

Ibrahim El-Sayed El-Kholy\*, Morcos Michael Mishrikey and Salah Loutfi Abdoul-Ela

Chemistry Department, Faculty of Science, Alexandria University, Moharram Bey,  
Alexandria, Egypt

Received April 30, 1982

The Michael reaction of ethyl cinnamates with deoxybenzoin gave ethyl 3,4,5-triaryl-5-oxopentanoates which were hydrolysed to the corresponding acids. The latter could be cyclized to the respective 3,4-dihydro-2H-pyran-2-ones which underwent ring opening with several nucleophiles to the corresponding acid derivatives. However, their reaction with ammonium acetate led to the formation of 3,4-dihydro-2-pyridones. The 3,4-dihydro-2-pyrones and pyridones were dehydrogenated to the corresponding 2-pyrones and 2-pyridones by fusion with sulfur.

*J. Heterocyclic Chem.*, **19**, 1329 (1982).

The 2H-Pyran-2-one ring is a central structural element of several naturally occurring and synthetically important compounds. A wide variety of methods are described in literature (1) for their synthesis. 4,5,6-Triaryl-2H-pyran-2-ones are usually prepared by the condensation of acetylenic esters with suitable ketones (2). However, the synthetic utility of this route is restricted by the difficulties encountered in the synthesis of acetylenic esters. In the present study, 4,5,6-triaryl-2-pyrones and 2-pyridones could be prepared in fairly good yields by dehydrogenation of the respective 3,4-dihydro derivatives. The reactions of the latter are also studied.

The preparative potentialities of the alkoxide-catalyzed

Michael reaction leading to compounds with two vicinal chiral centers have been extensively studied (3) and in some cases both diastereoisomers have been isolated (4). In the present study, the reaction of deoxybenzoin (1) with ethyl cinnamate (2a) in the presence of sodium ethoxide led to the formation of a mixture of *erythro* and *threo* ethyl 3,4,5-triphenyl-5-oxopentanoates 3a. Similar to 1,2,3,5-tetraphenylpentane-1,5-dione (5), the *erythro* configuration, 3a-*erythro*, was assigned to the high melting ester (major product) and the *threo* configuration, 3a-*threo*, to the low melting ester. However, in the reaction with ethyl *p*-methoxycinnamate (2b) only one ester 3b was obtained. The above esters 3a,b could be hydrolysed by alkali to the corresponding acids 3c,d (Scheme I).

Scheme 1

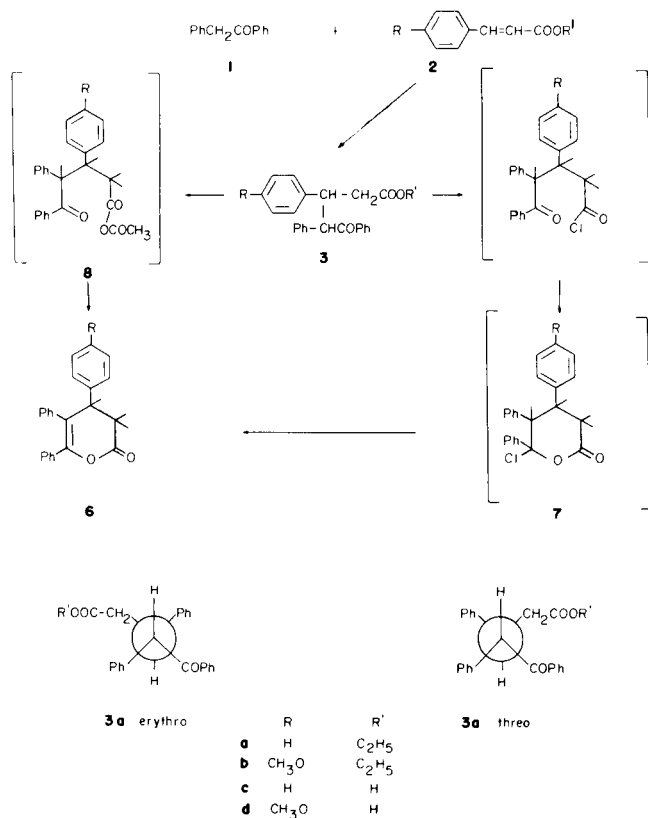


Table I

Infrared and Ultraviolet Spectra of 3,4,5-Triaryl-5-oxopentanoic Acids and Their Derivatives

	$\nu$ CO	IR (cm <sup>-1</sup> ) $\nu$ OH, NH <sub>2</sub> or NH	UV $\lambda$ max, nm (log $\epsilon$ )
3a erythro	1650, 1720		246 (4.12)
3a threo	1661, 1733		248 (4.21), 338 (a) (2.70)
3b	1685, 1733		228 (4.40), 246 (4.19), 285 (a) (3.13)
3c	1677, 1707	4150-4450	247 (4.16), 280 (a) (3.66)
3d	1680, 1705	3340-3520	228 (4.13), 247 (3.92)
13a	1680, 1660	3440	247 (4.10)
13b	1685, 1665	3460	227 (4.46), 247 (3.26), 282 (a) (3.61)
13c	1690, 1670	3400	220 (a) (4.40), 250 (a) (4.12), 265 (a) (4.05)
13e	1675, 1665		218 (4.06), 247 (4.01)
13f	1675, 1650	3200-3400	246 (4.11)
13g	1685, 1665	3280-3440	228 (4.24), 247 (a) (4.03), 277 (a) (3.23)
13h	1690, 1660	3440-3550	229 (4.53), 245 (a) (4.32), 282 (a) (3.73)
13i	1680, 1640	3160-3400	247 (3.97)
13j	1650, 1630	3320-3380	227 (4.28), 248 (a) (3.97), 277 (a) (3.74)

(a) Shoulder.

