Registry No. **1**, 91785-84-1; **2**, 91785-88-5; **3**, 91785-85-2; **4**, 91809-71-1; **5**, 91809-72-2; **6**, 91785-86-3; **7**, 91809-70-0; **8**, 91785-87-4; A, 2524-64-3; B, 6630-13-3; C_6H_5OH, 108-95-2; CH_3–*o*-C_6H_4–OH, 95-48-7; 4-chloro-3-methylphenol, 59-50-7; 2-methoxy-4-*n*-propylphenol, 2785-87-7; 4-(2,3-dichloropropyl)-2-methoxyphenol, 81480-43-5.

Literature Cited

(1) Zalkind, Y. S.; Dmitrieva, E. C.; *Plast. Massui*. **1934**, *4*, 28.
(2) Sullivan, J. D. U.S. Patent Appl. 98 877, 1970; *Chem. Abstr*. **1972**, *77*, 126221f.
(3) Kharlampovich, G. D.; Aksenova, T. F. *Khim. Prod. Koksovaniya Uglei Vestoka SSSR* **1965**, *3*, 180.
(4) Ohashi, K. Japan Patent 7660, 1951; *Chem. Abstr*. **1954**, *48*, 1415f.
(5) Raley, C. F. U.S. Patent 2 844 582, 1958; *Chem. Abstr*. **1959**, *53*, 3250i.
(6) Iovu, M.; Voina, E. *Fac. Pharm. Bucharest, Rom. Rev. Roum. Chim*. **1976**, *21*(3), 447.
(7) Celluloid Corp. Brit. British Patent 455 014, 1936; *Chem. Abstr*. **1937**, *31*, 1427⁷.
(8) Wilson, F. S. U.S. Patent 2 960 524, 1960; *Chem. Abstr*. **1961**, *55*, 8354e.
(9) Hoeflake, J. M. A. *Recl. Trav. Chim*. **1916**, *36*, 24.
(10) Holtschmidt, H.; Wilms, H. U.S. Patent 301 304 9, 1961; *Chem. Abstr*. **1962**, *57*, 4594i.
(11) Thomas, L. C.; Chittenden, R. A. *Chem. Ind*. **1961**, 1913.
(12) Nyquist, R. A. *Appl. Spectrosc*. **1957**, *11*, 161.
(13) Siddall, T. H.; Prohaska, C. A. *J. Am. Chem. Soc*. **1962**, *84*, 3467.
(14) Damico, J. N. *J. Assoc. Off. Anal. Chem*. **1966**; *49*(5), 1027.
(15) Szalontai, G. *J. Chromatogr*. **1976**, *124*(1), 9.
(16) Moskovskikh, V. V.; Kharlampovich, G. D.; Isaenko, L. A. *Zh. Fiz. Khim*. **1970**, *44*(11), 2891.
(17) Bhagat, S. D.; Mathur, R. K.; Siddhanta, N. N. *J. Chem. Eng. Data* **1982**, *27*, 209.

Received for review June 1, 1987. Revised October 20, 1987. Accepted July 13, 1988.

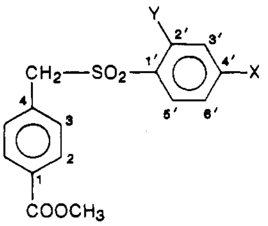
Synthesis and Spectral Studies of Some Alkyl [(Substituted Phenylsulfonyl)methyl]benzoate Derivatives. 3

Ali A. El-Bardan,* Ezzat A. Hamed, and Esmat F. Saad

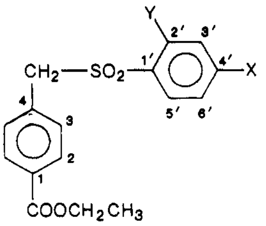
Chemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt

The synthesis, IR spectra, and proton NMR spectra of some alkyl [(substituted phenylsulfonyl)methyl]benzoate derivatives are reported.

As a continuation of our interest in substituted benzylphenyl sulfides and sulfones (*1–4*), a new series of methyl (**1a–h**) and ethyl (**2a–h**) [(substituted phenylsulfonyl)methyl]benzoates have been synthesized.



1



2

	X	Y
a	H	H
b	CH_3	H
c	OCH_3	H
d	NH_2	H

	X	Y
e	Cl	H
f	Br	H
g	NO_2	H
h	H	COOR

Experimental Section

Melting points are uncorrected. Infrared spectra (KBr pellets) were measured on a Pye Unicam Cambridge SP3-200 instrument and ^{1}H NMR spectra (acetone-d_6) on Varian XL200 with Me_4Si as internal standard. Elemental analyses were carried out in Cairo University, Egypt. The found elemental analysis data for carbon, hydrogen, and sulfur were in excellent agreement with those calculated.

