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Reaction of α,β-Unsaturated Ketones with Compounds containing an Active Methylene Group. A Synthesis of (3H)-1,2-Diazepin-3-one Derivatives

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1,3-Diaryl-2-propen-1-ones (IIa, b) reacted with methyl α-naphthylacetate (Ib) in the presence of sodium methoxide at room temperature, or under reflux to give only the corresponding 4,6-diaryl-3-[3̄-(1̄-3̄-diarylpropan-1̄-one)]-3-α-naphthyl-4-hydro-2H-pyran-2-ones (IIIa, b). However, on reacting the ketones (IIc—f) with ethyl phenylacetate (Ia) in the presence of sodium ethoxide at room temperature, or under reflux, the corresponding ethyl γ-aroyl-β-aryl-α-phenyl-butyrates (IVa—d) or 4,6-diaryl-3-[3̄-(1̄,3̄-diarylpropan-1̄-one)]-3-phenyl-4-hydro-2H-pyran-2-ones (IIIc, d), respectively, were obtained. The reaction of these compounds, (III) and (IV), with hydrazine hydrate gave the corresponding (3H)-1,2-diazepin-3-one (VI) and hydrazone (IX) derivatives, respectively.

The structures of the products were established by chemical and spectroscopic evidence.

Keywords——1,3-diaryl-2-propen-1-one; ethyl γ-aroyl-α,β-diarylbutyrate; 4,6-diaryl-3-[3̄-(1̄,3̄-diarylpropan-1̄-one)]-3-α-naphthyl-4-hydro-2H-pyran-2-one; (3H)-1,2-diazepin-3-one derivatives; spectroscopy

Introduction

The reaction of 1,3-diphenyl-2-propen-1-one with ethyl phenylacetate in the presence of sodium ethoxide has been reported to give the corresponding ethyl γ-benzoyl-α,β-diphenylbutyrate.[2—4)] The present investigation was intended to prepare new heterocyclic compounds and to throw further light on the reaction mechanism of α,β-unsaturated ketones with alkyl α-naphthyl- and phenylacetates, as well as to establish the structure and configuration of the products.

Results and Discussion

When 4-phenyl-(IIa) and 4-tolyl-(IIb)-1-phenyl-2-propen-1-ones were stirred with methyl α-naphthylacetate (Ib) in the presence of sodium methoxide in benzene, at room temperature for 24 hr or under reflux for 1 hr, the corresponding 4-aryl-3-α-naphthyl-3-[3̄-(1̄-3̄-diarylpropan-1̄-one)]-6-phenyl-4-hydro-2H-pyran-2-ones (IIIa, b) were obtained. Though the reaction of 1,3-diaryl-2-propen-1-ones (IIc, e) with ethyl phenylacetate (Ia) in the presence of sodium ethoxide under reflux for 1 hr gave the same pyran-2-ones (IIIc, d), lowering the reaction temperature to room temperature (24 hr) afforded the corresponding simple Michael addition products: ethyl γ-aroyl-β-aryl-α-phenylbutyrates (IVa, c). The reaction seems to proceed by 1,4-addition of the carbanion (A) to the double bond of the enone (II) (Chart 2) to give the ester (IV). However, the 2-pyrone derivatives (III) were obtained by Michael addition

