

Reaction of 3-Aryl-1-phenyl-2-propen-1-ones with Ethyl Phenylacetate

Yousuf A. Al-Farkh, Farouk H. Al-Hajjar (1) and Hayat S. Hamoud (Mrs.)

Petroleum and Petrochemicals Division, Kuwait Institute for Scientific Research, P. O. Box 24885
Safat, Kuwait

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3-Aryl-1-phenyl-2-propen-1-one I reacted with ethyl phenylacetate (II) in the presence sodium ethoxide at room temperature to give the corresponding ethyl β -aryl- γ -benzoyl- α -phenylbutyrate III. However, when the same ketones were refluxed with ethyl phenylacetate, they gave the corresponding 4-aryl-3,6-diphenyl-3,4-dihydro-2H-pyran-2-ones IV. The reactions of III and IV with hydrazine hydrate afforded the corresponding hydrazones VI and 2-pyridones VIII, respectively. The structure and configuration of the products are based on chemical and spectroscopic evidence.

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The reaction of 3-phenyl-(Ia) and 3-*p*-methoxyphenyl-(Ic)-1-phenyl-2-propen-1-ones with ethyl phenylacetate (II) in the presence of sodium ethoxide have been reported to give the corresponding ethyl β -aryl- γ -benzoyl- α -phenylbutyrate III (2,3a,b). The goal of the present investigation was to prepare new substituted heterocyclic compounds and to shed further light on the reaction mechanisms of α,β -unsaturated ketones with ethyl phenylacetate as well as to establish the structure and configuration of the products.

When 3-phenyl-(Ia), 3-*p*-tolyl-(Ib), 3-*p*-methoxyphenyl-(Ic), and 3-*p*-chlorophenyl-(Id)-1-phenyl-2-propen-1-ones were allowed to react with ethyl phenylacetate at room temperature for 24 hours in the presence of a suspension of sodium ethoxide in benzene, they gave rise to the corresponding ethyl β -aryl- γ -benzoyl- α -phenylbutyrate IIIa-d, whereas Ib and Id gave in addition to the ester III, a small amount of the corresponding 4-aryl-3,6-diphenyl-3,4-dihydro-2H-pyran-2-ones IVb,d. However, when the reaction was carried out under reflux for one hour, the corresponding 2-pyrones IVa-d were obtained in 85-93% yield. In all cases the reaction seems to proceed by

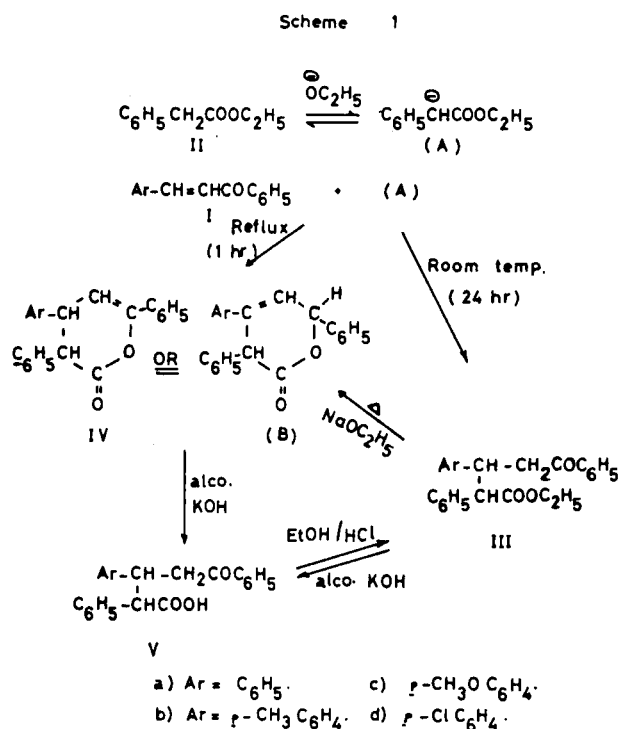


Table I

The Infrared, Electronic and Nuclear Magnetic Resonance Spectral Data of 4-Aryl-3,6-diphenyl-3,4-dihydro-2H-pyran-2-ones IVa-d

