

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

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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).

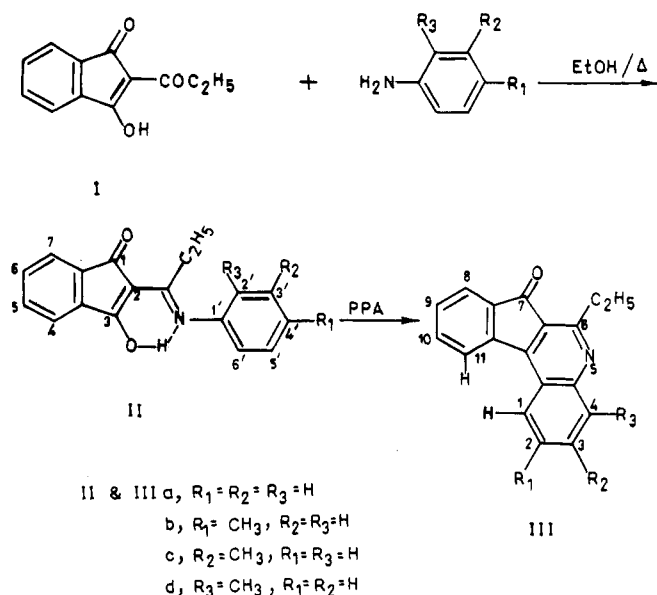
2-Propanoylindane-1,3-dione (I) upon refluxing with aniline and three isomeric toluidines in ethanol gave the corresponding anils (IIa-d) in excellent yields. The structures of these were confirmed by ¹H NMR spectral data (Table I). The IR spectrum of IIb shows absorptions at 1690 (C=O) and 1630 cm⁻¹ (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

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Table I. Characterization Data of Compounds II and III

no.	mp, °C	yield, %	$R_f \times 100$	$^1\text{H NMR}$ (CDCl_3), ppm
IIa	139	76	55	1.22 (t, 3 H, $J = 7$ Hz, $\text{CH}_2\text{-CH}_3$), 2.95 (q, 2 H, $J = 7$ Hz, CH_2), 7.15–7.90 (9 H, ArH), 12.35 (br s, 1 H, H-3 enolic, exchangeable with D_2O)
IIb	130	80	56	1.25 (t, 3 H, CH_3), 2.38 (s, 3 H, C-4' CH_3), 3.00 (d, 2 H, CH_2), 7.12 (d, 2 H, $J = 8$ Hz, H-2', H-6'), 7.27 (d, 2 H, $J = 8$ Hz, H-3', H-5'), 7.50–7.87 (m, 4 H, ArH), 12.25 (br s, 1 H, H-3 enolic, exchangeable with D_2O)
IIc	122	83	54	1.25 (t, 3 H, CH_3), 2.42 (s, 3 H, C-3' CH_3), 3.00 (q, 2 H, CH_2), 7.05–7.80 (m, 8 H, ArH), 12.15 (br s, 1 H, H-3 enolic, exchangeable with D_2O)
IId	136	82	53	1.20 (t, 3 H, CH_3), 2.35 (s, 3 H, C-2' CH_3), 2.95 (q, 2 H, $J = 7$ Hz, CH_2), 7.20–7.80 (m, 8 H, ArH), 12.15 (br s, 1 H, H-3 enolic, exchangeable with D_2O)
IIIa	118	55	52	1.35 (t, 3 H, $\text{CH}_2\text{-CH}_3$), 3.30 (q, 2 H, CH_2), 7.25–7.70 (m, 5 H, ArH), 7.75–8.05 (dd, 2 H, $J = 8$ and 2.5 Hz, H-4, H-11), 8.15 (d, 1 H, $J = 8$ Hz, H-1)
IIIb	113	60	54	1.35 (t, 3 H, $\text{CH}_2\text{-CH}_3$), 2.52 (s, 3 H, C-2 CH_3), 3.35 (q, 2 H, $J = 7$ Hz, CH_2), 7.40–7.70 (m, 4 H, ArH), 7.80–7.95 (m, 2 H, H-4, H-11), 8.10 (1 H, $J = 2.5$ Hz, H-1)
IIIc	115	45	51	1.35 (t, 3 H, $J = 7$ Hz, $\text{CH}_2\text{-CH}_3$), 2.45 (s, 3 H, C-3 CH_3), 3.30 (q, 2 H, CH_2), 7.2–7.95 (m, 6 H, ArH), 8.05 (d, 1 H, $J = 8$ Hz, H-1)
IIId	142	48	50	1.37 (t, 3 H, $J = 7$ Hz, $\text{CH}_2\text{-CH}_3$), 2.72 (s, 3 H, C-4 CH_3), 3.35 (q, 3 H, CH_2), 7.15–7.75 (m, 5 H, ArH), 7.90 (dd, 1 H, $J = 8$ and 2.5 Hz, H-11), 8.15 (dd, $J = 8$ and 2.5 Hz, H-1)