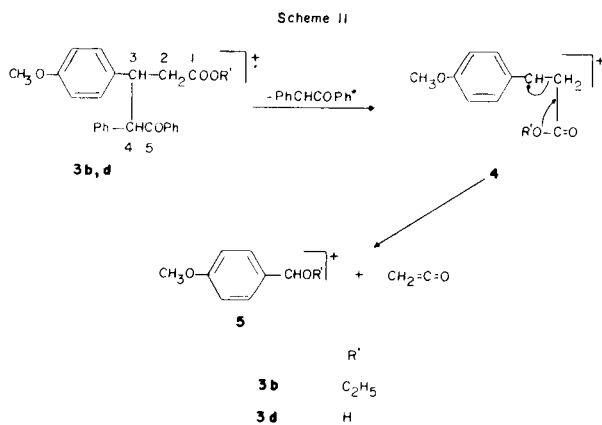
The infrared spectra of the esters and the acids showed a ketonic carbonyl in the range 1650-1685  $\text{cm}^{-1}$  as well as a CO ester (or acid) at 1705-1733  $\text{cm}^{-1}$  (Table I). Their ultraviolet spectra (Table I) exhibited an absorption maximum at 246-248 nm due to the  $\pi$ - $\pi^*$  band of the acetophenone moiety (6). Their  $^1\text{H}$  nmr spectra (Table II) showed a multiplet (2H) at  $\delta$  2.32-2.78 for the methylene (C-2), a multiplet (1H) at  $\delta$  3.80-4.00 for H-3 and a doublet (1H) ( $J = 11.0$  Hz) at  $\delta$  4.80-5.53 for H-4. The relatively high coupling constant for the latter signal is consistent with the *s-trans* conformation for H-3 and H-4 (7). It is worthy to mention that the above assignment is confirmed by the reported  $^1\text{H}$  nmr data for 1,2,3-triphenylhexane-1,5-dione (8), 1,2,3,5-tetra-phenylpentane-1,5-dione (5) and 1,2-diphenyl-4-oxopentane-3-carbonitrile (9) which gave similar patterns.

Table II

$^1\text{H}$  NMR Spectra ( $\delta$ ) of 3,4,5-Triaryl-5-oxopentanoic Acids and Their Derivatives in Deuteriochloroform (a)

	$\text{CH}_2$ (m)	H-3 (m)	H-4 (d)	Ar-H (m)	Others
<b>3a erythro</b>	2.49	3.89	5.10	7.67	1.01 t, 3.90 q ( $\text{C}_2\text{H}_5$ )
<b>3a threo</b>	2.78	3.93	4.80	7.40	1.02 t, 3.88 q ( $\text{C}_2\text{H}_5$ )
<b>3b</b> (b)	2.32	3.80	5.38	7.57	0.87 t, 3.77 q ( $\text{C}_2\text{H}_5$ ), 3.63 s ( $\text{OCH}_3$ )
<b>3c</b> (b)	2.41	4.00	5.53	7.63	
<b>3d</b> (b)	2.38	3.82	5.40	6.89	3.76 s ( $\text{OCH}_3$ )
<b>13a</b> (b)	2.34	3.89	5.34	7.36	6.41 m ( $\text{NH}_2$ )
<b>13b</b> (b)	2.19	3.96	5.30	7.27	3.58 s, ( $\text{OCH}_3$ ), 6.33 m ( $\text{NH}_2$ )
<b>13c</b> (b)	2.56	4.13	5.41	7.29	9.50 s (NH)
<b>13d</b>	2.47	4.44	5.38	7.46	2.62 s, 2.73 s ( $\text{N}(\text{CH}_3)_2$ )
<b>13e</b>	2.65	4.11	5.24	7.15	1.52 m, 3.37 m (piperidine)
<b>13f</b>	2.27	4.15	5.14	7.42	6.16 m ( $\text{NH}_2$ ), 9.09 s (NH)
<b>13g</b>	2.33	4.11	5.18	7.38	3.76 s ( $\text{OCH}_3$ ), 6.39 m ( $\text{NH}_2$ )
<b>13h</b> (b)	2.18	4.01	5.35	7.31	3.66 s ( $\text{OCH}_3$ ), 9.03 s (NH)
<b>13i</b> (b)	2.39	3.88	5.35	7.50	9.50 s (NH), 10.33 s (OH)
<b>13j</b>	2.20	3.73	5.10	7.28	3.43 s ( $\text{OCH}_3$ ), 9.96 m (NH and OH)

(a) s: Singlet, d: doublet ( $J = 11.0$  Hz), t: triplet ( $J = 7.0$  Hz), q: quartet ( $J = 7.0$  Hz), m: multiplet. (b) Spectra carried out in  $\text{DMSO}-d_6$ .



The structure of the 5-oxopentanoic acids and esters **3** was further confirmed from their mass spectra. The base peak in the spectra of the ester **3b** and the acid **3d** can be represented as the cation **4**, presumably arising by  $\text{C}_3$ - $\text{C}_4$  bond cleavage in the molecular ion. Subsequent skeletal rearrangement involving a four centered transition state accompanied by elimination of a ketene molecule accounts for the very prominent peaks corresponding to the cation **5** (Scheme II).

