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# SOME REACTIONS OF 2-CINNAMYLIDENE 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 University, 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-benzylidene-indan-1,3dione (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-2spiro-3-(1,4-diphenyl-piperidene)-5-spiro-2-indan1,3-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-dioxo-2indanyl)-indanyl)-cinnamyl]-malonate (X). Hydrolysis of (X) with alcoholic KOH gave  $\beta$ (1,3-dioxo-2-indanyl)- $\beta$ -cinnamyl-propionic acid (XI), which easily cyclised to 3,4,4,5tetrahydro-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<sub>3</sub> 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. HC1. 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)-5piro-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<sup>-1</sup> (C=0); NMR; 2.5 (t. CH<sub>2</sub>); 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=0), and 3400 (NH) cm<sup>-1</sup> 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<sub>2</sub> acetic acid 30%. The reaction mixture was warmed at room temperature overnight, and the solid product was collected. IR, 1725, 1695 and 695 cm<sup>-1</sup>, NMR, 305 (d. CH); 2.5 (d.CH) (Table 1).

Dimorpholinodihydrocinnamylidene-2,2-bisindan-1,3diøne (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<sup>-1</sup> (Table 1).

Dipiperidinodihydrocinnamylidene-2,2-bisindan-1, 3dione (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<sup>-1</sup>. (Table 1).

Table 1.

Compound							Analysis			
	Solvent of crystalization		Colour	Yield	m.p. (°C)	Molecular formula	Calcd.		Found	
			% 140 KuM A CM1-8				C%	H%	C%	H%
IIb	ethyl	alcohol	Brown	62	184	C <sub>27</sub> H <sub>18</sub> O <sub>4</sub>	79.78	4.43	80.13	3.90
III	"	"	Yellow	52	185	C34H25NO2	77.85	4.89	77.56	4.92
IV	>>	>>	>>	45	172	C <sub>25</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub>	79.76	4.26	79.42	4.74
V	acetic	acid	Orange	80	220	C <sub>27</sub> H <sub>18</sub> Br <sub>2</sub> O <sub>4</sub>	57.24	3.15	57.03	3.20
VI	"	,,	Brown	53	250	C35H36N2O6	72.41	6.20	72.98	5.96
VII	"	"	"	69	263	C <sub>37</sub> H <sub>40</sub> N <sub>2</sub> O <sub>4</sub>	77.10	6.94	76.95	6.85
VIII	ethyl	alcohol	Yellow	60	270	C <sub>31</sub> H <sub>29</sub> O <sub>6</sub>	75.00	5.68	74.96	5.68
IX	>>	>>	Brown	50	155	C <sub>27</sub> H <sub>16</sub> O <sub>3</sub>	83.50	4.14	83.98	4.14
Х	,,	"	Yellow	72	149	C <sub>25</sub> H <sub>24</sub> O <sub>6</sub>	71.42	5.71	71.38	5.59
XI	***		Colourless	s 55	i 155 - <sup>8</sup>	C <sub>20</sub> H <sub>16</sub> O <sub>4</sub>	75.00	5.00	75.01	5.10
XII	acetic	acid	Green	50	152	C <sub>20</sub> H <sub>13</sub> O <sub>2</sub>	79.58	4.62	79.58	4.53
XIV	ethyl	alcohol	Yellow	65	198	C <sub>21</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub>	73.26	4.65	73.20	4.41



VIII, R -Ethoxy.

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106

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;<sup>1</sup> (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<sup>-1</sup>.

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

(g)) best extents, 1.5; glassie, 3.0, yeast extract, 3.0; casers hydrolyzats, 4.0, poptoice, 6.0; and agar, 25.0. The cultures were recolated at  $3.7^{\circ}$  (or 48 fit, and then stored in a refriguration at  $5^{\circ}$ . All isolance were gran positive upores forming rods and were identified, so facillae specify using the artifects of (surgey's Manual of Determinative Instratorolegy. The culture expression instrument activity of antipute grootstrates.

Associate reponsion in a 500 mb coderal flate 100mb of matrice, anoth serie (collected at 121° for 15 min. The medium, after codiing, was incodured from the ager shuft amplically and allowed to prov at 30° for 24 hr on a rotary, shaker (designed and fabricated in the workshop of the PCSTR Laboratories, Labora rotating at the rate of 125 root

Annumation procedures for the production of protana, justication for to Hence Medium [15] was prepared by outiting bactopopicum from the availant chose compasition is shown below:

(g/1) giveose, 3.30, years extract 1.0, CuCO, 1.10, paplone 3.0, pH 7.0 or pH 9.0 adjusted as desired. ("ap water was replaced by distilled water, as large amount of salts present in the former retards the growth of micro myanisms). The wheat heat, or heat of other exteals or defatted, sepbeam, along with (notero thes 50 m) of 4.0 Means medium contained in a 300 mi control flash was modulated at 121° (seting 2 mi of 56 mi control flash was modulated by (tage bated at 30° for optimum period (48 hr in the cute of wheat bran, make han need on or not huss, and 4 days wheat bran, make han need on or not huss, and 4 days wheat bran, make han need was used as substate) for wheat defined scybears must was used as substate) for solved at find enzyme synthesis. for 4 hr, and the product was collected. IR. 1728 and  $1780 \text{ cm}^{;1}$ . (Table 1).

 $\beta$  - (1,3-dioxo - 2-indanyl) -  $\beta$ -cinnamyl -  $\alpha$  - cyanopropionic 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<sup>-1</sup> (Table 1).

## REFERENCES

- 1. M. V. Ionescu and O.K. Popescu, Bull. Soc. Chim. Fr., **51**, 1215 (1932).
- W.A. Mosher and J.E. Innes, J. Heterocyclic Chem., 7,
  1083 (1970).

Protesses break down proteins to insulter males peptidge, and (jaulie to the blading units of proteins serting acids. According to their mode of action the protein

Proteines are ortalized by all organisms. Some protances formed are extremed in the surrounding medium, and are called extra-callatar protoses, others return inside the call and are called baracellular protoses, others return inside the protesses and uncrobal prevents produced on 4 largeprotesses produced by a protocol of 4 largeprotesses and uncrobal prevents produced on 4 largeprotesses in many case more than one protesses is asoreprotesses. In many case more than one protesses is asoreted. Strains of *Barilites achietis* produce both a neutral and an algebra fragmentation terms is contrained by the second of the organism from the fits are are active protesses in proteflat file and meaning motions and the second in the life of the organism from the fits are are active period in the life the incomplete protess and straine period in the life define meaning motions work is an extra-cellular protesses of define the logarither work an extra-cellular protesses of representatives of bacilites sativity and bacilites protesses of representatives of bacilites sativity and bacilites carriers of representatives of sativity and bacilite carrier, produce a protesses after a carbonary phase (logarithme phase)

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#### MATERIALS AND METHODS -

Creations and growth: The from of Bacillas subtility, and in the present study, was isolated locally from the sub-