Compound	Infrared Spectra (Nujol)		Electronic Spectra (Ethanol)		Nmr Spectra (Deuteriochloroform)	
	cm ⁻¹	ν	λ max (nm)	ϵ	δ	Assignment (No. of Protons)
IVa	1720 (s)	C=O	284	6,990	7.96-6.70 (m)	(16) ArH+CH=
	1680 (s)	C=C	248	15,680	5.43-4.27 (m)	(2) >CHCH<
			225	46,740		
IVb	1718 (s)	C=O	248	14,680	7.95-6.50 (m)	(16) ArH+CH=
	1670 (s)	C=C			5.37-4.03 (m)	(2) >CHCH<
IVc	1715 (s)	C=O	246	14,200	2.05 (s)	(3) ArCH ₃
	1675 (s)	C=C			7.90-6.18 (m)	(15) ArH+CH=
					5.17-4.17 (m)	(2) >CHCH<
IVd	1720 (s)	C=O	247	15,920	3.53 (s)	(3) ArOCH ₃
	1675 (s)	C=C	220	17,140	8.07-6.40 (m)	(15) ArH+CH=
				5.73-4.13 (m)	(2) >CH-CH<	

Table II

The Infrared, Electronic and Nuclear Magnetic Resonance Spectral Data of Ethyl β -Aryl- γ -benzoyl- α -phenylbutyrates IIIa-d, β -Aryl- γ -benzoyl- α -phenylbutyric Acids Va-d and the Hydrazone Derivatives VIa-d

Compound	Infrared Spectra (Potassium bromide)		Electronic Spectra (Ethanol)		Nmr Spectra (Deuteriochloroform)	
	cm^{-1}	ν	λ max (nm)	ϵ	δ	Assignments (No. of Protons)
IIIa	1735 (s) 1690 (s)	COOEt COAr	243	12,310	7.97-6.80 (m) 4.23-2.97 (m) 3.87 (q) (J = 7 Hz) 0.90 (t) (J = 7 Hz)	(15) ArH (4) >CHCHCH ₂ (2) CH ₂ (3) CH ₃
IIIb	1730 (s) 1685 (s)	COOEt COAr	242	12,700	7.92-6.92 (m) 4.42-2.93 (m) 3.97 (q) (J = 7 Hz) 2.27 (s) 0.92 (t) (J = 7 Hz)	(14) ArH (4) >CHCHCH ₂ (2) CH ₂ (3) ArCH ₃ (3) CH ₃
IIIc	1735 (s) 1685 (s)	COOEt COAr	242	11,070	8.08-6.58 (m) 4.58-2.58 (m) 3.75 (s) 0.93 (t) (J = 7 Hz)	(14) ArH (6) >CHCHCH ₂ CH ₂ of ethyl (3) ArOCH ₃ (3) CH ₃
IIId	1735 (s) 1685 (s)	COOEt COAr	243	12,080	8.08-6.98 (m) 4.45-2.75 (m) 3.90 (q) (J = 7 Hz) 0.05 (t) (J = 7 Hz)	(14) ArH (4) >CHCHCH ₂ (2) CH ₂ (3) CH ₃
Va	3400-2500 (br) 1705 (s) 1690 (s)	OH COOH COAr	241	11,800	8.07-6.87 (m) 4.30-3.40 (m)	(15) ArH (4) >CHCHCH ₂
Vb	3400-2500 (br) 1700 (s) 1685 (s)	OH COOH COAr	278-271 (sh) 242	4,030 16,130	8.05-6.72 (m) 4.03-3.20 (m) 2.15 (s)	(14) ArH (4) >CH-CHCH ₂ (3) ArCH ₃
Vc	3400-2500 (br) 1700 (s) 1685 (s)	OH COOH COAr	242	12,260	8.13-6.40 (m) 4.17-3.23 (m) 3.65 (s)	(14) ArH (4) >CHCHCH ₂ (3) ArOCH ₃
Vd	3400-2500 (br) 1697 (s) 1685 (s)	OH COOH COAr	241	12,110	8.13-6.87 (m) 4.30-3.26 (m)	(14) ArH (4) >CHCHCH ₂
VIa	3360 (m) 3210 (m) 1730 (s)	NH ₂ COOEt	266	12,200	7.69-7.17 (m) 4.67 (br) 4.17-2.69 (m) 3.83 (q) (J = 7 Hz) 0.83 (t) (J = 7 Hz)	(15) ArH (2) NH ₂ (4) >CHCHCH ₂ (2) CH ₂ (3) CH ₃
VIb	3350 (m) 3220 (br) 1730 (s)	NH ₂ COOEt	266	11,085	7.73-7.0 (m) 4.53 (br) 3.90 (q) (J = 7 Hz) 4.17-2.67 (m) 2.30 (s) 0.87 (t) (J = 7 Hz)	(14) ArH (2) NH ₂ (2) CH ₂ (4) >CHCHCH ₂ (3) ArCH ₃ (3) CH ₃
VIc	3350 (m) 3220 (m) 1730 (s)	NH ₂ COOEt	267	13,050	7.90-6.60 (m) 4.60 (br) 4.23-2.23 (m) 3.53 (g) (J = 7 Hz) 3.63 (s) 0.87 (t) (J = 7 Hz)	(14) ArH (2) NH ₂ (4) >CHCHCH ₂ (2) CH ₂ (3) ArOCH ₃ (3) CH ₃
VI d	3340 (m) 3200 (m) 1730 (s)	NH ₂ COOEt	265	13,160	7.78-6.70 (m) 4.80 (br) 4.17-2.30 (m) 3.85 (q) (J = 7 Hz) 0.88 (t) (J = 7 Hz)	(14) ArH (2) NH ₂ (4) >CHCHCH ₂ (2) CH ₂ (3) CH ₃