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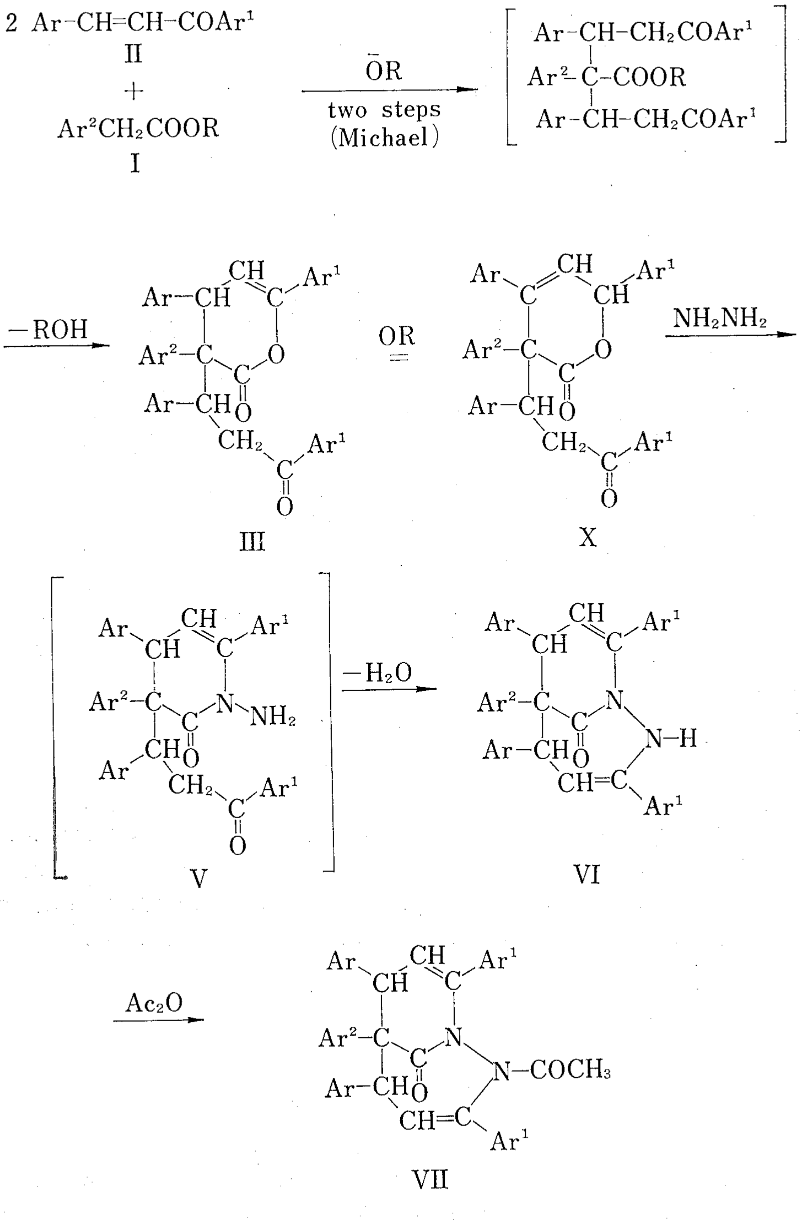
2) W. Borsche, *Chem. Ber.*, **42**, 4496 (1909).
3) R. Conner and D. Andrews, *J. Am. Chem. Soc.*, **56**, 2713 (1934).
4) A. Sammour, M.I.B. Salim, and M.S. Abd Elhalim, *Egypt J. Chem.*, **15**, 23 (1972).

between one mole of the acetate (I) and two moles of α,β-unsaturated ketone (II) with subsequent cyclization between the ester and the carbonyl group (Chart 1).

The structures of the above products were established spectroscopically and chemically.

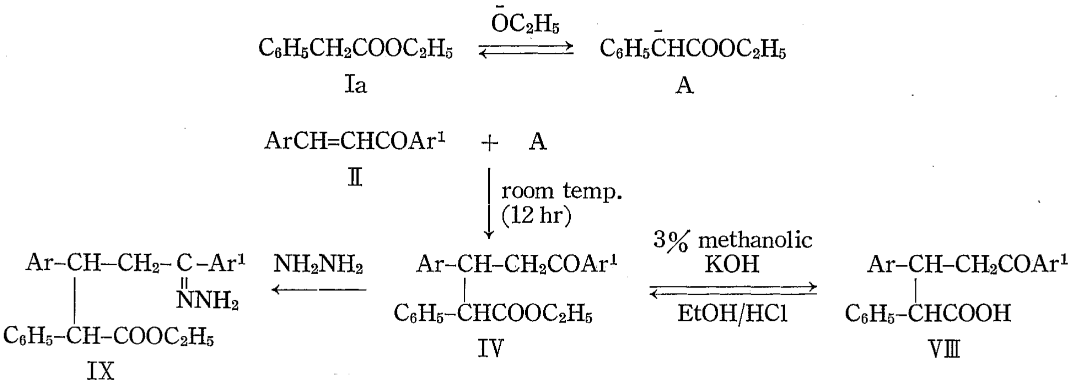


Compound (I): a) $Ar^2=C_6H_5$; $R=C_2H_5$.
b) $Ar^2=\alpha\text{-}C_{10}H_7$; $R=CH_3$.

Compounds (III), (VI) and (VII):
a) $Ar=Ar^1=C_6H_5$; $Ar^2=\alpha\text{-}C_{10}H_7$.
b) $Ar=p\text{-}CH_3C_6H_4$; $Ar=C_6H_5$; $Ar^2=\alpha\text{-}C_{10}H_7$.
c) $Ar=Ar^2=C_6H_5$; $Ar^1=p\text{-}Br.C_6H_4$.
d) $Ar=3,4\text{-}OCH_2OC_6H_3$; $Ar^1=Ar^2=C_6H_5$.

