

Nazar H. Al-Jobour and Mowafaq Y. Shandala

Department of Chemistry, College of Science, Mosul University, Mosul, Iraq

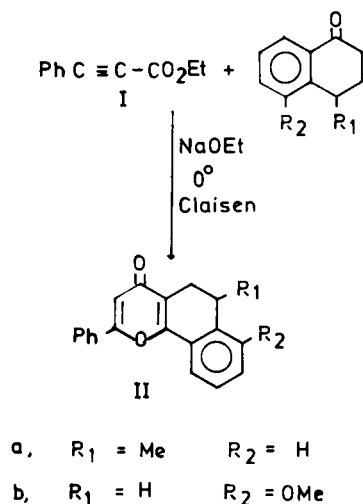
Received October 12, 1979

Reaction of phenylpropionic ester (I) with  $\alpha$ - and  $\beta$ -tetralones in the presence of sodium ethoxide yielded 5,6-dihydro-7,8-benzflavones and ethyl  $\beta$ -(2-tetralon-1-yl)cinnamates, as a result of Claisen and Michael reactions, respectively. The reaction of I with 3-ethoxy-2-cyclohexen-1-one and acetylcyclopropane in the presence of sodium ethoxide yielded acetylenic  $\beta$ -diketones and 2-aryl-6-cyclopropylpyran-4-ones, respectively. These products were identified on the basis of spectral and analytical data.

*J. Heterocyclic Chem.*, **17**, 941 (1980).

In the course of our study on the behavior of acetylenic esters towards compounds having active methylene groups, the synthesis of 2,6-diaryl-4-pyrones (1) and 5,6-dihydro-7,8-benzoflavones (2) has been well documented in the literature. These reactions seem to be of general application since they extend to compounds having an active methylene group attached to the carbon (3-7) and nitrogen (8) atoms. Because of the contribution of these reactions in synthetic organic chemistry, we now report similar condensation reactions involving the use of various ketones having active methylene groups. The compounds selected for this study were tetralones, 3-ethoxy-2-cyclohexen-1-one and acetylcyclopropane.

The condensation of ethyl phenylpropionate with  $\alpha$ -tetralone derivatives in the presence of sodium ethoxide yielded 5,6-dihydro-2-phenyl-naphtho[1,2-*b*]pyran-4-one (IIa,b) as a result of Claisen condensation followed by cyclization of the unisolated intermediate (Scheme 1).

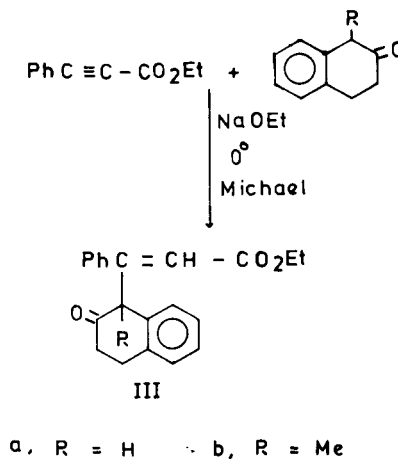


(Scheme 1)

The structure of the flavones IIa and IIb was supported by spectroscopic evidence. The ir spectral data showed an absorption band in the range of 1665 and 1620 cm<sup>-1</sup>, characteristic of the 4-pyrone structure (9). The nmr spec-

tral data of the compounds (IIa) and (IIb) showed a signal near  $\delta$  6.8 (singlet, olefinic H); the other signals are consistent with the proposed structure.

However, condensation of (I) with  $\beta$ -tetralone and 1-methyl- $\beta$ -tetralone in the presence of sodium ethoxide yielded ethyl  $\beta$ -(2-tetralon-1-yl)cinnamate (IIIa) and ethyl  $\beta$ -(1-methyl-2-tetralon-1-yl)cinnamate (IIIb), respectively, as main products. The reaction pathway seems to proceed by a simple Michael addition of the anion derived from  $\beta$ -tetralone with ethyl phenylpropionate (Scheme 2).



