

A Facile Synthesis of 1*H*-Indeno[1,2-*b*]quinolin-11-ones

David C. Lankin (1) and Hans Zimmer

Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221

Received May 5, 1972

The synthesis of the substituted 1*H*-indeno[1,2-*b*]quinolin-11-ones, (**2**), have previously been reported (2). However, most of these reported preparations are rather long and involved and, in some cases, employ intermediates which are not readily available. Thus, 3-(2-phenylquinolinyl)carboxylic acids, which are not conveniently available starting materials, were converted into their chlorides and ring closure was effected in low yields to **2** and substituted **2** species by a Friedel-Crafts reaction (2a). It was in connection with another research problem that it was necessary to prepare quantities of **2** for use in making spectral comparisons. Consequently, a facile synthetic route to the desired **2** was devised and is described here.

Reduction of the 2-(2-nitrobenzylidene)-1,3-indandiones, (**1a-c**), which were obtained by a condensation of 1,3-indandione with an aromatic aldehyde (3), with either sodium dithionite or stannous chloride gave the desired 1*H*-indeno[1,2-*b*]quinolin-11-ones, (**2a-c**) in low to moderate yields (4). The spectral data for **1a-c** and **2a-c**, most of which have not previously been reported, are summarized in Table I.

The reaction **1** → **2** probably involves the intermediate amine **3**, which when formed, immediately undergoes ring closure to give **2**. The involvement of such an amine, in which the 2-aminobenzene moiety is *cis* with respect

to a carbonyl carbon, has been postulated in some photochemical studies reported earlier by us (5). The reaction which is described here represents a general method for obtaining the 1*H*-indeno[1,2-*b*]quinolin-11-one ring system from readily available starting material in a simple two step reaction sequence (6).

EXPERIMENTAL

General Procedures.

Spectra were determined as follows: ir, chloroform solution, Perkin Elmer 700; uv, methanol solution, Unicam SP-800A; nmr, deuteriochloroform solution, Bruker HFX-10; mass spectra, Hitachi-Perkin Elmer RMU-7A operating at 70 v. Analyses by tlc involved Eastman Kodak precoated silica gel with fluorescent indicator as the adsorbent, eluted with chloroform and developed with iodine vapor and/or detected by ultraviolet light. Elemental analyses were performed by Galbraith Laboratories, Nashville, Tennessee, gave satisfactory results for all new compounds; all melting points are uncorrected.

Preparation of 2-(2-Nitrobenzylidene)-1,3-indandiones, (**1a-c**).

General Procedure.

A solution of equimolar amounts (30-50 mmoles) of 1,3-indandione and the substituted 2-nitrobenzaldehyde in 80-100 ml. of glacial acetic acid containing 2.5 ml. of concentrated sulfuric acid was stirred at room temperature for 12-24 hours. The reaction mixture was poured into 400 ml. of water and the resulting precipitate was filtered. The solid, which was obtained, was recrystallized from the appropriate solvent.

2-(2-Nitrobenzylidene)-1,3-indandione, (**1a**).

This compound was obtained as a yellow crystalline solid, m.p. 187-189° from 1-butanol (Lit. (3) 188°, $R_f = 0.51$, in 90% yield.

2-(4,5-Dimethoxyoxy-2-nitrobenzylidene)-1,3-indandione, (**1b**).

This compound was obtained as bright yellow crystals, m.p. 242-243.5° from isopropyl alcohol, $R_f = 0.46$, in 60% yield. The mass spectrum of **1a** showed a molecular ion at m/e 339.

Anal. Calcd. for $C_{18}H_{13}NO_6$: C, 63.72; H, 3.86; N, 4.13. Found: C, 63.65; H, 3.75; N, 3.82.

2-(4,5-Methylenedioxy-2-nitrobenzylidene)-1,3-indandione, (**1c**).

This compound was obtained as a bright yellow solid, m.p. 228-229° from methanol/acetone, $R_f = 0.48$, in 88% yield. The mass spectrum of **1c** showed a molecular ion at m/e 323.

Anal. Calcd. for $C_{17}H_9NO_6$: C, 63.16; H, 2.81; N, 4.33. Found: C, 62.81; H, 2.73; N, 4.02.