Compound (II): a) $Ar=Ar^1=C_6H_5$.
b) $Ar=p\text{-}CH_3C_6H_4$; $Ar^1=C_6H_5$.
c) $Ar=C_6H_5$; $Ar^1=p\text{-}BrC_6H_4$.
d) $Ar=p\text{-}Cl.C_6H_4$; $Ar^1=p\text{-}BrC_6H_4$.
e) $Ar=3,4\text{-}OCH_2OC_6H_3$; $Ar^1=C_6H_5$.
f) $Ar=3,4\text{-}OCH_2OC_6H_3$; $Ar=p\text{-}Cl.C_6H_4$.

Chart 1



Compound (IV): a) Ar=C_6H_5; Ar^1=p-BrC_6H_4
b) Ar=p-Cl·C_6H_4; Ar^1=p-Br·C_6H_4
c) Ar=3,4-$OCH_2OC_6H_3$; Ar^1=C_6H_5
d) Ar=3,4-$OCH_2OC_6H_3$; Ar^1=p-Cl·C_6H_4
Compound (VIII): a) Ar=C_6H_5; Ar^1=p-BrC_6H_4
b) Ar=3,4-$OCH_2OC_6H_3$; Ar^1=C_6H_5
Compound (IX): a) Ar=C_6H_5; Ar^1=p-BrC_6H_4
b) Ar=3,4-$OCH_2OC_6H_3$; Ar^1=C_6H_5
c) Ar=3,4-$OCH_2OC_6H_3$; Ar^1=p-Cl·C_6H_4

Chart 2

(i) Spectroscopic Evidence for the Structures of 3-[3-(1,3-Diarylpropan-1-one)]-3,4,6-triaryl-4-hydro-2H-pyran-2-ones (IIIa—d) and the Esters (IVa—d)

The infrared spectra of the 2-pyrones (IIIa—d) (Table III) show strong bands in the 1725—1715 cm^{-1}, 1693—1690 cm^{-1} and 1670—1660 cm^{-1} regions which are attributable to the two carbonyls and the >C=C< stretching frequencies of the 2-pyrone derivatives.[4-7] The NMR spectra of these pyrones show signals of methine and methylene protons in addition to the aromatic protons (Table III). Compound (IIIb) shows two signals at δ 2.07 and 1.93

Table I. Physicochemical Properties of 3,4,6-Triaryl-3-[3-(1,3-diaryl-propan-1-one]-4-hydro-2H-pyran-2-ones (IIIa—d) and Ethyl γ-Aroyl-α,β-diaryl-butyrates (IVa—d)

Compound No.	mp (°C)	Yield (%)	Formula	Analysis (%)							
				Calcd.				Found			
				C	H	Br	M.W.	C	H	Br	M.W. (MS)
IIIa	270—271[a]	72	$C_{42}H_{32}O_3$	86.28	5.52	—	584	86.25	5.77	—	584
IIIb	278—279[a]	78	$C_{44}H_{36}O_3$	86.25	5.92	—	612	86.41	5.80	—	612
IIIc	292—293[a]	68	$C_{38}H_{28}Br_2O_3$	65.91	4.08	23.08	690, 692, 694	66.11	4.08	22.98	690, 692, 694
IIId	260—261[b]	79	$C_{40}H_{30}O_7$	77.16	4.86	—	622	76.80	4.82	—	622
IVa	140—141[a]	85	$C_{25}H_{23}BrO_3$	66.53	5.14	17.70	450, 452	66.81	5.10	17.92	450, 452
IVb	182—183[b]	81	$C_{25}H_{22}BrClO_3$	61.81	4.56	16.45	484, 486, 488	61.82	4.63	16.51	484, 486, 488
IVc	142—143[b]	72	$C_{26}H_{24}O_5$	74.98	5.81	—	416	75.11	5.75	—	416
IVd	216—217[a]	78	$C_{26}H_{23}ClO_5$	69.26	5.14	Cl 7.86	450, 452	69.52	5.22	Cl 8.16	450, 452

[a] Crystallized from benzene-petroleum-ether (30—60°).
[b] Crystallized from benzene.