Michael addition of the carbanion (A) to the ketone to give III (2,3), followed by cyclization of the intermediate III to yield IV (cf. Scheme 1).

The structure of the pyrones IVa-d and the esters IIIa-d were established by both spectroscopic and chemical evidence.

(1) Spectroscopic Evidence.

The infrared spectra of the 2-pyrones IVa-d (Table I) show absorption in the $1720-1715\text{ cm}^{-1}$ and $1680-1670\text{ cm}^{-1}$ regions which are correlated to the carbonyl and the $>\text{C}=\text{C}<$ stretching frequencies of the 2-pyrone (4,5). The nmr spectra of these pyrones and the assignment of the signals are reported in Table I. The electronic spectra of these compounds show absorption in the region $248-246\text{ nm}$ attributed to the K-band of the styrene moiety (6). The alternative structure (B) (cf. Scheme 1) is excluded since the electronic absorption of these compounds are not affected by the substituents in the aryl group. The structure of the esters IIIa-d was rigidly confirmed from their spectral data (ir, nmr, and uv) (cf. Table II). Thus, the ir spectra show two strong bands at $1735-1730\text{ cm}^{-1}$ and $1690-1685\text{ cm}^{-1}$ correlated to the carbonyl group of ester and ketone (7a,b), respectively. The nmr spectra of the esters IIIa-d show signals attributed to the ethyl ester, methine and aromatic protons (Table II). The electronic spectra of these compounds are identical which indicates their structural analogy. They show absorption maxima in the range $243-242\text{ nm}$ (cf. Table II) which are very similar to the spectra of acetophenone (8a-c). Accordingly, this absorption band can be attributed to the $\pi-\pi^*$ band of the acetophenone moiety.