(Scheme 2)

The structure of products (IIIa) and (IIIb) was deduced from the spectral data. The ir spectral data showed the absence of an acetylenic linkage, while a broad strong absorption near 1700 cm<sup>-1</sup>, characteristic of the ester and the ketonic carbonyl groups. The nmr spectral data showed a singlet at  $\delta$  6.8 indicating an olefinic proton, while the presence of a signal at  $\delta$  4.33 (q) and  $\delta$  1.35 (t) was consistent with an ethoxy carbonyl group. Also, the presence of a singlet in the nmr spectrum of compound (IIIb), which integrated for the three protons of the methyl group, confirms that the anion is formed on C-1 rather than on C-3 of the  $\beta$ -tetralone system. The condensation of propionic

Table I  
The Ir and Nmr Spectral Data of Various Pyranones and Acetylenic  $\beta$ -Diketones

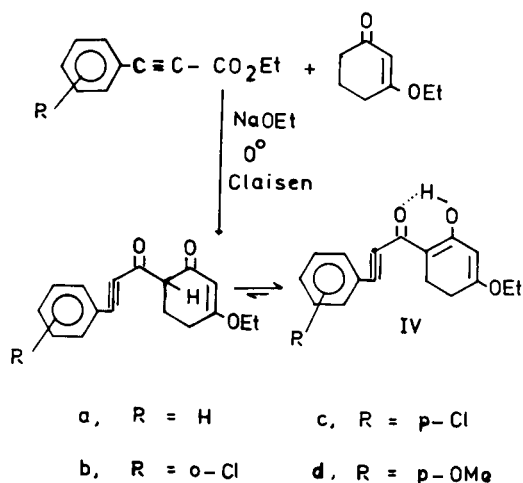
Compound No.	cm <sup>-1</sup>	Ir (chloroform) ( $\nu$ )	$\delta$	Nmr (deuteriochloroform) Protons
IIa	1665 1620	C=O	7.3-8.04 (m)	aromatic
		C=C	6.85 (s)	C=CH
			3.08 (d)	CH <sub>2</sub>
		2.98 (t)	:CH 1.3 (d)	CH <sub>3</sub>
IIb	1650 1615	C=O	7.4-8 (m)	aromatic
		C=C	6.86 (s)	C=CH
			3.92 (s)	OCH <sub>3</sub>
			2.74-3 (m)	CH <sub>2</sub> CH <sub>2</sub>
IIIa	1700-1710 (br) 1635	2 C=O	7.2-8.1 (m)	aromatic
		C=C	6.83 (s)	C=CH
			4.33 (q)	OCH <sub>2</sub>
			4.12 (s)	:CH
			2.46-3.1 (m)	CH <sub>2</sub> CH <sub>2</sub>
			1.35 (t)	CH <sub>3</sub>
IIIb	1690-1705 (br) 1625	2 C=O	7.08-7.88 (m)	aromatic
		C=C	6.75 (s)	C=CH
			4.31 (q)	OCH <sub>2</sub>
			2.47-2.84 (m)	CH <sub>2</sub> CH <sub>2</sub>
			1.87 (s)	:C-CH <sub>3</sub>
			1.37 (t)	CH <sub>3</sub>
IVa	2800-3300 (br) 1670 (w), 1655 (w) 1615 (st) 2220	OH (a)	7.3-7.9 (m)	aromatic
		2 C=O	5.4 (s)	C=CH
		C=C	3.88 (q)	OCH <sub>2</sub>
		C $\equiv$ C	2.4-3 (2t)	CH <sub>2</sub> CH <sub>2</sub>
			1.4 (t)	CH <sub>3</sub>
			12.8 (s)	C=COH (b)
IVb	2450-3200 (br) 1660 (w), 1650 (w) 1615 (st) 2210	OH (a)	7.2-7.87 (m)	aromatic
		2 C=O	5.48 (s)	C=CH
		C=C	4.05 (q)	OCH <sub>2</sub>
		C $\equiv$ C	2.33-3.07 (2t)	CH <sub>2</sub> CH <sub>2</sub>
			1.35 (t)	CH <sub>3</sub>
IVc	2600-3500 (br) 1670 (w), 1660 (w) 1620 (st) 2215	OH (a)	7.34-7.75 (m)	aromatic
		2 C=O	5.4 (s)	C=CH
		C=C	3.7 (q)	OCH <sub>2</sub>
		C $\equiv$ C	2.35-2.9 (2t)	CH <sub>2</sub> CH <sub>2</sub>
			1.4 (t)	CH <sub>3</sub>
IVd	2600-3200 (br) 1665 (w), 1655 (w) 1615 (st) 2220	OH (a)	6.95-7.67 (m)	aromatic
		2 C=O	5.37 (s)	C=CH
		C=C	3.95 (q)	OCH <sub>2</sub>
		C $\equiv$ C	3.85 (s)	OCH <sub>3</sub>
			2.4-2.9 (2t)	CH <sub>2</sub> CH <sub>2</sub>
Va	1665 1625	C=O	7.33-8 (m)	aromatic
		C=C	6.24-6.65 (2d)	2 C=CH
			1.8 (m)	:CH
			1.1 (m)	CH <sub>2</sub> CH <sub>2</sub>
Vb	1660 1615	C=O	7.2-7.8 (m)	aromatic
			6.75-7 (2d)	2 C=CH
		C=C	1.8 (m)	:CH
			1.3 (m)	CH <sub>2</sub> CH <sub>2</sub>