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5) T. Eicher and A. Hansen, *Tetrahedron Lett.*, **1967**, 1169.
6) T. Sasaki, K. Kanematsu, and A. Kakehi, *J. Org. Chem.*, **36**, 2451 (1971).
7) L. Mosti, P. Schenone, and G. Menozzi, *J. Heterocycl. Chem.*, **15**, 181 (1978).

attributable to two methyl protons present in different environments. The ultraviolet spectra of the compounds (III) give further support to the proposed structures. They show an absorption in the region 258—234 nm which is attributable to the K-band of the styrene moiety.[8] The alternative structure (X) (*cf.* Chart 1) is excluded since the absorption of these compounds should not be affected by substituents in the aryl group (Ar). The UV spectrum of (IIIc) shows absorption at 258 nm, attributable to the *p*-bromostyrene moiety.[9] Further support

Table II. Physicochemical Properties of (3)-1,2-Diazepin-3-one Derivatives (VIa—d), γ-Aroyl-α,β-diarylbutyric Acids (VIIIa, b) and the Hydrazone Derivatives (IXa—c)

Compound No.	mp (°C)	Yield (%)	Formula	Analysis Calcd. C	H	N	M.W.	Found C	H	N	M.W. (MS)
VIa	281—282[a]	88	$C_{42}H_{32}N_2O$	86.87	5.54	4.82	580	86.66	5.71	4.47	580
VIb	271—272[a]	82	$C_{44}H_{36}N_2O$	86.81	5.96	4.60	608	86.38	5.97	4.46	608
VIc[b]	278—279[c]	77	$C_{38}H_{28}Br_2N_2O$	66.29	4.10	4.07	686, 688, 690	65.91	4.08	3.95	686, 688, 690
VId	252—253[a]	79	$C_{40}H_{30}N_2O_5$	77.65	4.89	4.53	618	77.74	4.85	4.27	618
VIIIa[d]	231—232[e]	74	$C_{23}H_{19}BrO_3$	65.26	4.52	—	422, 424	65.51	4.48	—	422, 424
VIIIb	207—208[f]	78	$C_{24}H_{20}O_5$	74.21	5.19	—	388	74.03	5.11	—	388
IXa	129—130[c]	82	$C_{25}H_{25}BrN_2O_2$	64.52	5.41	6.02	464, 466	64.71	5.38	6.06	464, 466
IXb	110—111[f]	78	$C_{26}H_{26}N_2O_4$	72.54	6.09	6.51	430	72.81	6.21	6.83	—
IXc[g]	75— 76[f]	75	$C_{26}H_{25}ClN_2O_4$	67.17	5.42	6.03	464, 466	66.83	5.48	6.23	464, 466

a) Crystallized from benzene–petroleum -ether (30—60°).
b) Br%: Calcd.=23.21; Found=22.98.
c) Crystallized from methanol.
d) Br%. Calcd.=18.88; Found=19.21.
e) Crystallized from methanol–benzene.
f) Crystallized from benzene.
g) Cl% Calcd.=7.63; Found=7.87.

Table III. Infrared, Ultraviolet and Nuclear Magnetic Resonance Spectral Data for 3,4,6-Triaryl-3-[$\bar{3}$-($\bar{1}$-,$\bar{3}$-diaryl-propan-$\bar{1}$-one)]-4-hydro-2H-pyran-2-ones (IIIa—d)

Compound No.	Infrared spectra (Nujol) cm⁻¹	ν	Ultraviolet spectra (EtOH) λmax (nm)	ε	NMR spectra ($CDCl_3$) δ	Assignments (No. of protons)
IIIa	1725 (s)	C=O	284	16340	8.33—6.67 (m)	(27) ArH
	1690 (s)	C=O	249	27570	5.67—4.0 (m)	(5) 2-CH+>CH_2– +=CH–
	1660 (s)	C=C	225	66890		
IIIb	1725 (s)	C=O	299—293 (sh)	16620	8.0—6.33 (m)	(25) ArH
	1693 (s)	C=O	285	18940	5.50—4.0 (m)	(5) 2>CH+–CH_2– +=CH–
	1660 (s)	C=C	273	20610		
			258—234 (sh)	35560	2.07 (s)	(3) $ArCH_3$
			224	69200	1.93 (s)	(3) $ArCH_3$
IIIc	1715 (s)	C=O	258	29890	8.01—6.43 (m)	(23) ArH
	1670 (s)	C=C			5.61—3.98 (m)	(5) 2>CH+–CH_2– +=CH–
IIId	1715 (s)	C=O	288	10046	8.0—6.33 (m)	(21) ArH
	1670 (s)	C=C	246	30175	5.65 (s)	(4) 2–OCH_2O
					5.0—3.57 (m)	(5) 2>CH+–CH_2– +=CH–