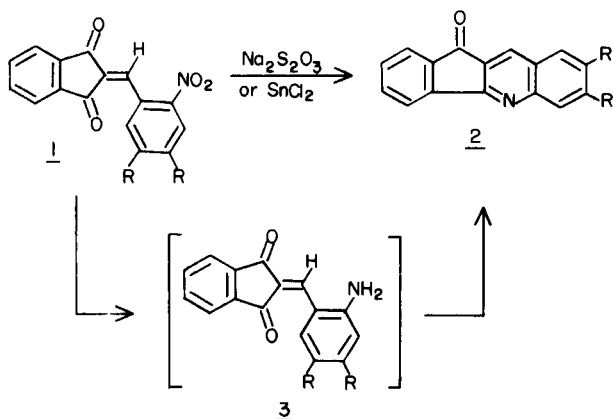
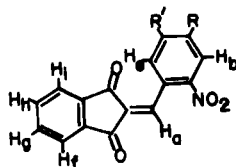
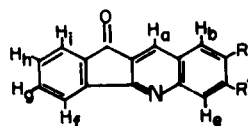


TABLE I

Spectral Properties of 2-Benzylidene-1,3-indandiones (**1a-c**) and 11*H*-Indeno[1,2-*b*]quinolin-11-ones, (**2a-c**)

	Infrared Data (a)		Ultraviolet Data (b)		Nmr Data	
	ν max (cm ⁻¹)	Assignment	λ max (nm)	ϵ	Chemical Shift (d)	Assignment (e)
1a	1740	C=O (c)	205 sh	17,200	1.74 (s)	H _a
	1698		220	19,500	1.74-2.96 (m)	H _b , H _c -H _i
	1645	C=C	243 sh	27,000		
	(R-H _c , R'-H _d)		255	31,000		
			261 sh	30,500		
		322.5	11,800			
1b	1735	C=O	208	18,500	1.69 (s)	H _d
	1697		245 sh	22,100	2.27 (s)	H _b
	1638	C=C	265 sh	22,000		
	(R-R' OCH ₃)		307	12,000		
			385	10,100	2.75 (s)	H _e
				1.69-2.43 (m)	H _f -H _i	
				5.95 (s)	-OCH ₃	
				5.97 (s)	-OCH ₃	
1c	1740	C=O	208	20,200	1.80 (s)	H _a
	1696		243 sh	27,900	2.31 (s)	H _b
	1643	C=C	258	30,600		
	(R-R' -OCH ₂ O-)		293	14,000		
			305 sh	13,700	2.61 (s)	H _e
		380	8,200	1.85-2.44 (m)	H _f -H _i	
				3.80 (s)	-O-CH ₂ -O-	



2a	1712	C=O (f)	205 sh	19,500	1.22 (m)	H _a , H _i (?)
	1620		C=N	211	21,700	2.00-2.67 (m)
	(R-H _c , R'-H _d)		220	21,100		
			226	21,000		
			241 sh	19,300		
			251 sh	22,000		
			274 sh	30,000		
			285	38,000		
			303	21,600		
			332	6,600		
	352	3,000				
	1710	C=O	209	23,000	1.80 (s)	H _a
	1620	C=N	230	22,500	2.00 (bd) J = 7.3	H _i (?)
			245	22,000		

2b (R-R'=OCH ₃)			255	17,800	(Hz)	
			298 sh	37,000	2.53 (s)	H _c
			310	47,900	2.90 (s)	H _b
					2.10-2.67 (m)	H _f -H _h (?)
					5.93 (s)	OCH ₃
					5.98 (s)	OCH ₃
	1715	C=O	208 sh	19,200	1.85 (s)	H _a
	1623	C=N	220	19,900		
			236.5	16,200	2.01 (bd), J = 7.3	H _i (?)
2c (R-R'=-OCH ₂ O-)			250	17,900	(Hz)	
			293	37,000	2.57 (s)	H _c
			305	40,400		
			315	33,400	2.90 (s)	H _b
					2.10-2.97 (m)	H _f -H _h (?)
				3.86 (s)	-OCH ₂ O-	

(a) Measured in chloroform solution. (b) Measured in methanol solution. (c) When measured in dichloromethane, (C=O) 1699 and 1738 cm⁻¹ and in carbon tetrachloride (C=O) 1702 and 1741 cm⁻¹. See I. Agranat, R. M. J. Loewenstein and E. D. Bergmann, *Israel J. Chem.*, **7**, 89 (1969). (d) All spectra were determined in deuteriochloroform. Shifts are reported as τ values with TMS as an internal reference. All spectra were run at 90 MHz. Multiplicities are as follows: (s) = singlet, (d) = doublet, (t) = triplet, (dd) = doublet of doublets, (td) = triplet of doublets, (m) = multiplet, and (bs) = broad singlet, and (bd) = broadened doublet. (e) All integrated areas are consistent with the assignments. A (?) indicates the assignment is tentative. (f) Measured in carbon tetrachloride solution (C=O) 1723 and (C=N) 1632 cm⁻¹. See N. H. Cromwell and R. A. Mitsch, *J. Org. Chem.*, **26**, 3812 (1961).

