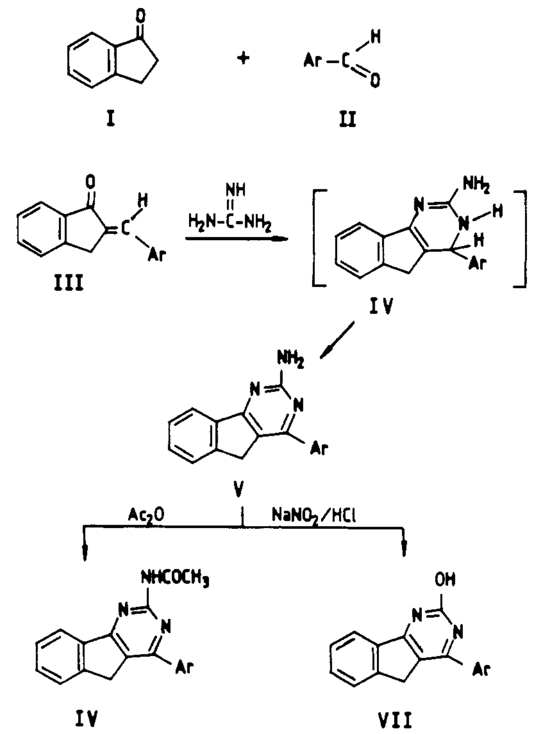
Scheme I



Compound	Ar	Compound	Ar
II-VIIa	C_6H_5	II-VIIf	p-ClC_6H_4
b	p-OCH_3-C_6H_4	g	o-ClC_6H_4
c	m-$OCH_3C_6H_4$	h	1-$C_{10}H_7$
d	p-Br-C_6H_4	i	2-$C_{10}H_7$
e	m-Br-C_6H_4	j	2-C_4H_3S
		k	2-C_4H_3O

itated material was filtered, washed with water, and dried. Crystallization from benzene gave 5*H*-2-amino-4-arylindeno[1,2-*d*]pyrimidines (V).

Acetylation of the 2-Aminopyrimidines (Vf,h). A mixture of the pyrimidine derivatives (1 g) and acetic anhydride (5 mL) was refluxed for 2 h. The product was poured in 30 mL of water-ethanol mixture (1:1) and cooled. The precipitated solid was filtered off. Crystallization from ethanol-water gave the corresponding 5*H*-2-acetamido-4-arylindeno[1,2-*d*]pyrimidines (VIf,h).

Reaction of 2-Aminopyrimidines Vf,h,j with Nitrous Acid. A solution of sodium nitrite (1.5 g) in water (10 mL) was added dropwise to a solution of the pyrimidine derivative (1.0 g) in glacial acetic acid (15 mL). The precipitated solid was crystallized from benzene to give the corresponding 5*H*-4-arylindeno[1,2-*d*]-2(1*H*)-pyrimidinone (VII).

Registry No. I, 83-33-0; IIa, 100-52-7; IIb, 123-11-5; IIc, 591-31-1; IId, 1122-91-4; IIe, 3132-99-8; IIf, 104-88-1; IIg, 89-98-5; IIh, 66-77-3; IIi, 66-99-9; IIj, 98-03-3; IIk, 98-01-1; IIIa, 5706-12-7; IIIb, 5706-14-9; IIIc, 110117-34-5; IIId, 5706-19-4; IIIe, 81975-58-8; IIIf, 5706-17-2; IIIg, 5706-16-1; IIIh, 92882-96-7; IIIi, 92882-97-8; IIIj, 5706-21-8; IIIk, 6072-51-1; Va, 110117-35-6; Vb, 110117-36-7; Vc, 110117-37-8; Vd, 110117-38-9; Ve, 110117-39-0; Vf, 110117-40-3; Vg, 110117-41-4; Vh, 110117-42-5; Vi, 110117-43-6; Vj, 110117-44-7; Vk, 110117-45-8; VIf, 110117-46-9; VIh, 110117-47-0; VIIf, 110117-48-1; VIIh, 110117-49-2; VIIj, 110117-50-5; guanidine hydrochloride, 50-01-1.

