

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, 2524-84-3; B, 6630-13-3; C₆H₅OH, 108-95-2; CH₃-o-C₆H₄-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.

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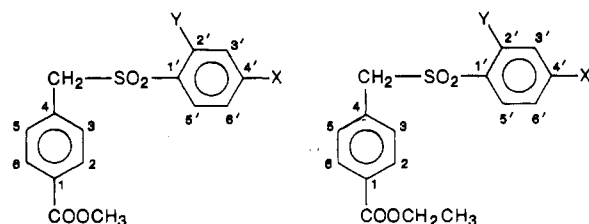
Synthesis and Spectral Studies of Some Alkyl [(Substituted Phenylsulfonyl)methyl]benzoate Derivatives. 3

All 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	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

Experimental Section

Melting points are uncorrected. Infrared spectra (KBr pellets) were measured on a Pye Unicam Cambridge SP3-200 instrument and ¹H NMR spectra (acetone-*d*₆) on Varian XL200 with Me₄Si 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; ¹H NMR δ 3.92 (s, methyl ester group, 3 H), 4.68 (s, CH₂, 2 H), 7.85 (d, C₂ and C₆, 2 H), 7.48 (d, C₃ and C₅, 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; ¹H NMR δ 2.45 (s, CH₃, 3 H), 3.90 (s, methyl ester group, 3 H), 4.65 (s, CH₂, 2 H), 7.98 (d, C₂ and C₆, 2 H), 7.35 (d, C₃ and C₅, 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; ¹H NMR δ 3.85 (s, OCH₃, 3 H), 3.90 (s, methyl ester group, 3 H), 4.58 (s, CH₂, 2 H), 7.92 (d, C₂ and C₆, 2 H), 7.03 (d, C₃ and C₅, 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; ¹H NMR δ 3.90 (s, methyl ester group, 3 H), 4.48 (s, NH₂, 2 H), 4.82 (s, CH₂, 2 H), 8.20 (d, C₂ and C₆, 2 H), 7.88 (d, C₃ and C₅, 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; ¹H NMR δ 3.82 (s, methyl ester group, 3 H), 4.70 (s, CH₂, 2 H), 7.81 (d, C₂ and C₆, 2 H), 7.19 (d, C₃ and C₅, 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; ¹H NMR δ 3.78 (s, methyl ester group, 3 H), 4.73 (s, CH₂, 2 H), 7.85 (d, C₂ and C₆, 2 H), 7.25 (d, C₃ and C₅, 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; ¹H NMR δ 3.86 (s, methyl ester group, 3 H), 4.92 (s, CH₂, 2 H), 8.22 (d, C₂ and C₆, 2 H), 7.38 (d, C₃ and C₅, 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; ¹H

NMR δ 3.88 (s, methyl ester groups, 6 H), 4.85 (s, CH₂, 2 H), 7.92 (d, C₂ and C₆, 2 H), 7.84 (d, C_{3'}, 1 H), 7.45 (d, C₃ and C₅, 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, CH₂, 2 H), 7.92 (d, C₂ and C₆, 2 H), 7.34 (d, C₃ and C₅, 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, CH₃, 3 H), 4.58 (s, CH₂, 2 H), 7.98 (d, C₂ and C₆, 2 H), 7.57 (d, C₃ and C₅, 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, OCH₃, 3 H), 4.59 (s, CH₂, 2 H), 7.90 (d, C₂ and C₆, 2 H), 7.05 (d, C₃ and C₅, 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, NH₂, 2 H), 4.62 (s, CH₂, 2 H), 8.19 (d, C₂ and C₆, 2 H), 7.82 (d, C₃ and C₅, 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, CH₂, 2 H), 7.92 (d, C₂ and C₆, 2 H), 7.31 (d, C₃ and C₅, 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, CH₂, 2 H), 8.00 (d, C₂ and C₆, 2 H), 7.39 (d, C₃ and C₅, 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, CH₂, 2 H), 8.39 (d, C₂ and C₆, 2 H), 7.38 (d, C₃ and C₅, 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'-Carboxyphenyl)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, CH₂, 2 H), 7.78 (d, C₂ and C₆, 2 H), 7.76 (d, C_{3'}, 1 H), 7.32 (d, C₃ and C₅, 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.

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

Mumtaz A. Quralshi* 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(7H)-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 indeno-

quinolines 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(7H)-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(7H)-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.