

SOME REACTIONS OF 2-CINNAMYLDENE AND 2-BENZYLIDENE-1,3-INDANDIONE

H. H. Hassan, A. A. Fadda, M. M. Yousif and E.M. Afsa

Chemistry Department, Faculty of Science, Mansoura Universtiy, Egypt

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INTRODUCTION

Detailed studies on Michael condensation of 2-arylideneindan-1, 3-dione (I) seem rather scarce in the literature [1,2]. In the present work 2-benzylideneindan-1,3-dione (Ia) and 2-cinnamylideneindan-1,3-dione (Ib) condensed with indan-1,3 - dione to give the corresponding 2,2-bis-indan-1,3-dione (IIa) and (IIb). Treatment of (Ia) with formaldehyde and benzylamine gave 1,3-indandione-2-spiro-3-(1,4-diphenyl-piperidene)-5-spiro-2-indan-1,3-dione (III). Hydrazine hydrate reacted with (Ia) to give 6-phenyl-6a-12,13-trihydro-bis-1,3-indenodiazepin-5,7-dione (IV). Heating bromine in acetic acid with (IIb) gave dibromodihydro-cinnamylidene-2,2-bis-indan-1,3-dione (V).

Reaction of (V) with morpholine, piperidene, and sodium ethoxide gave the corresponding dimorpholino, dipiperidino, and diethoxy dihydro derivative (VI, VII, VIII) respectively. Treatment of (IIa) with acetic anhydride and sodium acetate gave 10,11-dihydro-11-cinnamylidene-[1,2-b:2,1-e]pyrane-10,11-dione (IX). Diethoxymalonate reacted with (Ib) to give diethyl- $[\alpha(1,3\text{-dioxo-2-indanyl})\text{-indanyl}]\text{-cinnamyl}]\text{-malonate}$ (X). Hydrolysis of (X) with alcoholic KOH gave $\beta(1,3\text{-dioxo-2-indanyl})\text{-}\beta\text{-cinnamyl-propionic acid}$ (XI), which easily cyclised to 3,4,4,5-tetrahydro-2,5-dioxo-4-cinnamyl-2H - indeno [1,2-b]-3(2H)-Pyrane (XII) by refluxing in acetic anhydride.

EXPERIMENTAL

All melting points are uncorrected. The Pye Unicam SP 2000 spectrophotometer and the Varian 60 MHZ, in CDCl_3 solution were employed for IR and NMR spectra respectively.

Benzylidene & Cinnamylidene-2, 2-bis-indan-1, 3-dione (IIa, b):

Benzylidene & Cinnamylidene-2, 2-bis-indan-1, 3-dione (IIa, b): Equimolar quantities of each (Ia,b) (0.06 mole) and indan-1, 3-dione (0.06 mole), were dissolved separately in 50 ml sodium ethoxide, refluxed for 8 hr., and left to cool, acidified with dil. HCl. IIa was obtained as (3), IIb as shown in Table I, IR, 3010, 1725, 1665 and 1590 cm^{-1} .

1,3-Indandione - 2-spiro - 3-(1,4-diphenylpiperidene)-5-spiro-2-indeno-1,3-dione (III): After dissolving (0.06) mole of IIa in (0.12) mole of paraformaldehyde and (0.06) mole of benzylamine in acetic acid, the mixture warmed, and left at room temperature for 72 hr, and the solid was collected as shown in Table 1; IR, 1720 cm^{-1} (C=O); NMR; 2.5 (t. CH_2); 3(d. CH).

6-Phenyl-6a,12,13-trihydro-bis-1,5-indenodiazepine-5,7-dione (IV): (0.05 mole) of hydrazine hydrate was added to (0.05 mole) of IIa, in 50 ml. ethanol; the mixture was refluxed for 12 hr, in a waterbath, cooled, and the solid was collected. IR, 1660 (C=O), and 3400 (NH) cm^{-1} NMR; 2.9 (t. CH); 2.5 (d NH). (Table 1).

Dibromodihydro cinnamylidene-2,2-bis-1,3-indandione (V): (0.05 mole) of IIb was dissolved in 50 ml glacial acetic acid and followed by adding 10 ml of Br_2 acetic acid 30%. The reaction mixture was warmed at room temperature overnight, and the solid product was collected. IR, 1725, 1695 and 695 cm^{-1} , NMR, 305 (d. CH); 2.5 (d.CH) (Table 1).