General Procedure for the Synthesis of Methyl and Ethyl [(Substituted Phenylsulfonyl)methyl]benzoate. The sulfides and sulfones were prepared by previously reported procedures (*1*, *2*).

The sulfone esters **1a–h** and **2a–h** 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. The cooled reaction mixture was diluted with water and then washed with sodium bicarbonate solution. The solid products were recrystallized from dilute ethanol.

Methyl 4-[(Phenylsulfonyl)methyl]benzoate (1a). White crystals: yield 86%; mp 60–1 °C; ^{1}H NMR δ 3.92 (s, methyl ester group, 3 H), 4.68 (s, CH_2, 2 H), 7.85 (d, C_2 and C_6, 2 H), 7.48 (d, C_3 and C_5, 2 H), 7.64 (d, C_2' and C_6', 2 H), 7.51 (t, C_3', C_4', and C_5', 3 H).

Methyl 4-[(4′-Tolylsulfonyl)methyl]benzoate (1b). White solid: yield 83%; mp 156–7 °C; ^{1}H NMR δ 2.45 (s, CH_3, 3 H), 3.90 (s, methyl ester group, 3 H), 4.65 (s, CH_2, 2 H), 7.98 (d, C_2 and C_6, 2 H), 7.35 (d, C_3 and C_5, 2 H), 7.58 (d, C_2' and C_6', 2 H), 7.25 (d, C_3' and C_5', 2 H).

Methyl 4-[((4′-Methoxyphenyl)sulfonyl)methyl]benzoate (1c). White solid: yield 81%; mp 145–7 °C; ^{1}H NMR δ 3.85 (s, OCH_3, 3 H), 3.90 (s, methyl ester group, 3 H), 4.58 (s, CH_2, 2 H), 7.92 (d, C_2 and C_6, 2 H), 7.03 (d, C_3 and C_5, 2 H), 7.60 (d, C_2' and C_6', 2 H), 7.35 (d, C_3' and C_5', 2 H).

Methyl 4-[((4′-Aminophenyl)sulfonyl)methyl]benzoate (1d). Yellow solid: yield 76%; mp 175–6 °C; ^{1}H NMR δ 3.90 (s, methyl ester group, 3 H), 4.48 (s, NH_2, 2 H), 4.82 (s, CH_2, 2 H), 8.20 (d, C_2 and C_6, 2 H), 7.88 (d, C_3 and C_5, 2 H), 8.00 (d, C_2' and C_6', 2 H), 7.37 (d, C_3' and C_5', 2 H).

Methyl 4-[((4′-Chlorophenyl)sulfonyl)methyl]benzoate (1e). White crystals: yield 91%; mp 134–5 °C; ^{1}H NMR δ 3.82 (s, methyl ester group, 3 H), 4.70 (s, CH_2, 2 H), 7.81 (d, C_2 and C_6, 2 H), 7.19 (d, C_3 and C_5, 2 H), 7.72 (d, C_3' and C_5', 2 H), 7.57 (d, C_2' and C_6', 2 H).

Methyl 4-[((4′-Bromophenyl)sulfonyl)methyl]benzoate (1f). White solid: yield 94%; mp 152–4 °C; ^{1}H NMR δ 3.78 (s, methyl ester group, 3 H), 4.73 (s, CH_2, 2 H), 7.85 (d, C_2 and C_6, 2 H), 7.25 (d, C_3 and C_5, 2 H), 7.58 (d, C_2' and C_6', 2 H), 7.76 (d, C_3' and C_5', 2 H).

Methyl 4-[((4′-Nitrophenyl)sulfonyl)methyl]benzoate (1g). Yellow solid: yield 96%; mp 181–2 °C; ^{1}H NMR δ 3.86 (s, methyl ester group, 3 H), 4.92 (s, CH_2, 2 H), 8.22 (d, C_2 and C_6, 2 H), 7.38 (d, C_3 and C_5, 2 H), 7.90 (d, C_2' and C_6', 2 H), 7.98 (d, C_3' and C_5', 2 H).

Methyl 4-[((2′-Carbomethoxyphenyl)sulfonyl)methyl]benzoate (1h). White solid: yield 82%; mp 148–9 °C; ^{1}H

0021-9568/89/1734-0133$01.50/0 © 1989 American Chemical Society

NMR δ 3.88 (s, methyl ester groups, 6 H), 4.85 (s, CH_2, 2 H), 7.92 (d, C_2 and C_6, 2 H), 7.84 (d, C_3', 1 H), 7.45 (d, C_3 and C_5, 2 H), 7.52 (m, C_4', C_5', and C_6', 3 H).