Literature Cited

(1) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*; Methuen: London, 1966; p 149.
(2) Fuson, N.; Josien, M. L.; Shelton, E. M. *J. Am. Chem. Soc.* **1954**, *76*, 2526-2633.
(3) El-Rayyes, N. R. *J. Heterocycl. Chem.* **1982**, *19*, 415-419.
(4) French, H. S.; Wiley, L. *J. Am. Chem. Soc.* **1949**, *71*, 3702-3706.
(5) Roth, H. J.; Assadi, F. *Arch. Pharm.* **1970**, *149*, 303-307.
(6) Baltzly, R.; Wiley, L. *J. Am. Chem. Soc.* **1955**, *77*, 624-629.
(7) Braude, A. E.; Sondheimer, F.; Forbes, W. F. *Nature (London)* **1954**, *173*, 117-119.
(8) Abraham, R. J.; Loftus, P. *Proton and Carbon-13 NMR Spectroscopy*; Heyden: London, 1979; p 46.
(9) Baddar, F. G.; Al-Hajjar, F. H.; El-Rayyes, N. R. *J. Heterocycl. Chem.* **1976**, *13*, 257-268.
(10) El-Rayyes, N. R.; Ramadan, H. M. *J. Heterocycl. Chem.* **1987**, *24*, 589.
(11) Brown, D. J.; Short, L. N. *J. Chem. Soc.* **1953**, 331-337.
(12) El-Rayyes, N. R.; Ramadan, H. *J. Heterocycl. Chem.*, in press.

Received for review March 5, 1987. Accepted July 1, 1987. This work is part of the Research Project SC028 sponsored by Research Council, Kuwait University.

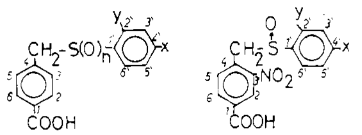
Synthesis and Spectral Studies of Some New Sulfides, Sulfoxides, and Sulfones. 2

Ahmed A. Kassem, Ali A. El-Bardan,* and El-Sayed M. E. Mansour

Chemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt

New substituted benzylphenyl sulfides, sulfoxides, and sulfones have been synthesized. Their structures were confirmed by IR, ^{1}H NMR, and mass spectra.

As a continuation of our interest in substituted benzylphenyl sulfides, sulfones, and sulfoxides, a new series has been synthesized. Sulfides (**1a-h**) and sulfones (**3a-h**) have been prepared by conventional procedures (*1-3*). The sulfoxides were prepared as described in the literature (*6*, *7*). The structures of the synthesized compounds were investigated by IR, ^{1}H NMR, and mass spectra.



n =(1)o ,(2)1 ,(3) 2 (4)

	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	COOH

The mass spectra (*9*, *10*) of **1a**, **1c**, **3a**, and **4b** were studied. The relative intensities of the most prominent peaks in their

0021-9568/87/1732-0483$01.50/0 © 1987 American Chemical Society

Table I. Yields, Melting Points, and ^{1}H NMR Spectra of the Compounds 4-[(Phenylthio)methyl]benzoic Acid (1a) and Its Derivatives 1b–h and 4-[(Phenylsulfonyl)methyl]benzoic Acid (3a) and Its Derivatives 3b–h