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8) C.G. Overberger and D. Tanner, *J. Am. Chem. Soc.*, **77**, 369 (1955).
9) O.H. Wheeler and C.B. Covarrubias, *Can. J. Chem.*, **40**, 1224 (1962).

for the structures of these compounds was obtained from their mass spectra, which showed peaks corresponding to $[M]^{\cdot+}$, $[M\text{–}ArCHCH_2COAr^1]^+$, which corresponds to the 3,4,6-triaryl-2H-pyran-2-one molecular ion (XI), $[ArCHCH_2COAr^1]^+$, $[M\text{–}COAr^1]^+$, and $[COAr^1]^+$ (Chart 3).

The structures and configurations of the esters (IVa—d), were confirmed by their spectral data (IR, UV, NMR and MS) (*cf.* Table IV). Thus, the IR spectra of these compounds show two strong bands at 1735—1725 cm^{-1} and 1789—1680 cm^{-1} attributable to the carbonyl groups of the ester and ketone, respectively. The UV spectra of these compounds are almost identical with each other, suggesting a structural similarity. They show absorption maxima in the range of 256—243 nm (*cf.* Table IV), close to the maxima in the spectra of acetophenone derivatives.[10]

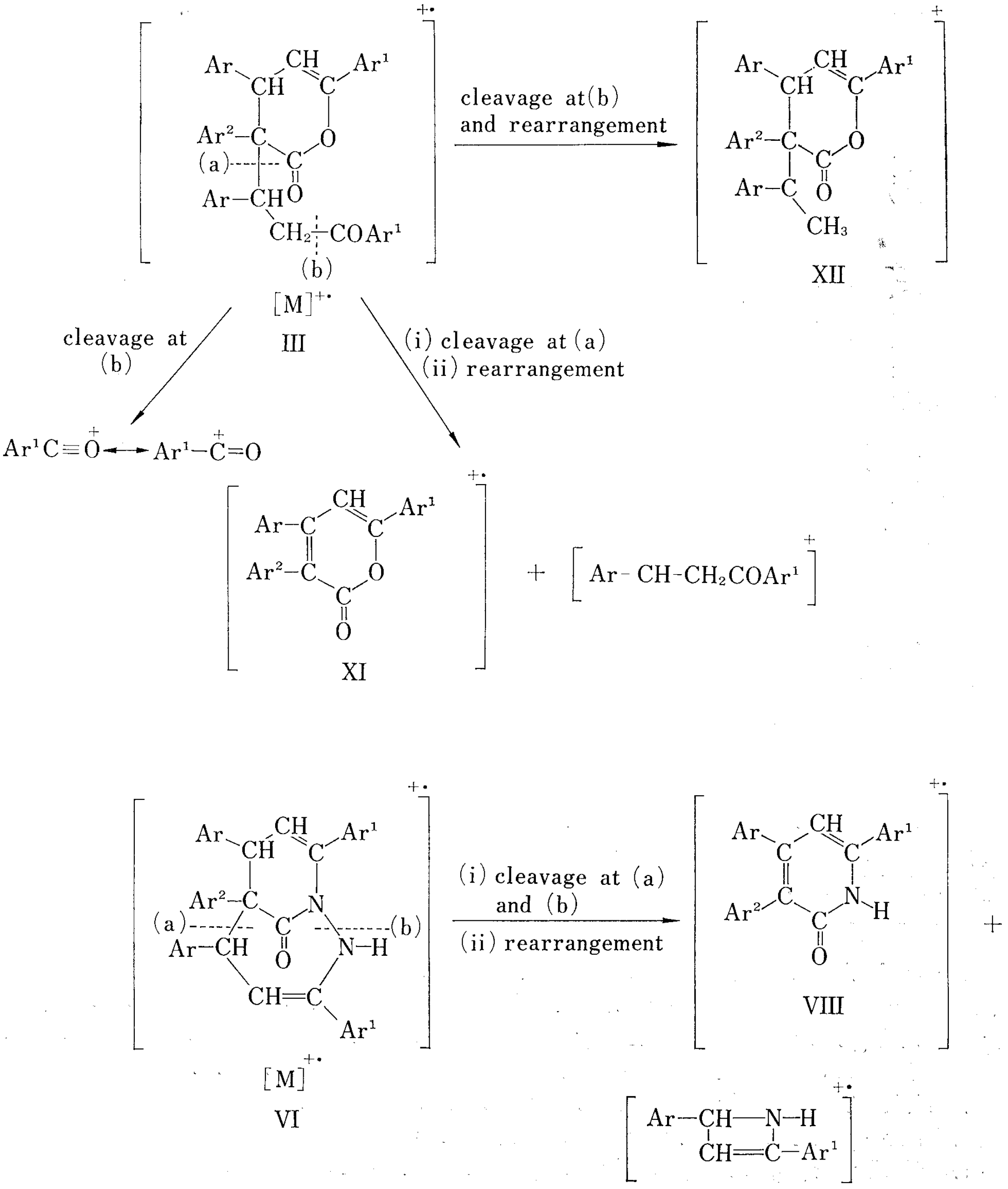

Chart 3

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[10] G. Adembri, P. Sarti-Fantono, and E. Belgodere, *Tetrahedron*, 22, 3149 (1966); E.A. Braude and F. Sondheimer, *J. Chem. Soc.*, **1955**, 3754; R.A. Morton, Ali Hassan and T.C. Calloway, *ibid.*, **1934**, 883.

Table IV. Infrared, Ultraviolet and Nuclear Magnetic Resonance Spectral Data for Ethyl γ-Aroyl-α,β-diaryl-butyrates (IVa—d), the Acids (VIIIa, b) and Hydrazones (IXa—c).

Compound No.	Infrared spectra (Nujol)		Ultraviolet spectra (EtOH)		NMR spectra ($CDCl_3$)	
	cm^{-1}	ν	λmax (nm)	ε	δ	Assignments (No. of protons)
IVa	1735 (s)	COOEt	256	17880	7.67—7.0 (m)	(14) ArH