Table I continued

Compound No.	cm <sup>-1</sup>	Ir (chloroform) (c) $\nu$	$\delta$	Nmr (deuteriochloroform) Protons
Vc	1655	C=O	7.1-7.9 (m)	aromatic
	1620	C=C	6.6-6.9 (2d)	2 C=CH
			1.8 (m)	:CH
			1.2 (m)	CH <sub>2</sub> CH <sub>2</sub>
Vd	1650	C=O	6.85-7.75 (m)	aromatic
	1615	C=C	6.2-6.6 (2d)	2 C=CH
			3.88 (s)	OCH <sub>3</sub>
			1.84 (m)	:CH
			1.08 (m)	CH <sub>2</sub> CH <sub>2</sub>

(a) Chelated. (b) Exchanged with deuterium oxide. (c) Abbreviations: s = singlet, m = multiplet, d = doublet, t = triplet, q = quartet, st = strong, w = weak, br = broad.

esters with 3-ethoxy-2-cyclohexen-1-one in the presence of sodium ethoxide at 0° yielded acetylenic  $\beta$ -diketones (IVa-d) (Scheme 3).

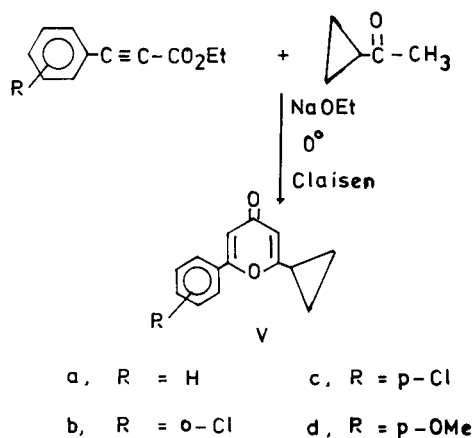


(Scheme 3)

No cyclization has been achieved during crystallization or by a base action on these diketones (IV) indicating their stability. However, an attempt to convert them into their corresponding pyran-4-ones is still under investigation. The structure of these compounds was elucidated from their spectral and analytical data. A sharp absorption in the range 2200-2220 cm<sup>-1</sup>, consistent with the presence of an acetylenic linkage, indicated that the reaction pathway proceeds through a Claisen condensation, while the nmr (enolic proton at  $\delta$  13.5) and ir (broad absorption 2500-3400 cm<sup>-1</sup>) data proved that the system was strongly enolised. These compounds gave a positive ferric chloride test and easily formed copper chelated (11).

The reaction of propiolic esters with acetylcyclopropane in the presence of sodium ethoxide gave 2-aryl-6-cyclo-

propylpyran-4-one (Va-d). The reaction pathway proceeded *via* Claisen condensation followed by cyclization of the unisolated diketonic intermediates (Scheme 4).



(Scheme 4)

The structure of these pyranones (V) was deduced from their spectral and elemental analysis. The ir spectral data showed no absorption for an acetylenic linkage, but a two-band system in the range of 1650-1665 and 1615-1625 cm<sup>-1</sup> could be assigned to the 4-pyrone structure. The nmr spectral data showed two doublets between  $\delta$  7.2-6.7 characteristic of the two olefinic protons (10). The rest of ir and nmr data are listed in the Experimental.

#### EXPERIMENTAL

Ir spectra were measured in chloroform with a Unicam SP 200 instrument. <sup>1</sup>H nmr spectra were determined with a Bruker Spectrospin 90 MHz for solutions in deuteriochloroform containing tetramethylsilane as internal standard. Compounds were analysed by the Max Plank Institute, Ruhr, West Germany. Melting points were measured on a Kofler hot stage and are uncorrected. Light petroleum ether with b.p. 60-80° was used for crystallization.