				^{1}H NMR (δ, ppm)						
compd	color	yield, %	mp, °C	$-CH_2$	C_2, C_6	C_3, C_5	C_2', C_6'	C_3', C_5'	$-NH_2$	$-CH_3$
1a	white	94	178–80	4.27 (s)	7.79 (d)	7.42 (d)	7.27 (m)	7.27 (m), C_4'		
1b	pale yellow	91	215–7	4.13 (s)	7.79 (d)	7.36 (d)	7.19 (d)	7.07 (d)		2.27 (s)
1c	pale yellow	85	153–5	4.09 (s)	7.83 (d)	7.24 (d)	7.18 (d)	6.72 (d)		3.73 s) (OCH_3)
1d	pale yellow	88	165–8	4.00 (s)	7.75 (d)	7.26 (d)	6.92 (d)	6.39 (d)	4.66 (s)	
1e	white	93	155–6	4.25 (s)	7.82 (d)	7.39 (d)	7.33 (d)	7.30 (d)		
1f	yellow	96	160	4.28 (s)	7.79 (d)	7.19 (d)	7.26 (d)	7.42 (d)		
1g	yellow	97	181–2	4.45 (s)	8.13 (d)	7.23 (d)	7.43 (d)	7.76 (d)		
1h	white	82	310	4.35 (s)	(C_2, C_6, C_3') 7.82 (d)		(C_3, C_5) 7.20 (d)	(C_4', C_5', C_6') 7.33 (m)		
3a	white	92	298	4.75 (s)	7.79 (d)	7.52 (d)	7.60 (d)	7.23 (d), C_4'		
3b	white	89	280	4.73 (s)	7.83 (d)	7.25 (d)	7.59 (d)	7.35 (d)		2.09 (s)
3c	white	78	>300	4.68 (s)	7.79 (d)	7.05 (d)	7.56 (d)	7.23 (d)		3.81 (s) (OCH_3)
3d	yellow	88	274	4.76 (s)	8.30 (d)	7.19 (d)	7.82 (d)	7.75 (d)	4.54 (s)	
3e	white	93	285	4.81 (s)	7.79 (d)	7.26 (d)	7.62 (s)	7.62 (s)		
3f	white	91	>300	4.73 (s)	7.89 (d)	7.19 (d)	7.76 (d)	7.63 (d)		
3g	pale yellow	58	>300	4.99 (s)	7.81 (d)	7.32 (d)	7.61 (d)	8.18 (d)		
3h	white	73	253	4.88 (s)	(C_2, C_6, C_3') 7.76 (2d)		(C3, C_5, C_6') 7.23 (d)		(C_4', C_5') 7.43 (m)	

Table II. Yields, Melting Points, and ^{1}H NMR Spectra of the Compound 4-[(Phenylsulfinyl)methyl]benzoic Acid (2a) and Its Derivatives 2b–h

				^{1}H NMR (δ, ppm)						
compd	color	yield, %	mp, °C	$-CH_2(\delta_A + \delta_B)/2$	C_2, C_6	C_3, C_5	C_2', C_6'	C_3', C_5'	$-NH_2$	$-CH_3$
2a	white	92	241	4.28 (q)	8.00 (d)	7.23 (d)	7.12 (m)	7.12 (m), C_4'		
2b	white	78	253	4.19 (q)	8.10 (d)	7.32 (d)	7.15 (d)	7.00 (d)		2.29 (s)
2c	white	75	239	4.20 (q)	8.03 (d)	7.10 (d)	7.18 (d)	7.00 (d)		3.52 (s) (OCH_3)
2d	pale brown	93	228	4.23 (q)	8.10 (d)	7.21 (d)	7.13 (d)	6.97 (d)	4.15 (s)	
2e	white	91	255	4.29 (q)	8.06 (d)	7.18 (d)	7.12 (m)	7.12 (m)		
2f	pale yellow	95	250	4.30 (q)	7.92 (d)	7.18 (d)	7.12 (d)	7.52 (d)		
2g	yellow	78	281	4.37 (q)	7.92 (d)	7.10 (d)	7.38 (d)	8.12 (d)		
2h	white	72	230	4.36 (q)	(C_2, C_6, C_3') 8.00 (d)	(C_3, C_5, C_6') 7.31 (d)		(C_4', C_5') 7.00 (t)		

Table III. Yields, Melting Points, and ^{1}H NMR Spectra of the Compound 4-[(Phenylsulfinyl)methyl]-3-nitrobenzoic Acid (4a) and Its Derivatives 4b–h