Scheme I



1700 cm^{-1} indicative of a $\text{C}=\text{O}$ group.

Experimental Section

All the melting points are uncorrected. IR spectra in KBr disks were recorded on a Beckman IR-20 spectrophotometer. $^1\text{H NMR}$ spectra were recorded on R-32 Perkin-Elmer (90 MHz) spectrometer in deuteriochloroform using tetramethylsilane as an internal standard. The solvent system for TLC was benzene–ethyl acetate (8:2).

The elemental analysis data for all eight compounds appear in Table II.

Materials. Anilines were procured from BDH India. 2-Propanoylindan-1,3-dione (I) was prepared by the reported method (13).

α -(1,3-Dioxolindan-2-yl)propylideneanilines (IIa–d). A mixture of 2-propanoylindan-1,3-dione (1.2 g, 0.01 mol) and pure anilines (0.012 mol) in ethanol (30 mL) was refluxed for 3 h. The solid product obtained on cooling was crystallized from ethanol to afford green needles of anils (IIa–d) (Table I).

6-Ethylindeno[2,1-c]quinolin-7(7H)-ones (IIIa–d). The anil II (4 mmol) was added to a freshly prepared PPA (5 g of P_2O_5 + 3 mL of H_3PO_4) and heated to 120 °C for 6 h, cooled,

Table II. Analyses of Compounds II and III

no.	mol formula	anal. %, calcd (found)		
		C	H	N
IIa	$\text{C}_{18}\text{H}_{15}\text{O}_2\text{N}$ (277)	77.97 (77.71)	5.41 (5.34)	5.05 (4.99)
IIb	$\text{C}_{19}\text{H}_{17}\text{O}_2\text{N}$ (291)	79.03 (79.28)	5.84 (5.79)	4.81 (4.75)
IIc	$\text{C}_{19}\text{H}_{17}\text{O}_2\text{N}$ (291)	79.03 (78.19)	5.84 (5.80)	4.81 (4.88)
IId	$\text{C}_{19}\text{H}_{17}\text{O}_2\text{N}$ (291)	79.03 (78.73)	5.84 (5.78)	4.81 (4.77)
IIIa	$\text{C}_{18}\text{H}_{13}\text{ON}$ (259)	88.39 (88.16)	5.01 (4.94)	5.40 (5.37)
IIIb	$\text{C}_{19}\text{H}_{15}\text{ON}$ (273)	86.03 (85.85)	5.49 (5.52)	5.12 (5.03)
IIIc	$\text{C}_{19}\text{H}_{15}\text{ON}$ (273)	86.03 (86.00)	5.49 (5.38)	5.12 (5.07)
IIId	$\text{C}_{19}\text{H}_{15}\text{ON}$ (273)	86.03 (85.98)	5.49 (5.51)	5.12 (5.14)

poured into cold water, and made alkaline with NH_4OH . It was extracted with CHCl_3 , and the extracts were dried over anhydrous MgSO_4 . The solvent was distilled, and the residue upon crystallization from petroleum ether–benzene mixture afforded shining yellow needles of indenoquinolinones (IIIa–d) (Table I).

Registry No. I, 46383-33-9; IIa, 117067-89-7; IIb, 117067-90-0; IIc, 117067-91-1; IId, 117067-92-2; IIIa, 117067-93-3; IIIb, 117067-94-4; IIIc, 117067-95-5; IIId, 117067-96-6; 4-MeC₆H₄NH₂, 106-49-0; 3-MeC₆H₄NH₂, 108-44-1; 2-MeC₆H₄NH₂, 95-53-4; aniline, 62-53-3.

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