Reduction of (1a-c).

General Procedure A.

To a solution of 2.0 g. of **1** in 800 ml. of hot (60-70°) 95% ethanol was added an aqueous solution of sodium dithionite (15 g./30 ml. water). The red color of the solution, which initially formed, gradually faded to yellow and, after stirring for a total of 0.5-1.0 hours, the solution was cooled and filtered. The resulting solid was recrystallized from the appropriate solvent affording the 11*H*-indeno[1,2-*b*]quinolin-11-ones, (**2a-c**).

General Procedure B.

To 15.0 g. of stannous chloride dihydrate which was dissolved in 150-200 ml. of concentrated hydrochloric acid was added 5.0 g. of **1**. The solution was stirred at room temperature for 24 hours. The reaction mixture was cooled to 0° and slowly neutralized with ammonium hydroxide solutions to pH 8-9. The resulting precipitate was filtered and dried. The dried solid was combined with sand and extracted with chloroform in a Soxhlet apparatus until the liquid in the extraction thimble was essentially colorless (2-4 days). The chloroform was evaporated and the solid which was obtained was recrystallized from the appropriate solvent providing the 11*H*-indeno[1,2-*b*]quinolin-11-ones (**2a-c**).

11*H*-Indeno[1,2-*b*]quinolin-11-one, (**2a**).

This compound was obtained as a yellow solid which was sublimed (160-170°/4 mm), m.p. 173-174° (Lit. 7, 174-175°, Lit. 8, 176°, R_f = 0.25, in 18% yield (Procedure A) and 45% yield (Procedure B).

7,8-Dimethoxy-11*H*-indeno[1,2-*b*]quinolin-11-one, (**2b**).

This compound was obtained as a deep yellow crystalline solid, m.p. 287-289° from pyridine (Lit. 2b, 290-290.5°, pyridine),

R_f = 0.24, in 58% yield (Procedure A) and 51% yield (Procedure B).

7,8-Methylenedioxy-11*H*-indeno[1,2-*b*]quinolin-11-one, (**2c**).

This compound was obtained as a yellow solid, m.p. 243-245° from acetic acid (Lit. 2b, 245-246°, acetic acid), R_f = 0.36, in 37% yield (Procedure A) and 14% yield (Procedure B).

The spectral data for **1a-c** and **2a-c** are summarized in Table I.

Acknowledgement.

Support for this work on PHS Grant EH-00159-02 is gratefully acknowledged.

REFERENCES

- (1) Environmental Health Trainee, 1968-1970.
- (2a) W. Borsche and F. Sinn, *Ann. Chem.*, **538**, 283 (1939); (b) W. Borsche and W. Ried, *ibid.*, **554**, 269 (1943); (c) E. Noelting and H. Blum, *Ber.*, **34**, 2467 (1901).
- (3) I. Agranat, R. M. J. Loewenstein, and E. D. Bergmann, *Israel J. Chem.*, **7**, 89 (1969).
- (4) Yields were not optimized.
- (5a) H. Zimmer, D. C. Armbruster, S. P. Kharidia, and D. C. Lankin, *Tetrahedron Letters*, 4053 (1969); (b) H. Zimmer and R. Walter, *Z. Naturforsch.*, **18b**, 669 (1963); (c) H. Zimmer, F. Haupter, J. Rothe, W. E. J. Schrof, and R. Walter, *ibid.*, **18b**, 165 (1963).
- (6) All 2-nitrobenzaldehydes and the 1,3-indandione used in this study were obtained from Aldrich Chemical Company, Milwaukee, Wisconsin.
- (7) N. H. Cromwell and R. A. Mitsch, *J. Org. Chem.*, **26**, 3812 (1961).
- (8) R. Oberkobusch, *Chem. Ber.*, **86**, 975 (1953).