Table II

Melting Points, Percentage Yields and Analytical Results of Pyran-4-ones and Acetylenic  $\beta$ -Diketones

Compound No.	M.p. (°C)	Yield %	Formula	Analyses %			
				Calcd. C	H	Found C	H
IIa	138 (a)	44	C <sub>20</sub> H <sub>16</sub> O <sub>2</sub>	83.33	5.55	83.03	5.77
IIb	190-192 (a)	58	C <sub>20</sub> H <sub>16</sub> O <sub>3</sub>	78.94	5.26	78.71	5.45
IIIa	124 (d)	33	C <sub>21</sub> H <sub>20</sub> O <sub>3</sub>	78.75	6.25	78.55	6.31
IIIb	140-142 (d)	41	C <sub>22</sub> H <sub>22</sub> O <sub>3</sub>	79.04	6.58	78.85	6.62
IVa	137 (a)	21	C <sub>17</sub> H <sub>16</sub> O <sub>3</sub>	76.00	5.86	76.12	5.97
IVb	112 (c)	31	C <sub>17</sub> H <sub>16</sub> ClO <sub>3</sub>	67.43	4.95	67.35	5.08
IVc	126-128 (c)	25	C <sub>17</sub> H <sub>15</sub> ClO <sub>3</sub>	67.43	4.95	67.32	5.12
IVd	118 (a)	29	C <sub>18</sub> H <sub>18</sub> O <sub>4</sub>	72.48	6.04	72.15	5.85
Va	106 (c)	58	C <sub>14</sub> H <sub>12</sub> O <sub>2</sub>	78.96	5.65	79.24	5.66
Vb	246-248 (b)	38	C <sub>14</sub> H <sub>11</sub> ClO <sub>2</sub>	68.15	4.46	67.95	4.55
Vc	230-232 (a)	24	C <sub>14</sub> H <sub>11</sub> ClO <sub>2</sub>	68.15	4.46	67.88	4.42
Vd	188 (c)	47	C <sub>15</sub> H <sub>14</sub> O <sub>3</sub>	74.38	5.78	74.26	5.73
		Calcd.	Found			Calcd.	Found
(IVb)		11.73	11.71	(Vb)		14.4	14.23
(IVc)		11.73	11.65	(Vc)		14.4	14.33

(a) Recrystallized from benzene/light petroleum ether. (b) Recrystallized from benzene/methanol. (c) Recrystallized from methanol. (d) Recrystallized from light petroleum ether (80-100°).

#### Condensation of Tetralones with Ethyl Phenylpropionate.

Tetralone (1 mmole) and ethyl phenylpropionate (1 mmole) were added successively to an ice-cold suspension of sodium ethoxide (1 mmole) in dry ether (150 ml). The mixture becomes reddish brown and was kept at 0° for 72 hours. It was then mixed with water (200 ml.) and acidified with dilute sulphuric acid. Extraction with ether, washing with saturated sodium bicarbonate solution, drying (sodium sulfate) and evaporation of the solvent afforded the corresponding benzflavones (IIa,b) or the tetralon-1-ylcinnamates (IIIa,b).

#### Condensation of 3-Ethoxy-2-cyclohexen-1-one with Ethyl Arylpropionates.

The ketone (1 mmole), arylpropionic ester (1 mmole) and sodium ethoxide (1 mmole) in dry ether (150 ml.) were allowed to stand for 48 hours at 0° and then for 72 hours at room temperature. The yellowish-red mixture after treatment as described in the previous reaction, gave the corresponding 3-ethoxy-6-arylpropionyl-2-cyclohexen-1-one (IVa-d).

#### Condensation of Acetylcyclopropane with Arylpropionic Esters.

Acetylcyclopropane (1 mmole) and arylpropionic ester (1 mmole) were added successively to an ice-cold suspension of sodium ethoxide (1 mmole) in dry ether (150 ml.). The reaction mixture which acquires an orange colour was kept at 0° for 48 hours and then for 36 hours at room temperature. After the usual workup as described in the earlier example,

it afforded the corresponding 2-aryl-6-cyclopropylpyran-4-one (Va-d). The proportions of the resulting compounds indicated by the yield, analytical and spectral data, are listed in the Tables I and II.

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