Treatment of the triaryl-5-oxopentanoic acids **3c, d** with thionyl chloride or acetic anhydride and sodium acetate led to the formation of the corresponding 4,5,6-triaryl-3,4-dihydro-2H-pyran-2-ones **6a, b**, respectively. Lactonization with thionyl chloride is assumed to proceed via an intermediate formation of an acid chloride which most probably has the cyclic structure **7**. Cyclization with acetic anhydride involves acylation of the  $\delta$ -keto acid at the carbonyl group with the formation of the mixed anhydride **8** and subsequent elimination of acetic acid (**10**). Acylation at the carbonyl group with the formation of the acetate of the enol form is also possible (**11**) (Scheme I).

The infrared spectra of the dihydropyrones **6a, b** exhibited a strong lactone carbonyl absorption in the range 1775-1780  $\text{cm}^{-1}$  (**12**) (Table III). Their ultraviolet spectra

Table III

Infrared and Electronic Spectra of 4,5,6-Triaryl-2-pyrones, 2-Pyridones and Their 3,4-Dihydro Derivatives

	IR ( $\text{cm}^{-1}$ )		UV
	$\nu$ CO	$\nu$ NH	$\lambda$ max, nm, (log $\epsilon$ )
<b>6a</b>	1755		(a) 217 (c) (4.30), 270 (3.98) (b) 246 (3.97)
<b>6b</b>	1780		(a) 225 (4.33), 275 (3.99) (b) 227 (4.30), 247 (4.17) (a) 245 (4.13)
<b>14a</b>	1685	3300	(a) 224 (4.38), 240 (c) (4.14), 284 (3.71)
<b>14b</b>	1685	3220-3240	(a) 224 (4.38), 240 (c) (4.14), 284 (3.71)
<b>15a</b>	1721 (d)		(a) 230 (4.19), 253 (4.27), 340 (3.94)
<b>15b</b>	1734		(a) 230 (4.29), 252 (4.31), 320 (4.12)
<b>16b</b>	1735		(a) 230 (4.28), 248 (c) (4.20), 338 (4.05)
<b>21b</b>	1640	3000-3120	(a) 227 (c) (4.29), 255 (4.31), 305 (c) (4.00)
<b>22b</b>	1610	3000-3160	(a) 247 (4.49), 280 (c) (4.25)

(a) Spectra carried out in methanol. (b) Spectra carried out in 0.1 *M* methanolic sodium methoxide. (c) Shoulder. (d) Taken from reference (19a).

showed an absorption maximum in the region 270-275 nm (Table III) which can be attributed to the stilbene moiety of the molecule (**13**). In 0.1 *M* methanolic sodium methoxide this band disappeared with the development of a band at 246-248 nm characterizing the spectra of the 5-oxopent-

anoates suggesting a facile ring opening of the lactone ring of the 3,4-dihydropyrones with methoxide ion. Their  $^1\text{H}$  nmr spectra (Table IV) gave a typical ABX pattern. The methylene protons (AB) appeared as a multiplet (2H) at  $\delta$  3.02-3.12 and the H-4 proton (X) as a double of doublets centered at  $\delta$  4.06-4.13.

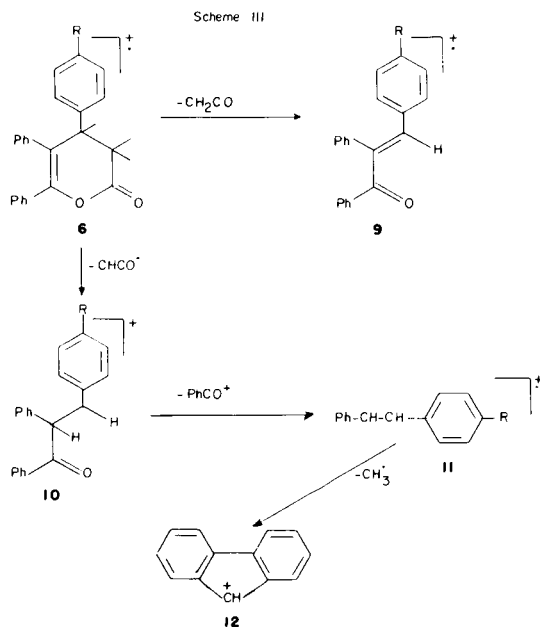
Table IV

$^1\text{H}$  NMR Spectra ( $\delta$ ) of 4,5,6-Triaryl-2-pyrones, 2-Pyridones and Their 3,4-Dihydro Derivatives in Deuteriochloroform (a)

	H-3	H-4	Ar-H (m)	Others (s)
<b>6a</b> (b)	3.02 (m)	4.13 (dd)	7.12	
<b>6b</b>	3.12 (m)	4.06 (dd)	7.10	3.78 (OCH <sub>3</sub> )
<b>14a</b>	2.85 (m)	4.01 (m)	7.03	
<b>14b</b>	3.06 (m)	3.94 (m)	7.21	3.85 (OCH <sub>3</sub> )
<b>15a</b>	6.35 (s)		7.10	
<b>15b</b>	6.30 (s)		7.12	3.70 (OCH <sub>3</sub> )
<b>16b</b>			7.03	3.72 (OCH <sub>3</sub> )
<b>21a</b> (b)	6.42 (s)		7.10	
<b>21b</b>	6.51 (s)		6.90	3.75 (OCH <sub>3</sub> )
<b>22b</b>	6.60 (s)		7.00	3.75 (OCH <sub>3</sub> )