	1683 (s)	COAr			4.17—2.33 (m)	(6) $\rangle$CH–$\overset{\mid}{\mathrm{C}}$H–$CH_2$–+$OCH_2$–
					0.85 (t) (J=7 Hz)	(3) –CH_3
IVb	1725 (s)	COOEt	256	18300	7.67—7.17 (m)	(13) ArH
	1689 (s)	COAr	222—213 (sh)	22090	4.07—2.8 (m)	(6) $\rangle$CH–$\overset{\mid}{\mathrm{C}}$H–$CH_2$–+$OCH_2$–
					0.92 (t) (J=7 Hz)	(3) –CH_3
IVc	1730 (s)	COOEt	243	15210	7.73—6.43 (m)	(13) ArH
	1680 (s)	COAr			5.91 (s)	(2) OCH_2O
					4.21—2.81 (m)	(6) $\rangle$CH–$\overset{\mid}{\mathrm{C}}$H–$CH_2$–+$OCH_2$–
					0.93 (t) (J=7 Hz)	(3) –CH_3
IVd	1725 (s)	COOEt	295—269 (sh)	6760	7.83—6.67 (m)	(12) ArH
	1685 (s)	COAr	249	18410	5.87 (s)	(2) OCH_2O
					4.17—2.83 (m)	(6) $\rangle$CH–$\overset{\mid}{\mathrm{C}}$H–$CH_2$–+$OCH_2$–
					0.93 (t) (J=7 Hz)	(3) –CH_3
VIIIa	3400—2500 (br.)	OH	255	21540	7.83—6.83 (m)	(14) ArH
	1693 (s)	C=O			4.33—3.33 (m)	(4) $\rangle$CH–$\overset{\mid}{\mathrm{C}}$H–$CH_2$–
VIIIb	3500—2500 (br.)	OH	285	6360	8.07—6.4 (m)	(13) ArH
	1695 (s)	CO	240	17570	5.73 (s)	(2) OCH_2O
	1680 (s)	COAr			4.07—3.33 (m)	(4) $\rangle$CH–$\overset{\mid}{\mathrm{C}}$H–$CH_2$–
IXa	3340 (s)	NH_2	269	15000	7.83—6.80 (m)	(14) ArH
	3260 (br.)				4.67 (br.)	(2) NH_2
	3180 (br.)				4.17—2.33 (m)	(6) $\rangle$CH–$\overset{\mid}{\mathrm{C}}$H–$CH_2$–+$OCH_2$–
	1730 (s)	COOEt			0.83 (t)	(3) –CH_3
IXb	3410 (br.)	NH_2	265	14110	7.91—6.81 (m)	(13) ArH
	3300 (w)				5.91 (s)	(2) OCH_2O
	3200 (m)				4.72 (br.)	(2) NH_2
	1730 (s)	COOEt			4.22—2.36 (m)	(6) $\rangle$CH–$\overset{\mid}{\mathrm{C}}$H–$CH_2$–+$OCH_2$–
					0.91 (t) (J=7 Hz)	(3) –CH_3
IXc	3400 (br.)	NH_2	276	13880	7.83—6.6 (m)	(12) ArH
	3320 (w)				5.90 (s)	(2) OCH_2O
	3240 (w)				4.83 (br.)	(2) NH_2
	1730 (s)	COOEt			4.17—2.33 (m)	(6) $\rangle$CH–$\overset{\mid}{\mathrm{C}}$H–$CH_2$–+$OCH_2$–
					0.93 (t) (J=7 Hz)	(3) –CH_3