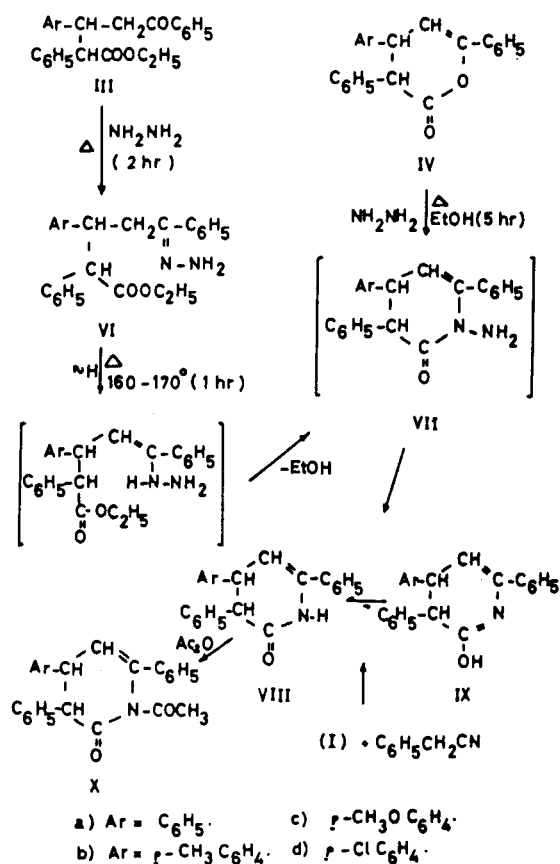
(2) Chemical Evidence.

When the pyrones IVa-d were subjected to alkaline cleavage, β -aryl- γ -benzoyl- α -phenylbutyric acids Va-d were obtained. The structure assigned to the acids was established by esterification with ethanol in the presence of sulfuric acid to give the corresponding esters IIIa-d. Further evidence for the structure of the acids Va-d is forthcoming from their spectral data. Thus, their nmr spectra show chemical shifts which can be assigned to the different protons of these compounds (cf. Table II). Their ir spectra (Table II) show bands in the regions $1705-1697\text{ cm}^{-1}$ and $1690-1685\text{ cm}^{-1}$ which can be correlated to the $\nu\text{ C}=\text{O}$ of the carboxyl and the benzoyl groups (7b,c), respectively, in addition to the broad band at $3400-2500\text{ cm}^{-1}$ ($\nu\text{ OH}$ of COOH). The electronic spectra of these acids are identical which indicates their structural analogy and similar to the spectra of the corresponding esters IIIa-d, can be attributed to the $\pi-\pi^*$ band of the acetophenone moiety (8a-c).

The structure of the esters IIIa-d was also established by their chemical reactions. Thus, the heating of esters

IIIa-d with sodium ethoxide in benzene on a boiling water-bath for 30 minutes, yielded the corresponding 2-pyrones IVa-d. On alkaline hydrolysis, the esters IIIa-d gave the corresponding acids Va-d. Adequate evidence for the assigned structure was supported by their reaction under reflux with hydrazine hydrate to give the hydrazones VIa-d. The structure of the hydrazone derivatives VIa-d was confirmed from their spectral data. Thus, their ir spectra show two sharp bands in the regions $3360-3340\text{ cm}^{-1}$ and $3220-3200\text{ cm}^{-1}$ which are attributed to $\nu\text{ NH}_2$ (7d) and a strong band at 1730 cm^{-1} correlated to the carbonyl group of the ester (7a). These values confirmed our results that the hydrazine hydrate has only reacted with the carbonyl group of the ketonic ester III, (cf. Table II). The nmr spectra show a broad band (NH_2), in addition to the methine and the ethyl ester protons (Table II). The electronic spectra of these compounds are similar to the spectra of the acetophenone hydrazone (8a). Although Sammour, *et al.*, (2) failed to synthesize a cyclic product from the reaction of ester IIIa,c with hydrazine hydrate; 2-pyridone derivatives VIIIa-d were separated in 90-94% yield when the hydrazones (VIa-d) were heated at $160-170^\circ$ for one hour or by refluxing the esters IIIa-d and hydrazine hydrate in *n*-butanol or ethanol for 8 hours. The latter compounds VIIIa-d were identical with the products obtained by the