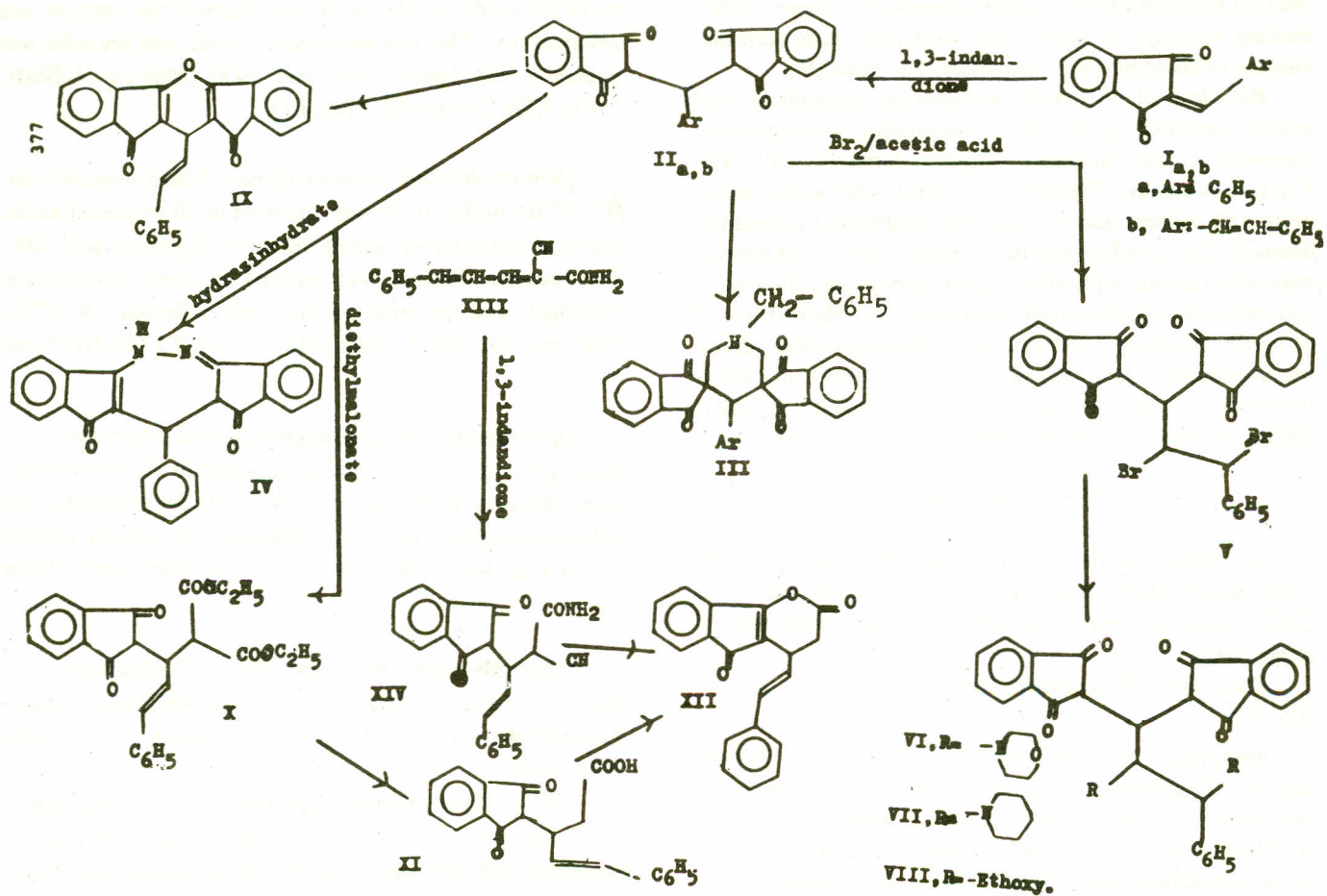
Dimorpholinodihydrocinnamylidene-2,2-bisindan-1,3-dione (VI): (0.10 mole) of morpholine in 10 ml methanol was added to (0.05 mole) of V in 10 ml methanol, the volume completed to 50 ml, refluxed 2 hr, cooled and the product collected. IR, 3010, 1725, and 1665 cm^{-1} (Table 1).