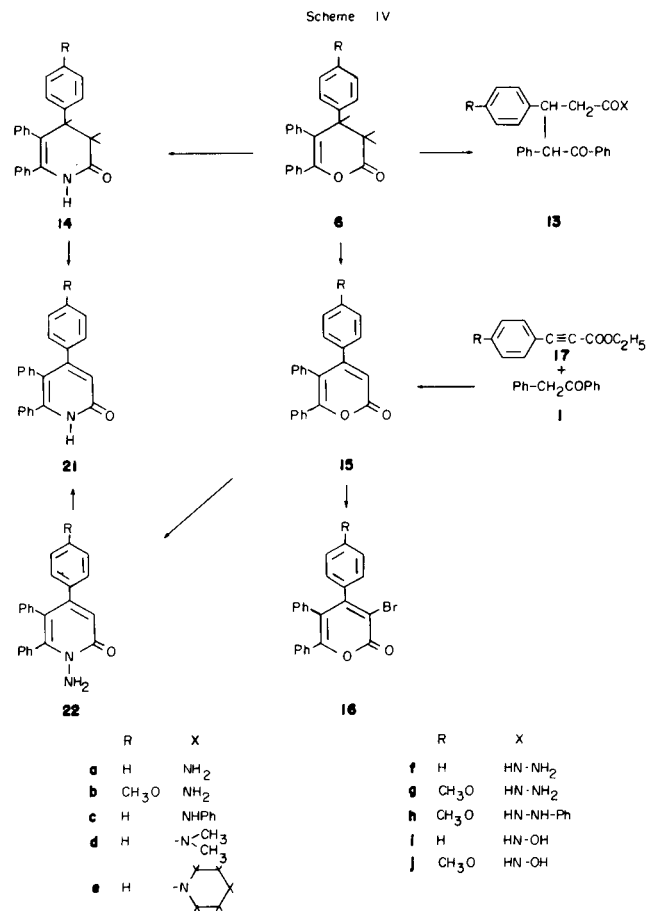
(a) s: Singlet, dd: double of doublets, m: multiplet. (b) Spectra carried out in DMSO-d<sub>6</sub>.

While relatively little has been published concerning the mass spectra of  $\gamma$ - and  $\delta$ -lactones (14), it appears that no such study has been reported for 3,4-dihydro-2-pyrones. In the present work, the structure of the dihydropyrones **6a,b** was supported by their mass spectra. A main fragmentation pathway involves the elimination of a keten molecule from the molecular ion *via* a retro Diels-Alder reaction giving rise to the radical cation **9**. A similar behaviour was observed in the photolysis of 6-methyl- (15)



and 4,4-dimethyl-6-isopropyl-3,4-dihydro-2H-pyran-2-ones (16). Meanwhile, a different fragmentation route is also possible involving elimination of CHCO radical giving the cation **10**. Subsequent loss of a benzoyl cation and a methyl radical accounts for the species **11** and **12**, respectively (Scheme III).

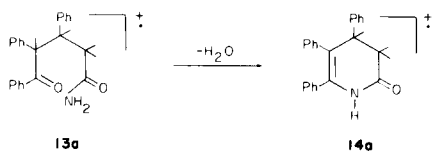
As  $\delta$ -lactones, 3,4-dihydro-2H-pyran-2-ones are easily cleaved by nucleophilic reagents. Thus, **6a,b** gave with alkali the corresponding acids **3c,d**, with ammonia, aniline, dimethylamine and piperidine, the corresponding acid amides **13a-e** were obtained. Also their reactions with hydrazine hydrate and phenylhydrazine led to the formation of the acid hydrazides **13f-h** while with hydroxylamine, the hydroxamic acids **13i,j** were formed (Scheme IV). The open chain structure of the above acid deriva-



tives was evident from their infrared, ultraviolet and  $^1\text{H}$  nmr spectra which were quite similar to the spectra of the parent acids and esters (Tables I, II).

On the other hand, the reaction of the dihydropyrones **6a,b** with ammonium acetate gave the 3,4-dihydro-2-pyridones **14a,b**, respectively, which presumably arose by cyclization of the initially formed acid amides **13a,b**. The susceptibility of the open chain amides to thermal cyclodehydration is supported by the observation of an intense

peak at  $m/e$  325 ( $M-H_2O$ ) in the mass spectrum of 3,4,5-triphenyl-5-oxopentanoic acid amide (**13a**) which can be attributed to the molecular ion of the corresponding 3,4-dihydro-2-pyridone **14a**.



Consistent with their cyclic structures, the infrared spectra of the dihydropyridones **14a,b** showed a single carbonyl absorption at  $1685\text{ cm}^{-1}$  for the cyclic amide carbonyl as well as a broad NH absorption in the range  $3220\text{--}3300\text{ cm}^{-1}$  (Table III). Their  $^1\text{H}$  nmr spectra exhibited two multiplets at  $\delta$  2.85-3.06 (2H) for the ring methylene (C-3) and  $\delta$  3.94-4.01 (1H) for the H-4 (Table IV). The appreciable deshielding (about 0.53 ppm) in the chemical shift of the methylene protons relative to the open chain derivatives is probably attributed to the anisotropic effect of the neighbouring cyclic carbonyl.

Among the methods used for the synthesis of 2H-pyran-2-one derivatives is the dehydrogenation of the respective 3,4-dihydro derivatives. Direct dehydrogenation in boiling cymene over palladium on carbon has been described in the case of a triterpenoid unsaturated lactone (17). Halogenation and subsequent dehydrohalogenation was extensively used for the preparation of 2-pyrene derivatives sub-

stituted in the 6- or 5- and 6- positions (18). In the present work, 4,5,6-triphenyl- (**15a**) and 4-(*p*-methoxyphenyl)-5,6-diphenyl- (**15b**) 2H-pyran-2-ones were prepared in good yield by fusion of the respective 3,4-dihydro derivatives **6a,b** with sulfur. Dehydrogenation of **6a** was also accomplished, in lower yield, by treatment with chloranil. Moreover, while *N*-bromosuccinimide affected dehydrogenation (40% yield) of **6a,b**, subsequent bromination was observed for **6b** giving 3-bromo-4-(*p*-methoxyphenyl)-5,6-diphenyl-2H-pyran-2-one (**16b**).