Scheme 2



reaction of 2-pyrones IVa-d with hydrazine hydrate in boiling ethanol (*cf.* Scheme 2). The compound VIIIb was also separated from the reaction of phenylacetonitrile with the ketone 1b in the presence of sodium ethoxide. Further evidence for the structure of 2-pyridones VIIIa-d was obtained from their ir, nmr, and uv spectra (*cf.* Table III). Thus, their ir spectra show a broad band in the range 3300-3240 cm^{-1} which is correlated to ν NH in addition to a strong band at 1680-1670 cm^{-1} that can be ascribed to the ν C=O of the pyridone ring (9). The nmr spectra of VIIIa-d show signals attributed to the methine and aromatic protons. The electronic spectra of these compounds show an absorption between 249-248 nm which can be attributed to the K-band of the styrene moiety (6). When the 2-pyridone VIIIa was treated with acetic anhydride, it gave the corresponding *N*-acetyl derivative Xa. This reaction gives a further evidence for the structure of these compounds as 2-pyridone and not as 2-hydroxypyridine (IX) (9). The structure of the latter compound was substantiated by its ir, uv and nmr spectra (Table III). The formation of 2-pyridones VIIIa-d from IV may proceed *via* the intermediate formation of VII followed by hydrolysis (10) (*cf.* Scheme 2).

EXPERIMENTAL

All the melting points are uncorrected. The ir spectra were recorded using a Perkin-Elmer 577 Grating Infrared Spectrophotometer. The nmr spectra were measured on JEOL JNM-PM Spectrometer using TMS as internal standard. The electronic spectra were measured on a Beckman Spectrophotometer ACTA using scan speed $\frac{1}{4}$ nm/second and chart 10 nm/inch. The purity of the analytical samples was checked by tlc (silica gel). Microanalyses were determined by Dr. Alfred Bernhardt, West Germany. Evaporation was performed on rotary evaporators *in vacuo*.

Reaction of 3-Aryl-1-phenyl-2-propen-1-ones with Ethyl Phenylacetate (II).

a) Under Reflux. General Procedure.

Ethyl phenylacetate (II) (0.015 mole) and the ketone (I) (0.015 mole) were added successively to a suspension of sodium ethoxide (0.015 mole) in dry benzene (50 ml. per 1.0 g. of ketone). The reaction mixture, which gradually acquired a deep orange color, was heated on a boiling water-bath for one hour with occasional stirring, then poured into cold dilute hydrochloric acid (10%; 100 ml.) and extracted with benzene. The benzene layer was shaken with sodium hydrogen carbonate solution, dried (sodium sulfate) and evaporated. The residue was crystallized from a suitable solvent to give the corresponding 4-aryl-3,6-diphenyl-3,4-dihydro-2*H*-2-pyran-2-one IV as colorless crystals. The results are reported in Table IV.

Table III

The Infrared, Electronic and Nuclear Magnetic Resonance Spectral Data of 4-Aryl-3,6-diphenyl-3,4-dihydro-2(1*H*)pyridones VIIIa-d and the *N*-acetyl derivative IXa

Compound	Infrared Spectra (Nujol)		Electronic Spectra (Ethanol)		Nmr Spectra (Deuteriochloroform)	
	cm^{-1}	ν	λ max (nm)	ϵ	δ	Assignment (No. of Protons)
VIIIa	3240 (br)	NH	248	14,020	7.52-6.68 (m)	(17) ArH+CH+=NH
	1680 (s)	C=O of pyridone			5.35-3.52 (m)	(2) >CHCH<
	1610 (s)	C=C				
VIIIb	3240 (br)	NH	248	14,180	7.58-6.42 (m)	(16) ArH+CH+=NH
	1670 (s)	C=O of pyridone			5.10-3.52 (m)	(2) CHCH
	1605 (m)	C=C			2.03 (s)	(3) ArCH ₃
VIIIc	3300 (s)	NH	249	15,110	7.60-6.30 (m)	(16) ArH+CH+=NH
	1670 (s)	C=O of pyridone			4.95-4.21 (m)	(2) >CHCH<
	1600 (s)	C=C			3.53 (s)	(3) ArOCH ₃
VIIId	3240 (br)	NH	249	15,100	8.12-6.45 (m)	(16) ArH+CH+=NH
	1670 (s)	C=O of pyridone			5.00-4.21 (m)	(2) >CHCH<
	1600 (m)	C=C				
Xa	1730 (s)	NCOCH ₃	249	13,250	7.60-6.36 (m)	(16) ArH+CH=
	1670 (s)	C=O of pyridone			5.00-3.20 (m)	(2) >CHCH<
	1600 (m)	C=C			2.40 (s)	(3) COCH ₃