The mass spectra of these compounds give further support to the proposed structures, showing peaks corresponding to $[M]^{\cdot+}$, $[M-C_2H_5OH]^{\cdot+}$, $[M-C_6H_5CHCOOC_2H_5]^+$, $[Ar-CH.CH_2-COAr^1]^+$, and $[COAr^1]^+$.

(ii) Chemical Evidence

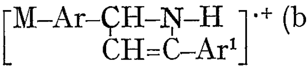
The chemical reactions of the 2-pyrones (IIIa—d) provided further evidence for the assigned structures. Thus, the reaction of these compounds with hydrazine hydrate in boiling ethanol gave the corresponding (3H)-1,2-diazepin-3-one derivatives (VIa—d). The structures of these compounds were identified from their spectral data (IR, UV, NMR, and MS) (Table V). Thus, their IR spectra show a broad band in the range of 3400—3230 cm^{-1} attributable to ν_{NH} in addition to two strong bands in the region of 1675—1670 cm^{-1} that can be ascribed to $\nu_{C=C}$ and $\nu_{C=O}$ of the 1,2 diazepin-3-one system. The NMR spectra of these compounds provided further evidence for their structure, showing signals due to the olefinic, methylene and aromatic protons. The UV spectra of these compounds show absorption maxima between 261—241 nm which can be attributed to the K-band of the styrene moiety.[8] The mass spectra of these compounds also support the assigned structures, showing peaks corresponding to $[M]^{\cdot+}$ and  $\left[\begin{array}{l}M\text{–}Ar\text{–}\underset{|}{C}H\text{–}\underset{|}{N}\text{–}H\\ \qquad CH{=}C\text{–}Ar^1\end{array}\right]^{\cdot+}$ (base peak), formed by cleavage at (a) and (b) and rearrangement (Chart 3). Further evidence for the structure of the (3H)-1,2-diazepin-3-one derivatives was obtained from the treatment of (VIa) with acetic anhydride, which gave the corresponding N-acetyl derivative (VIIa); the structure of this was substantiated by its spectral data (Table V).

Table V. Infrared, Ultraviolet and Nuclear Magnetic Resonance Spectral Data for (3)-1,2-Diazepin-3-one Derivatives (VIa—d) and the N-Acetyl Derivative (VIIa)

Compound No.	Infrared spectra (Nujol)		Ultraviolet spectra (EtOH)		NMR spectra ($CDCl_3$)	
	cm^{-1}	ν	λmax (nm)	ε	δ	Assignments (No. of protons)
VIa	3230(br.)	NH	298—290(sh)	10740	8.00—6.77(m)	(28) ArH+NH
	1675(s)	C=O	273	14870	5.33—3.67(m)	(4) $2{>}CH+2CH=$
	1673(m)	C=C	276—268(sh)	17320		
			249	26990		
			225	71860		
VIb	3400(s)	NH	298—290(sh)	12010	8.0—6.33(m)	(26) ArH+NH
	1673(s)	C=O	287—277(sh)	14750	5.67—3.67(m)	(4) $2{>}CH+2CH=$
	1771(m)	C=C	275—269(sh)	15660	1.90(s)	(3) $ArCH_3$
			246	26750	2.05(s)	(3) $ArCH_3$
VIc	3300(br.)	NH	261	32330	7.83—6.5(m)	(24) ArH+NH
	1675(s)	C=O			5.17—3.33(m)	(4) $2{>}CH+2CH=$
	1670(m)	C=C				
VId	3240(br.)	NH	292—271(sh)	12650	7.50—6.17(m)	(22) ArH+NH
	1675(s)	C=O	241	34020	5.77(s)	(2) OCH_2O
	1672(m)	C=C			5.65(s)	(2) OCH_2O
					5.0—3.17(m)	(4) $2{>}CH+2CH=$
VIIa	1740(s)	$NCOCH_3$	254	31350	7.67—6.67(m)	(27) ArH
	1670(s)	CO of pyridone			5.17—3.67(m)	(4) $2{>}CH+2CH=$
	1660(m)	${>}C=C{<}$			2.36	(3) $COCH_3$

The formation of (3H)-1,2-diazepin-3-one derivatives (VI) from 2-pyrones (III) may proceed via the intermediate formation of 1-amino-2-pyridone derivatives (V),[11] followed by cyclization (Chart 1).