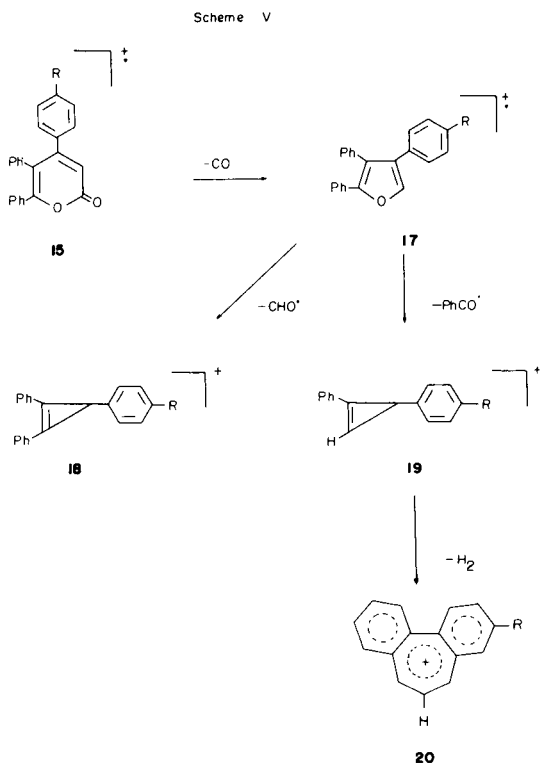
It is worthy to mention that 4-(*p*-methoxyphenyl)-5,6-diphenyl-2H-pyran-2-one (**15b**) which is not reported in the literature, was also prepared (15% yield) by a different route involving the condensation of deoxybenzoin (**1**) with ethyl *p*-methoxyphenylpropiolate (**17b**) in the presence of sodium ethoxide (Scheme IV).

The infrared spectra of the **15a,b** and **16b** showed a carbonyl stretching frequency at  $1735\text{ cm}^{-1}$  characteristic of 2-pyrones (19) and their  $^1\text{H}$  nmr spectra showed the H-3 ring proton signal at  $\delta$  6.30 (20) (Table IV). The mass spectra of **15a,b** gave a very prominent ( $M\text{-CO}$ ) peak (**17**) which generally characterizes the fragmentation of 2-pyrones (21). Subsequent elimination of CHO or PhCHO radicals from the furan species **17** gave the stable cyclopropenyl cations **18** or **19**, respectively, which is usually observed in the mass spectra of furans (22). The stable cation **20** is assumed to be formed by loss of a hydrogen molecule from **19** (19b) (Scheme V).

Table V

	Mp °C	Formula	C	Calcd. %		Analytical Data		Found %	
				H	N	C	H	N	
<b>3a erythro</b>	184	$C_{25}H_{24}O_3$	80.6	6.5		80.6	6.5		
<b>3a threo</b>	92	$C_{25}H_{24}O_3$	80.6	6.5		80.3	6.1		
<b>3b</b>	173	$C_{26}H_{26}O_4$	77.6	6.5		77.5	6.4		
<b>3c (a)</b>	242	$C_{23}H_{20}O_3$	80.2	5.8		80.0	5.6		
<b>3d</b>	218	$C_{24}H_{22}O_4$	77.0	5.9		77.0	6.0		
<b>6a</b>	132	$C_{23}H_{18}O_2$	84.6	5.6		84.9	5.8		
<b>6b</b>	129	$C_{24}H_{20}O_3$	80.9	5.7		81.2	5.9		
<b>13a</b>	240	$C_{23}H_{21}NO_2$	80.4	6.2	4.1	80.5	6.3	3.9	
<b>13b</b>	212	$C_{24}H_{23}NO_3$	77.2	6.2	3.8	76.8	6.3	3.8	
<b>13c</b>	224	$C_{29}H_{25}NO_2$	83.0	6.0	3.3	83.1	6.0	3.1	
<b>13d</b>	210	$C_{25}H_{25}NO_2$	80.8	6.8	3.8	80.5	7.1	3.5	
<b>13e</b>	163	$C_{26}H_{29}NO_2$	81.7	7.1	3.4	81.6	7.1	3.2	
<b>13f</b>	206	$C_{23}H_{22}N_2O_2$	77.1	6.2	7.8	76.8	5.8	7.5	
<b>13g</b>	156	$C_{24}H_{24}N_2O_3$	74.2	6.2	7.2	73.9	6.1	7.0	
<b>13h</b>	165	$C_{30}H_{28}N_2O_3$	77.6	6.1	6.0	77.5	6.2	6.0	
<b>13i</b>	168	$C_{23}H_{21}NO_3$	76.8	5.9	3.8	76.7	5.6	3.5	
<b>13j</b>	147	$C_{24}H_{23}NO_4$	74.0	5.9	3.6	73.7	6.0	3.5	
<b>14a</b>	155	$C_{23}H_{19}NO$	84.9	5.9	4.3	84.7	5.7	4.0	
<b>14b</b>	157	$C_{24}H_{21}NO_2$	81.1	6.0	3.9	81.5	6.3	4.1	
<b>15b</b>	164	$C_{24}H_{18}O_3$	81.3	5.1		81.4	5.3		
<b>16b (b)</b>	156	$C_{24}H_{17}BrO_2$	66.5	3.9		66.5	3.9		
<b>21b</b>	304	$C_{24}H_{19}NO_2$	81.6	5.4	4.0	81.8	5.2	3.9	
<b>22b</b>	152	$C_{24}H_{20}N_2O_2$	78.2	5.5	7.6	78.5	5.7	7.9	

(a) Reference (25), mp  $240^\circ$ . (b) Calcd. for Br: 18.5. Found: 18.8.