***Ethyl 4-[(Phenylsulfonyl)methyl]benzoate* (*2a*).** White solid: yield 89%; mp 158–9 °C; ^1H NMR δ 1.35 (t, methyl ester group, 3 H), 4.32 (q, methylene ester group, 2 H), 4.63 (s, CH_2, 2 H), 7.92 (d, C_2 and C_6, 2 H), 7.34 (d, C_3 and C_5, 2 H), 7.57 (t, C_3', C_4', and C_5', 3 H), 7.71 (d, C_2' and C_6', 2 H).

***Ethyl 4-[(4′-Tolylsulfonyl)methyl]benzoate* (*2b*).** White solid: yield 81%; mp 123–4 °C; ^1H NMR δ 1.38 (t, methyl ester group, 3 H), 4.36 (q, methylene ester group, 2 H), 2.42 (s, CH_3, 3 H), 4.58 (s, CH_2, 2 H), 7.98 (d, C_2 and C_6, 2 H), 7.57 (d, C_3 and C_5, 2 H), 7.82 (d, C_2' and C_6', 2 H), 7.35 (d, C_3' and C_5', 2 H).

***Ethyl 4-[((4′-Methoxyphenyl)sulfonyl)methyl]benzoate* (*2c*).** White solid: yield 73%; mp 149–50 °C; ^1H NMR δ 1.38 (t, methyl ester group, 3 H), 4.37 (q, methylene ester group, 2 H), 3.90 (s, OCH_3, 3 H), 4.59 (s, CH_2, 2 H), 7.90 (d, C_2 and C_6, 2 H), 7.05 (d, C_3 and C_5, 2 H), 7.60 (d, C_2' and C_6', 2 H), 7.32 (d, C_3' and C_5', 2 H).

***Ethyl 4-[((4′-Aminophenyl)sulfonyl)methyl]benzoate* (*2d*).** Deep yellow solid: yield 78%, mp 154–5 °C; ^1H NMR δ 1.38 (t, methyl ester group, 3 H), 4.34 (q, methylene ester group, 2 H), 4.52 (s, NH_2, 2 H), 4.62 (s, CH_2, 2 H), 8.19 (d, C_2 and C_6, 2 H), 7.82 (d, C_3 and C_5, 2 H), 8.00 (d, C_2' and C_6', 2 H), 7.32 (d, C_3' and C_5', 2 H).

***Ethyl 4-[((4′-Chlorophenyl)sulfonyl)methyl]benzoate* (*2e*).** White solid: yield 91%, mp 169–70 °C, ^1H NMR δ 1.38 (t, methyl ester group, 3 H), 4.37 (q, methylene ester group, 2 H), 4.68 (s, CH_2, 2 H), 7.92 (d, C_2 and C_6, 2 H), 7.31 (d, C_3 and C_5, 2 H), 7.70 (d, C_2' and C_6', 2 H), 7.58 (d, C_3' and C_5', 2 H).

***Ethyl 4-[((4′-Bromophenyl)sulfonyl)methyl]benzoate* (*2f*).** White solid: yield 88%; mp 181 °C; ^1H NMR δ 1.38 (t, methyl ester group, 3 H), 4.34 (q, methylene ester group, 2 H), 4.70 (s, CH_2, 2 H), 8.00 (d, C_2 and C_6, 2 H), 7.39 (d, C_3 and C_5, 2 H), 7.76 (d, C_2' and C_6', 2 H), 7.65 (d, C_3' and C_5', 2 H).

***Ethyl 4-[((4′-Nitrophenyl)sulfonyl)methyl]benzoate* (*2g*).** Pale yellow solid: yield 92%; mp 159–60 °C; ^1H NMR δ 1.38 (t, methyl ester group, 3 H), 4.35 (q, methylene ester group, 2 H), 4.82 (s, CH_2, 2 H), 8.39 (d, C_2 and C_6, 2 H), 7.38 (d, C_3 and C_5, 2 H), 8.70 (d, C_2' and C_6', 2 H), 8.79 (d, C_3' and C_5', 2 H).