Table IV

4-Aryl-3,6-diphenyl-3,4-dihydro-2H-pyran-2-ones (IVa-d)

Compound	Yield (%)	M.p. °C	Formula	Calcd. %		Found %	
				C	H	C	H
IVa	92	279-280 (a)	C ₂₃ H ₁₈ O ₂	84.64	5.56	84.42	5.45
IVb	95	272-273 (b)	C ₂₄ H ₂₀ O ₂	84.68	5.92	84.43	5.89
IVc (c)	89	238-239 (a)	C ₂₄ H ₂₀ O ₃	80.88	5.66	80.69	5.87
IVd (d)	90	222-223 (a)	C ₂₃ H ₁₇ ClO ₂	75.56	4.75	75.80	4.79

(a) Crystallized from benzene. (b) Crystallized from methanol-benzene. (c) OCH₃ %: Calcd. for = 8.71; Found = 8.52. (d) Cl%: Calcd. for = 9.83; Found = 9.93.

Table V

Ethyl β-Aryl-γ-benzoyl-α-phenylbutyrates (IIIa-d) and their Acids (Va-d)

Compound	Yield (%)	M.p. °C	Formula	Calcd. %		Found %	
				C	H	C	H
IIIa (3a)	82	153-154 (a)	C ₂₅ H ₂₄ O ₃	80.62	6.50	80.71	6.53
IIIb	72	142-143 (b)	C ₂₆ H ₂₆ O ₃	80.80	6.78	80.61	6.84
IIIc (2)	81	133-134 (a)	C ₂₆ H ₂₆ O ₄	77.59	6.51	77.62	6.73
IIId (c)	78	158-159 (a)	C ₂₅ H ₂₃ ClO ₃	73.79	5.70	73.73	5.70
Va (3a)	97	239-240 (b)	C ₂₃ H ₂₀ O ₃	80.21	5.85	80.30	5.62
Vb	98	224-225 (b)	C ₂₄ H ₂₂ O ₃	80.42	6.19	80.59	6.29
Vc	96	205-206 (d)	C ₂₄ H ₂₂ O ₄	76.99	5.92	76.80	5.84
Vd (e)	98	215-216 (b)	C ₂₃ H ₁₉ ClO ₃	72.92	5.06	72.89	5.15

(a) Crystallized from methanol. (b) Crystallized from benzene. (c) Cl %: Calcd. for = 8.71; Found = 8.62. (d) Crystallized from benzene-methanol. (e) Cl %: Calcd. for = 9.36; Found = 9.62.

The alkaline aqueous layer was acidified with dilute sulfuric acid and extracted with ether. Evaporation of the solvent gave phenylacetic acid, m.p. and mixed m.p. 76-77°.

b) At Room Temperature. General Procedure.

Ethyl phenylacetate (II) (0.015 mole) and the ketone (I) (0.015 mole) were added successively to a suspension of sodium ethoxide (0.015 mole) in dry benzene. The reaction mixture was left at room temperature for 24 hours with occasional stirring, then poured into cold dilute hydrochloric acid solution and worked up as in method (a) to give the corresponding ethyl β-aryl-γ-benzoyl-α-phenylbutyrate III as colorless crystals. The results are reported in Table V. In the case of Ib and Id, the product contained, in addition to the esters IIIb and IIIc, the corresponding 4-aryl-3,6-diphenyl-3,4-dihydro-2H-pyran-2-ones IVb (5% yield) and IVd (7% yield). These were separated from the corresponding esters III by fractional crystallization from benzene.

β-Aryl-γ-benzoyl-α-phenylbutyric Acid V. General Procedure.

The pyrone IV (1.0 g.) or the ester III was refluxed on a boiling water-bath with 5% methanolic potassium hydroxide (50 ml.) for one hour. The solvent was evaporated and the residue diluted with water, then extracted with ether to remove the neutral fraction. The aqueous alkaline solution was acidified and extracted with ether. Evaporation of the dried ether gave an oil, which solidified upon trituration with light-petroleum (b.p. 30-60°). The colorless solid was crystallized from a suitable solvent to give the corresponding β-aryl-γ-benzoyl-α-phenylbutyric acid V. The results are reported in Table V.