Triaryl-2-pyridones can be obtained from the corresponding 2-pyrones either by direct reaction with ammonia (19a, 23) or by their reaction with hydrazine hydrate followed by deamination with nitrous acid (19a, 24). However, in the present study 4,5,6-triphenyl- (21a) and 4-(*p*-methoxyphenyl)-5,6-diphenyl- (21b) 2-pyridones were prepared by dehydrogenation of the respective 3,4-dihydro derivatives 14a,b using sulfur. It is worthy to mention that 21b was also prepared from the 2-pyrone 15b *via* the amino pyridone 22b and subsequent reaction with nitrous acid (Scheme IV). The infrared spectra of the 2-pyridones 21a,b showed a carbonyl absorption at 1640  $\text{cm}^{-1}$  and an NH band at 3000-3120  $\text{cm}^{-1}$ . Their  $^1\text{H}$  nmr spectra showed the H-3 ring proton as a singlet at  $\delta$  6.51 (Table IV).

## EXPERIMENTAL

Microanalyses were performed by the Microanalysis Unit, Cairo University, Cairo. Infrared spectra were measured with a Unicam SP 1025 spectrophotometer for potassium bromide pellets or in Nujol. Electronic spectra were measured for solutions in methanol with a Unicam SP 1750 spectrophotometer. The  $^1\text{H}$  nmr spectra were recorded on a Varian EM-390 90 MHz spectrophotometer with TMS as internal standard. Mass spectra were recorded at 70 eV with an AEI MS-9 spectrometer coupled to a DS-50 data system using a direct insertion probe for introduction of samples.

Ethyl 3,4,5-Triaryl-5-oxopentanoates (Tables I, II, V).

To a cold suspension of sodium ethoxide (1.8 g, 0.026 mole) in dry ether (120 ml), ethereal solutions of deoxybenzoin (5 g, 0.026 mole) and ethyl cinnamate or *p*-methoxycinnamate (4.6 g, 0.026 mole) were suc-

cessively added and the reaction mixture was kept at 20° for 24 hours with occasional shaking. The pentanoic esters (50% yield) precipitated on pouring the reaction mixture onto ice-water mixture, and were crystallized from ethanol. More of the esters were obtained from the ethereal solution after washing with water, drying (sodium sulfate) followed by evaporation; ms: *m/e* (relative abundance) 3b:  $M^+$  402 (7), 357 (2), 251 (2), 224 (4), 223 (18), 211 (3), 210 (20), 209 (7), 208 (17), 207 (100), 197 (4), 196 (26), 195 (7), 179 (4), 178 (7), 167 (12), 166 (16), 165 (98), 161 (5), 152 (18), 137 (9), 135 (15), 134 (17), 121 (13), 119 (10), 115 (14), 105 (68), 91 (16), 89 (6), 77 (88).

*Threo* ethyl 4,5,6-triphenyl-5-oxopentanoate was obtained from the ethanolic mother liquor from the crystallization of the *erythro* isomer after dilution with water.

3,4,5-Triaryl-5-oxopentanoic Acids (Tables I, II, V).

A solution of ethyl 3,4,5-triaryl-5-oxopentanoate (2 g, 0.0049 mole) in ethanol (20 ml) was refluxed with potassium hydroxide (2 g, 0.036 mole) for two hours. The reaction mixture was then poured onto ice-water mixture (150 ml), acidified with 10% sulfuric acid and the separated pentanoic acid (90-95% yield) was filtered and crystallized from glacial acetic acid; ms: *m/e* (relative abundance) 3d:  $M^+$  374 (8), 227 (3), 223 (6), 210 (15), 209 (4), 197 (9), 196 (57), 195 (6), 180 (16), 179 (100), 167 (11), 166 (7), 165 (15), 152 (16), 138 (9), 137 (89), 134 (7), 119 (6), 115 (13), 109 (9), 105 (57).

4,5,6-Triaryl-3,4-dihydro-2H-pyran-2-ones (Tables III, IV, V).

They were prepared by two methods:

(i) A solution of 3,4,5-triaryl-5-oxopentanoic acid (1 g, 0.0028 mole) in acetic anhydride (20 ml) was refluxed with anhydrous sodium acetate (2 g) for two hours. The reaction mixture was then poured onto an ice-water mixture and the separated 3,4-dihydropyrene (60-65% yield) was filtered and crystallized from ethanol.