				^{1}H NMR (δ, ppm)							
compd	color	yield, %	mp °C	$-CH_2(\delta_A + \delta_B)/2$	C_2	C_5	C_6	C_2', C_6'	C_3', C_5'	$-NH_2$	$-CH_3$
4a	pale yellow	98	201	4.48 (q)	8.39 (s)	7.23 (d)	8.03 (d)	7.19 (m)	7.19 (m), C_4		
4b	pale yellow	77	206	4.39 (q)	8.33 (s)	7.16 (d)	8.00 (d)	7.00 (m)	7.00 (m)		2.33 (s)
4c	pale yellow	85	199	4.40 (q)	8.33 (s)	7.03 (d)	8.03 (d)	7.29 (d)	7.19 (d)		3.79 (s) (OCH_3)
4d	pale brown	90	228	4.42 (q)	8.39 (s)	6.92 (d)	8.05 (d)	7.26 (d)	7.18 (d)	4.30 (s)	
4e	pale yellow	94	226–7	4.49 (q)	8.36 (s)	7.36 (d)	8.03 (d)	7.23 (m)	7.23 (m)		
4f	white	92	233	4.50 (q)	8.34 (s)	7.81 (d)	8.03 (d)	7.29 (d)	7.69 (d)		
4g	yellow	88	235	4.59 (q)	8.38 (s)	7.15 (d)	8.00 (d)	7.56 (d)	8.26 (d)		
4h	white	93	195–7	4.58 (q)	8.18 (s)	(C_6, C_3') 7.86 (d)	(C_5, C_6') 7.46 (d)	(C_4', C_5') 7.07 (m)			

fragmentation patterns are recorded in Tables IV and V.

The IR spectra of all the compounds studied in the present work contained a broad band at 3100 cm^{-1} (–OH) and a sharp band at 1680–1700 cm^{-1} (C=O). In the case of sulfides, the spectrum showed the characteristic stretching band of the (C–S) at 630–650 cm^{-1}. The sulfones exhibited strong absorption bands at 1350 and 1150 cm^{-1} (SO_2). The sulfoxides showed in their IR spectra, besides others, an absorption band at 1010–1035 cm^{-1} (SO).

Due to the diastereotropic benzylic protons of the sulfoxides **2a–h**, they showed an AB ^{1}H NMR quartet (*3*, *7*, *8*) centered at $(\delta A + \delta B)/2 = 4.19–4.37$, and for the sulfoxides **4a–h**, at $(\delta A + \delta B)/2 = 4.39–4.59$.

Experimental Section

Melting points are uncorrected. Infrared spectra were recorded on a Pye Unicam Cambridge Sp 3-200 instrument, ^{1}H NMR spectra on a Varian XL 200 with Me_4Si as internal standard in DMSO-d_6 solvent, and mass spectra on a Varian Mat. GMbH CH 7. Elemental analyses were performed by the firms Beller, Göttingen, and Pascher, Bonn, West Germany. The found elemental analysis data were in excellent agreement with those calculated.

General Procedure for the Synthesis of Sulfides 1a–h. 4-Chloromethylbenzoic acid (*4*, *5*) (0.1 mol) in ethanol and the sodium salt of the thiol compound (Aldrich Chemical Co.) (0.1

Table IV. Relative Intensities of the Most Prominent Peaks in the Mass Spectra of 4-[(Phenylthio)methyl]benzoic Acid (1a) and 4-[(4′-Methoxyphenylthio)methyl]benzoic Acid (1c)

m/*e*	rel intens, %	*m*/*e*	rel intens, %
244	16.08	109	2.15
136	100.00	91	50.74
135	14.62	77	3.43
119	36.26	65	8.68
110	8.14		
1c			
274	82.34	107	12.45
139	100.00	92	8.75
136	10.24	91	6.26
135	12.68	65	4.11
119	5.36		

Table V. Relative Intensities of the Most Prominent Peaks in the Mass Spectra of 4-[(Phenylsulfonyl)methyl]benzoic Acid (3a) and 4-[(4′-Methylphenylsulfinyl)methyl]-3-nitrobenzoic Acid (4b)

m/*e*	rel intens, %	*m*/*e*	rel intens, %
3a			
276	8.36	135	100.00
199	2.54	121	3.76
167	6.52	119	32.18
166	47.81	118	10.21
149	26.32	91	42.17
136	94.16	77	8.38
4b			
319	2.46	136	4.24
303	2.05	135	1.86
246	6.48	124	17.86
180	78.54	123	11.32
164	8.52	119	1.65
163	2.43	91	44.38
140	24.82	89	6.53
139	100.00		

mol) were refluxed for 1–2 h. Cooling, dilution, and acidification with aqueous hydrochloric acid (in the case of **1d**, acidification with acetic acid) gave a solid, which was purified by crystallization from aqueous ethanol.