Esterification of β-Aryl-γ-benzoyl-α-phenylbutyric Acids Va-d. General Procedure.

This was accomplished by refluxing the acid (2.0 g.) with absolute ethyl alcohol (8 ml.) and a few drops of concentrated sulfuric acid on a boiling water-bath for 4 hours. The product was crystallized from a suitable solvent to give the corresponding ester III as colorless leaflets in 82-90% yield (cf. Table V).

Conversion of Ethyl β-Aryl-γ-benzoyl-α-phenylbutyrate III to the Corresponding Pyrones IV. General Procedure.

The solution of the ester III (0.019 mole) in dry benzene (50 ml.) was stirred with a suspension of sodium ethoxide (1.31 g.) on a boiling water-bath for one hour. The reaction mixture was poured into cold water and the benzene layer was evaporated. The residue was crystallized from a suitable solvent to give the corresponding pyrone IV in 89-92% yield.

The alkaline aqueous layer was acidified with dilute sulfuric acid and extracted with benzene. Evaporation of the solvent gave the corresponding acid in 5-10% yield.

Reaction of Ethyl β-Aryl-γ-benzoyl-α-phenylbutyrates IIIa-d with Hydrazine Hydrate. General Procedure.

A mixture of the ester III (2 g.) and hydrazine hydrate (99% w/w; 3 ml.) were refluxed in ethanol (25 ml.) for 2 hours (11). The reaction mixture was concentrated, diluted with water and the precipitated solid was crystallized from a suitable solvent to give the corresponding hydrazone VI. The results are reported in Table VI.

Table VI

The Hydrazone Derivatives (VIa-d) and 4-Aryl-3,6-diphenyl-3,4-dihydro-2(1H)pyridones (VIIIa-d)

Compound	Yield (%)	M.p. °C	Formula	Calcd. %			Found %		
				C	H	N	C	H	N
VIa (2)	81	110-111 (a)	C ₂₅ H ₂₆ N ₂ O ₂	77.69	6.78	7.25	77.81	6.61	7.46
VIb	78	108-109 (b)	C ₂₆ H ₂₈ N ₂ O ₂	77.97	7.05	6.99	78.47	6.98	6.76
VIc (2)	80	105-106 (b)	C ₂₆ H ₂₈ N ₂ O ₃	74.97	6.78	6.73	75.14	6.92	6.81
VId (c)	79	102-103 (a)	C ₂₅ H ₂₅ ClN ₂ O ₂	71.33	5.99	6.66	71.38	5.95	6.35
VIIIa	92	280-281 (b)	C ₂₃ H ₁₉ NO	84.89	5.88	4.3	85.01	5.86	4.6
VIIIb	90	266-267 (b)	C ₂₄ H ₂₁ NO	84.92	6.24	4.13	85.21	6.20	4.62
VIIIc	88	272-273 (d)	C ₂₄ H ₂₁ NO ₂	81.10	5.95	3.94	81.38	5.93	3.66
VIII d (e)	87	257-258 (d)	C ₂₃ H ₁₈ ClNO	76.77	5.04	3.89	76.34	4.86	4.11

(a) Crystallized from cyclohexane (tlc gave only one spot); reported m.p. for VIa 160° (2). (b) Crystallized from benzene-cyclohexane (tlc gave only one spot); reported m.p. for VIc 163° (2). (c) Cl %: Calcd. for = 8.42; Found = 8.12. (d) Crystallized from benzene. (e) Cl %: Calcd. for = 9.85; Found = 10.11.

4-Aryl-3,6-diphenyl-3,4-dihydro-2-(1H)pyridones (VIIIa-d). General Procedure.

A solution of the pyrone IV (2.0 g.) in ethanol (25 ml.) was refluxed with hydrazine hydrate (99% w/w; 3 ml.) on a boiling water-bath for 5 hours. The reaction mixture was concentrated and then diluted with water. The precipitated solid was crystallized from a suitable solvent to give the corresponding 2-pyridones VIIIa-d as colorless crystals. The results are reported in Table VI.