(ii) 3,4,5-Triaryl-5-oxopentanoic acid (1 g, 0.0028 mole) was refluxed with thionyl chloride (25 ml) for 30 minutes. After removal of excess of thionyl chloride under reduced pressure, the dihydropyrene (90-95% yield) separated and was crystallized from ethanol; ms: *m/e* (relative abundance) 6a:  $M^+$  326 (25), 285 (10), 284 (36), 283 (10), 256 (3), 207 (4), 206 (8), 191 (4), 189 (3), 180 (3), 179 (16), 178 (27), 167 (13), 165 (7), 152 (7), 151 (4), 139 (3), 131 (3), 115 (13), 106 (11), 105 (100), 103 (7), 102 (5), 91 (11), 89 (6), 78 (11), 77 (78); 6b:  $M^+$  356 (100), 329 (12), 317 (13), 315 (79), 314 (98), 313 (25), 299 (10), 284 (10), 238 (15), 237 (12), 224 (10), 210 (61), 208 (12), 207 (22), 206 (88), 205 (16), 198 (34), 195 (25), 178 (54), 177 (13), 176 (10), 168 (15), 165 (62), 162 (16), 136 (31), 135 (85), 122 (23), 120 (12), 115 (25), 108 (97), 106 (23), 105 (98), 102 (8), 92 (23), 78 (18), 77 (95).

The above 3,4-dihydro-2H-pyran-2-ones gave the corresponding 3,4,5-triaryl-5-oxopentanoic acids on refluxing their ethanolic solutions with hydrochloric acid or potassium hydroxide for two hours.

Preparation of Derivatives of 3,4,5-Triaryl-5-oxopentanoic Acids (Tables I, II, V).

These derivatives were generally prepared by refluxing an ethanolic solution of the 4,5,6-triaryl-2H-pyran-2-one with the appropriate amine, hydrazine or hydroxylamine for 2-8 hours and subsequent addition of water and were crystallized from ethanol or methanol.

The reaction with phenylhydrazine gave better results when the reactants were kept in toluene at 20° for 24 hours.

The above derivatives could be hydrolyzed to the parent acids when their solutions in glacial acetic acid were refluxed with concentrated hydrochloric acid for one hour.

4,5,6-Triaryl-3,4-dihydro-2-pyridones (Tables III, IV, V).

A solution of 4,5,6-triaryl-3,4-dihydro-2H-pyran-2-one (0.5 g, 0.0015 mole) in glacial acetic acid (20 ml) was refluxed with ammonium acetate (1.30 g, 0.0168 mole) for 4-6 hours. The dihydropyridones (60-65% yield) separated after removing the solvent under reduced pressure and addition of water and were crystallized from ethanol.

Dehydrogenation of 4,5,6-Triaryl-3,4-dihydro-2H-pyran-2-ones (i) With Sulfur.

4,5,6-Triaryl-3,4-dihydro-2H-pyran-2-one (1 g, 0.0030 mole) and sulfur (1.5 g) were finely ground together and fused for 2-6 hours at 170-190°. The reaction mixture after cooling was extracted several times with hot ethanol which afforded after evaporation the corresponding 4,5,6-triaryl-2-pyrone (60-70% yield).

4-(*p*-Methoxyphenyl)-5,6-diphenyl-2H-pyran-2-one was also prepared (15% yield) by condensation of deoxybenzoin with ethyl *p*-methoxyphenylpropionate in the presence of sodium ethoxide in dry ether at 0°; ms: m/e (relative abundance) **15a**: M<sup>+</sup> 324 (100), 298 (3), 297 (25), 296 (98), 268 (7), 267 (25), 265 (5), 247 (3), 192 (3), 191 (17), 190 (3), 189 (13), 165 (7), 162 (5), 126 (3), 106 (4), 105 (46), 77 (37); **15b**: M<sup>+</sup> 354 (55), 343 (4), 342 (20), 328 (3), 327 (25), 326 (100), 298 (4), 297 (15), 221 (12), 178 (11), 176 (3), 106 (3), 105 (42), 97 (4), 77 (33).

(ii) With Chloranil.

A solution of the dihydropyrone **6a** (1 g, 0.0030 mole) in dry benzene (15 ml) was refluxed with chloranil (1 g, 0.0040 mole) for five hours. After concentration the corresponding pyrone **15b** was obtained (30% yield).

(iii) With *N*-Bromosuccinimide.

A solution of the dihydropyrone **6a,b** (1 g, 0.0030 mole) in carbon tetrachloride (15 ml) was refluxed with NBS (0.66 g, 0.0037 mole) and a crystal of benzoyl peroxide for 8 hours. The reaction mixture in the case of **6a** gave after concentration the pyrone **15a** (40% yield), while in the case of **6b**, 3-bromo-4-(*p*-methoxyphenyl)-5,6-diphenyl-2H-pyran-2-one was obtained (40% yield). The latter was also prepared by bromination of the pyrone **15b** in carbon tetrachloride.

4,5,6-Triaryl-2-pyridones (Tables III, IV, V).

They were prepared (40-50% yield) by fusion of 4,5,6-triaryl-3,4-dihydro-2-pyridones (0.5 g, 0.0014 mole) with sulfur (1 g) for one hour at 190-210°.

4-(*p*-Methoxyphenyl)-5,6-diphenyl-2-pyridone was also prepared (70% yield) by treatment of a solution of 1-amino-4-(*p*-methoxyphenyl)-5,6-diphenyl-2-pyridone (0.2 g, 0.00054 mole) in glacial acetic acid (3 ml) with aqueous sodium nitrite (0.3 g). The amino-pyridone was prepared by refluxing the pyrone **15b** with 98% hydrazine hydrate in ethanol for 3 hours.

Acknowledgement.

We are grateful to Mr. Mel Micke, Department of Biochemistry, Madison, Wisconsin, U.S.A., for measuring the mass spectra.