Dipiperidinodihydrocinnamylidene-2,2-bisindan-1, 3-dione (VII) and Diethoxy-dihydrocinnamylidene-2, 2-bis-1, 3-indandione (VIII): We similarly obtained a compound (VI) (Table 1).

10a,11-dihydrocinnamylidindeno-[1,2-b:2,1-e]pyran-10,12-dione (IX): (0.06 mole) of IIb was refluxed in acetic anhydride (50 ml), and 2 g of sodium acetate for 4 hrs, cooled, and the product was collected. IR, 1660, 1230 and 1015 cm^{-1} . (Table 1).

Table 1.

Compound	Solvent of crystallization	Colour	Yield %	m.p. (°C)	Molecular formula	Analysis			
						Calcd.		Found	
						C%	H%	C%	H%
IIb	ethyl alcohol	Brown	62	184	C ₂₇ H ₁₈ O ₄	79.78	4.43	80.13	3.90
III	" "	Yellow	52	185	C ₃₄ H ₂₅ NO ₂	77.85	4.89	77.56	4.92
IV	" "	"	45	172	C ₂₅ H ₁₆ N ₂ O ₂	79.76	4.26	79.42	4.74
V	acetic acid	Orange	80	220	C ₂₇ H ₁₈ Br ₂ O ₄	57.24	3.15	57.03	3.20
VI	" "	Brown	53	250	C ₃₅ H ₃₆ N ₂ O ₆	72.41	6.20	72.98	5.96
VII	" "	"	69	263	C ₃₇ H ₄₀ N ₂ O ₄	77.10	6.94	76.95	6.85
VIII	ethyl alcohol	Yellow	60	270	C ₃₁ H ₂₉ O ₆	75.00	5.68	74.96	5.68
IX	" "	Brown	50	155	C ₂₇ H ₁₆ O ₃	83.50	4.14	83.98	4.14
X	" "	Yellow	72	149	C ₂₅ H ₂₄ O ₆	71.42	5.71	71.38	5.59
XI	" "	Colourless	55	155	C ₂₀ H ₁₆ O ₄	75.00	5.00	75.01	5.10
XII	acetic acid	Green	50	152	C ₂₀ H ₁₃ O ₂	79.58	4.62	79.58	4.53
XIV	ethyl alcohol	Yellow	65	198	C ₂₁ H ₁₆ N ₂ O ₃	73.26	4.65	73.20	4.41



Diethyl-[\alpha-(1,3-dioxo-2-indanyl)-cinnamyl] malonate (X): (0.06 mole) of Ib and (0.06 mole) of diethylmalonate were dissolved in 50 ml sodium ethoxide, refluxed for 8 hr, cooled, poured into ice water, acidified with dil. HCl, and the product collected. IR 2900, 1750, 1720, 1610 and 1270 cm^{-1} (Table 1).

\beta-(1,3-dioxo-2-indanyl)-\beta-cinnamyl propionic acid (XI): A solution of aqueous KOH (20 ml, 5%) was added to a boiling solution of (X) (4 g in 50 ml ethanol), refluxed for 2 hrs, acidified with dil HCl, and heated at 80° for another 2 hr and the product was collected. IR, 2910, 1720, 1660 and 1595 cm^{-1} .

3,4,4a,5-tetrahydro-2,5-dioxocinnamyl-2(H)-indeno [1,2-b]-3-(2H)-pyran (XII): (0.06 mole) of XI or XIV and one g of sodium acetate were refluxed in 20 ml acetic anhydride

for 4 hr, and the product was collected. IR. 1728 and 1780 cm^{-1} . (Table 1).

\beta-(1,3-dioxo-2-indanyl)-\beta-cinnamyl-\alpha-cyano-propionic acid (XIV): (0.05 mole) of cinnamylidene cyanoacetamide XIII was dissolved in 50 ml sodium ethoxide, refluxed 2 hr, cooled, poured into ice water, then acidified with 30 ml acetic acid, and the product was collected. IR, 2240, 1720, 3300 and 1680 cm^{-1} (Table 1).

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