The same product was also separated in 90-94% yield on heating the hydrazones VIa-d for one hour in an oil-bath at 160-170°.

Reaction of 3-p-Tolyl-1-phenyl-2-propen-1-one (Ib) with Phenylacetonitrile.

Phenylacetonitrile (0.015 mole) and the ketone (Ib) (0.015 mole) were added successively to a suspension of sodium ethoxide (0.015 mole) in dry benzene (50 ml. per 1.0 g. of ketone). The reaction mixture, which gradually acquired a yellow color, was left overnight at room temperature with occasional stirring, then poured into cold dilute hydrochloric acid (100 ml.) and extracted with benzene. The benzene layer was shaken with sodium hydrogen carbonate solution, dried (sodium sulfate) and evaporated. The residue was crystallized from benzene-cyclohexane to give 4-tolyl-3,6-diphenyl-3,4-dihydro-2(1H)pyridone (VIIIb) in colorless crystals, m.p. and mixed m.p. 266-267°, yield = 78%.

The alkaline aqueous layer was acidified with dilute sulfuric acid and extracted with benzene. Evaporation of the solvent gave phenylacetic acid m.p. and mixed m.p. 76-77°.

1-Acetyl-3,4,6-triphenyl-3,4-dihydro-2(1H)pyridone (Xa).

A mixture of acetic anhydride (3 ml.) and the pyridone VIIIa (1.0 g.) was heated in an oil-bath (125-130°) for 30 minutes. The reaction product was treated with 50% ethanol (20 ml.) and the precipitated solid was crystallized from benzene-cyclohexane to give the titled compound IXa as colourless leaflets m.p. 266-267°, yield = 88%.

Anal. Calcd. for C₂₅H₂₁NO₂: C, 81.72; H, 5.76; N, 3.81.
Found: C, 81.89; H, 5.88; N, 4.11.

REFERENCES AND NOTES

- (1) Author to whom all inquiries should be addressed.
- (2) A. Sammour, M. I. B. Selim and M. S. Abd Elhalim, *Egypt. J. Chem.*, 15, 23 (1972).
- (3a) W. Borsche, *Ber.*, 42, 4496 (1909); (b) R. Conner and D. Andrews, *J. Am. Chem. Soc.*, 56, 2713 (1934).
- (4) T. Eicher and A. Hansen, *Tetrahedron Letters*, 1169 (1967); Y. H. Hayasi and H. Nozaki, *Tetrahedron*, 27, 3085 (1977); T. Sasaki, K. Kanematsu and A. Kakehi, *J. Org. Chem.*, 36, 2451 (1971).
- (5) L. Mosti, P. Schenone and G. Menozzi, *J. Heterocyclic Chem.*, 15, 181 (1978).
- (6) C. G. Overberger and D. Tanner, *J. Am. Chem. Soc.*, 77, 369 (1955).
- (7) L. J. Bellamy, "The Infrared Spectra of Complex Molecules", Methuen, London, 1966, pages: (a) 179, (b) 132, (c) 162, (d) 249.
- (8a) G. Adembri, P. Sarti-Fantoni and E. Belgodere, *Tetrahedron*, 22, 3149 (1966); (b) E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, 3754 (1955); (c) R. A. Morton, Ali Hassan and T. C. Calloway, *ibid.*, 883 (1934).
- (9) A. Sakurai and H. Midoriakwa, *Bull. Chem. Soc. Japan*, 40, 1680 (1967); R. H. Wiley and J. Q. Esterle, *J. Org. Chem.*, 22, 1257 (1957); S. F. Mason, *J. Chem. Soc.*, 4874 (1957).
- (10) F. G. Baddar, F. H. Al-Hajjar and N. R. El-Rayyes, *J. Heterocyclic Chem.*, 13, 195 (1976); I. E. Kholy, F. K. Rafla and G. Soliman, *J. Chem. Soc.*, 4490 (1961).
- (11) When the reaction mixture was refluxed for 8 hours in ethanol or in 1-butanol, the corresponding 2-pyridone VIII was separated.