## REFERENCES AND NOTES

- (1) L. Cavaliere, *Chem. Rev.*, **41**, 525 (1947); N. P. Shusherina, N. D. Dmitrieva, E. A. Luk'yanets and R. Ya Levina, *Russ. Chem. Rev.*, **36** 175 (1967); R. Livingstone, "Rodd's Chemistry of Carbon Compounds", S. Coffey, ed, Vol. IV, Heterocyclic Compounds, Part E, 1977, p 9.
- (2) S. Ruhemann, *J. Chem. Soc.*, 457 (1910); G. Soliman and I. E. El-Kholy, *ibid.*, 1755 (1954); I. E. El-Kholy, F. K. Rafla and M. M. Mishrikey, *J. Org. Chem.*, **31**, 2167 (1966).
- (3) E. D. Bergmann, D. Ginsburg and R. Pappo, "Organic Reactions", Vol. 10, John Wiley and Sons, New York, 1959, p 179.
- (4) J. Stevanovsky and A. Bozilova, *Monatsh. Chem.*, **99**, 798 (1968); J. Stevanovsky and L. Viteva, *Commun. Dept. Chem. Bulg. Acad. Sci.*, **4**, 99 (1971); *Chem. Abstr.*, **75**, 88270v (1971); *ibid.*, **4**, 159 (1971); *Chem. Abstr.*, **76**, 24872f (1972); Y. N. Stevanovsky and L. Z. Viteva, *Monatsh. Chem.*, **111**, 1287 (1980); *ibid.*, **112**, 125 (1981).
- (5) A. M. Baradel, R. Longera and J. Dreux, *Bull. Soc. Chim. France*, 252 (1970).
- (6) R. A. Morton, A. Hassan and T. C. Calloway, *J. Chem. Soc.*, 883 (1934); E. A. Braude and F. Sondheimer, *ibid.*, 3754 (1955); G. Adembri, P. S. Arti-Fantoni and E. Belgodere, *Tetrahedron*, **22**, 3149 (1966).
- (7) C. A. Kingsburg and W. B. Thornton, *J. Org. Chem.*, **31**, 1000 (1966).
- (8) A. M. Baradel, J. Dreux, R. Longera, P. Lazio and H. Riviere, *Bull. Soc. Chim. France*, 3543 (1966).
- (9) A. M. Baradel, R. Longera and J. Dreux, *ibid.*, 255 (1970).
- (10) R. B. Woodward, F. Sondheimer, T. Taub, K. Heusler and W. M. McLamore, *J. Am. Chem. Soc.*, **74**, 4223 (1952).
- (11) L. Hagemayer and D. Hull, *Ind. Eng. Chem.*, **41**, 2920 (1949); E. S. Rothman, S. Serota, T. Perstein and D. Swern, *J. Org. Chem.*, **27**, 3123 (1962).
- (12) L. Mosti, P. Schenone and G. Menozzi, *J. Heterocyclic Chem.*, **15**, 181 (1978).
- (13) H. Suzuki, *Bull. Chem. Soc. Japan*, **33**, 381 (1960).
- (14) L. Friedman and F. R. Long, *J. Am. Chem. Soc.*, **75**, 2832 (1953); W. H. McFadden, E. A. Day and M. J. Diamond, *Anal. Chem.*, **37**, 89 (1965); E. Hankanen, R. Moisio and P. Karvonen, *Acta Chem. Scand.*, 370 (1965); B. J. Millard, *Org. Mass Spectrom.*, **1**, 279 (1968).
- (15) A. Yogev and Y. Mazur, *J. Am. Chem. Soc.*, **87**, 3520 (1965).
- (16) H. Nozaki, Z. Yamaguti, T. Okada, R. Noyori and M. Kawanisi, *Tetrahedron*, **23**, 3993 (1967).
- (17) D. Rosenthal, P. Grabowich, E. Saba and J. Fried, *J. Am. Chem. Soc.*, **85**, 3971 (1963).
- (18) W. Jacobs and A. Scott, *J. Biol. Chem.*, **87**, 601 (1930); N. P. Shusherina, E. A. Luk'yanets and R. Ya Levina, *Zh. Obshch. Khim.*, **34**, 2507 (1964); *Zh. Org. Khim.*, **1**, 2226 (1965).
- (19a) I. E. El-Kholy, F. K. Rafla and G. Soliman, *J. Chem. Soc.*, 4490 (1961); (b) R. Hayasi and H. Nozaki, *Tetrahedron*, **27**, 3085 (1971); (c) N. N. Magdesieva, N. M. Koloskova and LeNgi, *Khim. Geterotsikl. Soedin.*, 1475 (1977).
- (20) W. H. Pirkle and W. V. Turner, *J. Org. Chem.*, **40**, 1617 (1975); I. E. El-Kholy, M. M. Mishrikey and H. M. Fuid-Alla, *J. Heterocyclic Chem.*, **14**, 845 (1977).
- (21) H. Budzikiewicz, C. Djerassi and D. H. Williams, "Mass Spectrometry of Organic Compounds", Holden Day, Inc., 1967, p 208; W. H. Pirkle and M. Dines, *J. Am. Chem. Soc.*, **90**, 2318 (1968); W. H. Pirkle and W. V. Turner, *J. Org. Chem.*, **40**, 1644 (1975).
- (22) C. Spitteller, *Advan. Heterocyclic Chem.*, **7**, 305 (1966).
- (23) I. E. El-Kholy, F. K. Rafla and G. Soliman, *J. Chem. Soc.*, 2588 (1959).
- (24) I. E. El-Kholy, M. M. Mishrikey and H. M. Fuid-Alla, *J. Heterocyclic Chem.*, **12**, 129 (1975).
- (25) E. J. Cragoe, Jr., A. M. Pietruszkiewicz and C. M. Robb, *J. Org. Chem.*, **23**, 971 (1958).