General Procedure for the Synthesis of Sulfoxides. The sulfoxides **2a–h** can be prepared by oxidation of the sulfides **1a–h** with 1 equiv of *m*-chloroperbenzoic acid (Aldrich) in chloroform at −10 °c for 24 h. The solid sulfoxide was purified by crystallization from aqueous dioxane. The sulfoxides **4a–h** can be prepared by oxidation of the corresponding nitrosulfides (**1a–h**) (*1*) under the same conditions.

General Procedure for the Synthesis of Sulfones 3a–h. The sulfides **1a–h** were treated in a mixture of acetic acid (60%)–water (40%) and acidified to 3 M with sulfuric acid. An excess of 30% hydrogen peroxide was added dropwise, and at the end of the addition precipitation occurred. The mixture was refluxed for 24 h before dilution with water. The product was purified by crystallization from aqueous dioxane.

The yields, melting points, and the ^{1}H NMR data of the prepared compounds are shown in Tables I, II, and III.

Registry No. **1a**, 88382-49-4; **1b**, 88382-50-7; **1c**, 110046-23-6; **1d**, 110046-24-7; **1e**, 88382-51-8; **1f**, 110046-25-8; **1g**, 110046-26-9; **1h**, 110046-27-0; **2a**, 110046-28-1; **2b**, 110046-29-2; **2c**, 110046-30-5; **2d**, 110046-31-6; **2e**, 110046-32-7; **2f**, 110046-33-8; **2g**, 110046-34-9; **2h**, 110046-35-0; **3a**, 71964-92-6; **3b**, 110046-36-1; **3c**, 110046-37-2; **3d**, 110046-38-3; **3e**, 110046-39-4; **3f**, 110046-40-7; **3g**, 110046-41-8; **3h**, 110046-42-9; **4a**, 110046-43-0; **4b**, 110046-44-1; **4c**, 110046-45-2; **4d**, 110046-46-3; **4e**, 110046-47-4; **4f**, 110046-48-5; **4g**, 110046-49-6; **4h**, 110046-50-9; C_6H_5SNa, 930-69-8; 4-$H_3CC_6H_4SNa$, 10486-08-5; 4-$H_3COC_6H_4SNa$, 19488-09-6; 4-$H_2NC_6H_4SNa$, 6976-04-1; 4-ClC_6H_4SNa, 18803-44-6; 4-BrC_6H_4SNa, 13457-82-4; 4-$O_2NC_6H_4SNa$, 13113-79-6; 2-$HO_2CC_6H_4SNa$, 134-23-6; 4-$ClCH_2C_6H_4CO_2H$, 1642-81-5.

Literature Cited

(1) Kassem, A. A.; El-Bardan, A. A. *J. Chem. Eng. Data* **1986**, *31*, 496.
(2) Schönberg, A.; Iskander, Y. *J. Chem. Soc.* **1942**, 90–95.
(3) Russel, G. A.; Pecoraro, J. M. *J. Org. Chem.* **1979**, *44*, 3990.
(4) *Chem. Abstr.* **1970**, *72*, 332; 89881 V.
(5) El-Bardan A. A. Ph.D. Dissertation, University of Alexandria, Alexandria, Egypt, 1985.
(6) Russel, G. A.; Ochrymowez, L. A. *J. Org. Chem.* **1970**, *35* 2106.
(7) Nishio, M. *Chem. Pharm. Bull. Jpn.* **1962**, *17*, 262.
(8) Nishio, M. *Chem. Pharm. Bull. Jpn.* **1967**, *15*, 1609.
(9) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; Wiley: New York, 1981.
(10) Mclafferty, F. M. *Interpretation of Mass Spectra*; Benjamin: New York, 1966.

Received for review December 17, 1986. Accepted June 23, 1987.