***Ethyl 4-[((2′-Carbethoxyphenyl)sulfonyl)methyl]benzoate* (*2h*).** White solid: yield 86%; mp 101–2 °C; ^1H NMR δ 1.40 (t, methyl ester groups, 6 H), 4.32 (q, methylene ester groups, 4 H); 4.86 (s, CH_2, 2 H), 7.78 (d, C_2 and C_6, 2 H), 7.76 (d, C_3', 1 H), 7.32 (d, C_3 and C_5, 2 H), 7.48 (m, C_4', C_5', and C_6', 3 H).

Registry No. **1a**, 59584-27-9; **1b**, 117687-51-1; **1c**, 117687-52-2; **1d**, 117687-53-3; **1e**, 117687-54-4; **1f**, 117687-55-5; **1g**, 117687-56-6; **1h**, 117687-57-7; **2a**, 56571-79-0; **2b**, 117687-58-8; **2c**, 117687-59-9; **2d**, 117687-60-2; **2e**, 117687-61-3; **2f**, 117687-62-4; **2g**, 117687-63-5; **2h**, 117687-64-6; 4-[(phenylsulfonyl)methyl]benzoic acid, 71964-92-6; 4-[(4′-tolylsulfonyl)methyl]benzoic acid, 110046-36-1; 4-[((4′-methoxyphenyl)sulfonyl)methyl]benzoic acid, 110046-37-2; 4-[((4′-aminophenyl)sulfonyl)methyl]benzoic acid, 110046-38-3; 4-[((4′-chlorophenyl)sulfonyl)methyl]benzoic acid, 110046-39-4; 4-[((4′-bromophenyl)sulfonyl)methyl]benzoic acid, 110046-40-7; 4-[((4′-nitrophenyl)sulfonyl)methyl]benzoic acid, 110046-41-8; 4-[((2′-carboxyphenyl)sulfonyl)methyl]benzoic acid, 110046-42-9.

Literature Cited

(1) Kassem, A.; El-Bardan, A. *J. Chem. Eng. Data* **1986**, *31*, 496.
(2) Kassem, A.; El-Bardan, A.; Mansour, S. *J. Chem. Eng. Data* **1987**, *32*, 483.
(3) Shöenberg, A.; Iskander, Y. *J. Chem. Soc.* **1942**, 90–95.
(4) Russell, G. A.; Pecoraro, J. M. *J. Org. Chem.* **1979**, *44*, 3990.

Received for review March 28, 1988. Revised July 22, 1988. Accepted August 26, 1988.

New and Convenient Synthesis of Indeno[2,1-*c*]quinoline Derivatives

Mumtaz A. Quraishi* and Som N. Dhawan

Department of Applied Chemistry, Institute of Technology, Banaras Hindu University, Varanasi 221 005, India

2-Propanoylindane-1,3-dione (I) was condensed with aniline and three isomeric toluidines to give the corresponding anils (IIa–d), which on treatment with polyphosphoric acid afforded the corresponding 6-ethylindeno[2,1-*c*]quinolin-7(7*H*)-ones (IIIa–d). The structures of these were established by elemental analyses and IR and ^1H NMR spectral data.

Introduction

The reported (*1–4*) biological activity of azafluorenes and their benzoanalogues (indenoquinolines) led to the elaboration of few synthetic procedures for building up of these aza hydrocarbons (*5–11*). However, the syntheses of indenoquinolines are either too lengthy or commence with substrates which are not readily available. Moreover, there appears to be no report on the synthesis of indeno[2,1-*c*]quinolines bearing an alkyl group at C-6. The present paper describes a convenient synthesis of indeno[2,1-c]quinolin-7(7*H*)-ones (IIIa–d) (Scheme I).

2-Propanoylindane-1,3-dione (I) upon refluxing with aniline and three isomeric toluidines in ethanol gave the corresponding anils (IIa–d) in excellent yields. The structures of these were confirmed by ^1H NMR spectral data (Table I). The IR spectrum of IIb shows absorptions at 1690 (C=O) and 1630 cm^{-1} (C=N). ^1H NMR spectra of these compounds revealed the presence of enolic H (Table I). The anils (IIa–d) on treatment with polyphosphoric acid (PPA) yielded the corresponding 6-ethylindeno[2,1-*c*]quinolin-7(7*H*)-ones (IIIa–d). Such cyclization reactions catalyzed by PPA are reported in the case of α-(1,3-dioxocyclohexyl-2-yl)ethylideneanilines (*12*). The structures of these (IIIa–d) were established by ^1H NMR spectral data (Table I). The IR spectrum of IIIb exhibits absorption at

---

* Address correspondence to this author at G/1, Arvind Colony, Banaras Hindu University, Varanasi 221 005, India.

0021-9568/89/1734-0134$01.50/0 © 1989 American Chemical Society