$: C, 67.55; H, 5.96; S, 10.59. Found: C, 67.90; H, 5.90; S, 10.6.

Ethyl 4-[(4'-aminophenylthio)methyl] benzoate (**4d**). Yellow oil, yield 48%, $n_D^{20} > 1.70$; UV (EtOH): λ_{max} = 208 nm (ε = 11830); ^{1}H NMR (acetone-d_6): δ 1.40 (t, 3 H, CH_3 ester), 3.30 (s, 2 H, 4'—NH_2), 3.92 (s, 2 H, CH_2 benzylic), 4.38 (q, 2 H, CH_2 ester), 7.05 (d, 2 H, $H_{3',5'}$), 7.25 (d, 2 H, $H_{2',6'}$), 7.28 (d, 2 H, $H_{3,5}$), 8.00. (d, 2 H, $H_{2,6}$). Anal. Calcd. for $C_{16}H_{17}NO_2S$: C, 66.90; H, 5.92; S, 11.14. Found: C, 67.20; H, 5.70; S, 11.10.

Ethyl 4-[(4'-chlorophenylthio)methyl] benzoate (**4e**). Colorless plates, yield 90%, m.p. 64°C, UV (MeOH): λ_{max} = 247 nm (ε = 23300); ^{1}H NMR (acetone-d_6): δ 1.45 (t, 3 H, CH_3 ester), 4.18 (s, 2 H, CH_2 benzylic), 4.40 (q, 2 H, CH_2 ester), 7.28 (d, 2 H, $H_{2',6'}$), 7.35 (d, 2 H, $H_{3',5'}$), 7.50 (d, 2 H, $H_{3,5}$), 8.06. (d, 2 H, $H_{2,6}$). Anal. Calcd. for $C_{16}H_{15}ClO_2S$: C, 62.74; H, 4.89; S, 10.44. Found: C, 62.30; H, 4.80; S, 10.10.

Ethyl 4-[(4'-bromophenylthio)methyl] benzoate (**4f**). Colorless crystals, yield 95%, m.p. 86°C, UV (MeOH): λ_{max} = 248 nm (ε = 32200); ^{1}H NMR (acetone-d_6): δ 1.46 (t, 3 H, CH_3 ester), 4.22 (s, 2 H, CH_2 benzylic), 4.42 (q, 2 H, CH_2 ester), 7.34 (d, 2 H, $H_{2',6'}$), 7.48 (d, 2 H, $H_{3',5'}$), 7.42 (d, 2 H, $H_{3,5}$), 7.98. (d, 2 H, $H_{2,6}$). Anal. Calcd. for $C_{16}H_{15}BrO_2S$: C, 54.70; H, 4.27; S, 9.12. Found: C, 55.20; H, 4.40; S, 9.10.

Ethyl 4-[(4'-nitorphenylthio)methyl] benzoate (**4g**). Yellow crystals, yield 84%, m.p. 105°C, UV (MeOH): λ_{max} = 250 nm (ε = 33200); ^{1}H NMR (acetone-d_6): δ 1.42 (t, 3 H, CH_3 ester), 4.32 (s, 2 H, CH_2 benzylic), 4.43 (q, 2 H, CH_2 ester), 7.22 (d, 2 H, $H_{3,5}$), 7.64 (d, 2 H, $H_{2',6'}$), 8.00 (d, 2 H, $H_{3',5'}$), 8.18. (d, 2 H, $H_{2,6}$). Anal. Calcd. for $C_{16}H_{15}NO_4S$: C, 60.56; H, 4.73; S, 10.12. Found: C, 60.40; H, 4.60; S, 10.00.

Ethyl 4-[(2'-carboxyphenylthio)methyl] benzoate (**4h**). Colorless crystals, yield 93%, m.p. 285°C, UV (MeOH): λ_{max} = 223 nm (ε = 23230); ^{1}H NMR (acetone-d_6); δ 1.40 (t, 3 H, CH_3 ester), 4.28 (s, 2 H, CH_2 benzylic), 4.41 (q, 2 H, CH_2 ester), 7.28 (t, 2 H, $H_{4',5'}$), 7.38 (d, 2 H, $H_{3,5}$), 7.50 (d, 1 H, $H_{6'}$), 7.75 (d, 1 H, $H_{3'}$), 8.10. (d, 2 H, $H_{2,6}$). Anal. Calcd. for $C_{17}H_{16}O_4S$: C, 64.55; H, 5.06; S, 10.13. Found: C, 64.90; H, 5.40; S, 10.00.

Ethyl 4-[(2'-carboethyoxyphenylthio)methyl] benzoate (**4j**). Colorless crystals, yield 90%, m.p. 88°C, UV (EtOH): λ_{max} = 223 nm (ε = 23660); ^{1}H NMR (acetone-d_6): δ 1.36, 1.42 (tt, 6 H, 2 CH_3 ester), 4.32 (s, 2 H, CH_2 benzylic), 4.35, 4.38 (qq, 4 H, 2 CH_2 ester), 7.25 (t, 2 H, $H_{4',5'}$), 7.40 (d, 2 H, $H_{3,5}$), 7.46 (d, 1 H, $H_{6'}$), 7.72 (d, 1 H, $H_{3'}$), 8.08. (d, 2 H, $H_{2,6}$). Anal. Calcd. for $C_{19}H_{20}O_4S$: C, 66.27; H, 5.81; S, 9.30. Found: C, 66.60; H, 5.90; S, 9.00.

Action of 5% Sodium Hydroxide Solution. Methyl or ethyl 4-[(4-substituted phenylthio)methyl]-3-nitrobenzoate **1a–i**, **2a–hj**, (0.1 mole) were treated with 5% sodium hydroxide (5 mL) and refluxed for 1 hr. Upon cooling, dilution with water and acidification, a mixture of diaryl disulfide[24–26] (Table II) and 4-methyl-3-nitrobenzoic acid[22] was obtained and separated by fractional crystallization.

TABLE II

Yield % and m.p.s of diaryl disulfides

Disulfide	Yield %	Melting point °C
$(PhS)_2$	90	60 (lit[26] 61°)
$(4\text{-}CH_3\text{-}PhS)_2$	85	58.9° (lit[27] 57°)
$(4\text{-}CH_2OPhS)_2$[a]	70	46°
$(4\text{-Br-}PhS)_2$	95	110° (lit[28] 112°)
$(4\text{-Cl-}OhS)_2$	90	72° (lit[26] 73°)
$(4\text{-}NO_2\text{-}PhS)_2$	93	186° (lit[29] 182°)
$(4\text{-}NH_2\text{-}PhS)_2$	80	87° (lit[30] 85°)
$(2\text{-HOOC-}OhS)_2$	72	288° (lit[28] 290°)

[a]Satistactory sulfur analysis.

The same procedure with methyl and ethyl 4-[(4′-substituted phenylthio)methyl] benzoates, (**3a–i**) and (**4a–hj**), respectively, gave 4-methylbenzoic acid in addition to the corresponding diaryl disulfide.

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