The structure of the esters (IVa—d) was also established by studying their chemical reactions. Thus, on alkaline hydrolysis, the esters (IVa, c) gave the corresponding γ-aroyl-α, β-diarylbutyric acids (VIIIa, b). The structures assigned to these acids were confirmed by esterification with ethanol in the presence of sulfuric acid to give the corresponding esters (IVa, c). The proposed structures of these acids were supported by their IR, UV, NMR and MS spectra data. The IR spectra (Table IV) showed bands at 1695—1680 cm^{-1} attributable to $\nu_{C=O}$ of the carboxyl and the aroyl groups,[12,13a,b] in addition to a broad band at 3500—2500 cm^{-1} ($\nu_{OH\ of\ COOH}$). The ultraviolet spectra of these acids are identical, reflecting their structural similarity, and are similar to the spectra of the corresponding esters. They show absorption maxima in the range of 240—255 nm which can be attributed to the π-π^* band of acetophenone derivatives. Their NMR data are listed in Table IV. The mass spectra of these compounds show peaks corresponding to $[M]^{\cdot+}$, $[M-CO_2]^{\cdot+}$, and $[Ar^1CO]^+$. Further evidence for the structure of the esters was obtained from their reaction with

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hydrazine hydrate to give the corresponding hydrazones (IXa—c). The structure of these hydrazones was established from their spectral data. The IR spectra show three bands in the regions of 3410—3340 cm^{-1}, 3320—3200 cm^{-1} and 3240—3180 cm^{-1} which are attributable to ν_{NH_2}[13c)] and a strong band at 1730 cm^{-1} [13a)] due to the carbonyl group of the ester. These values confirmed that the hydrazine hydrate had only reacted with the carbonyl group of the ketonic ester (IV) (*cf.* Chart 2). The NMR spectra of these hydrazones showed a broad band (NH_2) that disappeared on addition of D_2O, in addition to methine and ethyl ester protons (Table IV). The UV spectra of these compounds were similar to that of acetophenone hydrazone.[10)] The mass spectra of these compounds also support the structures, showing peaks of $[M]^{\cdot+}$, $[M-C_6H_5CHCOOC_2H_5]^+$, $[C_6H_5CHCOOC_2H_5]^+$, and $[ArCHCH_2C(N-NH_2)Ar^1]$.

Experimental

Melting points are uncorrected. Ultraviolet and infrared spectra were measured with a Beckman ACTA machine at a scan speed of 0.25 nm/second (Chart 10 nm/inch) and a Perkin-Elmer 577 grating infrared spectrophotometer, respectively. NMR spectra were measured in $CDCl_3$ solution, with tetramethylsilane as an internal standard, using a JEOL JNM-PM spectrometer. MS spectra were measured with Varian MAT 311A mass spectrometer. The purity of the analytical samples was checked by TLC (silica gel). Microanalyses were carried out by Dr. Bernhardt, West Germany. Evaporation was performed *in vacuo* on rotary evaporators.

Reaction of 1,3-Diaryl-2-propen-1-ones with Alkyl Arylacetates——(a) Under Reflux. General Procedure Alkyl arylacetate (I) (0.015 mol) and the ketone (II) (0.015 mol) were added successively to a suspension of sodium alkoxide (0.015 mol) 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 (Na_2SO_4) and concentrated. The residue was crystallized from a suitable solvent to give the corresponding 3,4,6-triaryl-3-[$\bar{3}$-($\bar{1}$,$\bar{3}$-diarylpropan-$\bar{1}$-one)]-4-hydro-2H-pyran-2-one (III) as colorless crystals. The data are listed in Table I.

Acidification of the alkaline aqueous layer with hydrochloric acid gave α-naphthylacetic acid, mp and mixed mp 131—132° (in the case of methyl α-naphthylacetate) and phenylacetic acid, mp and mixed mp 76—77° (in the case of ethyl phenylacetate).

(b) At Room Temperature. General Procedure: Alkyl arylacetate (I) (0.015 mol) and the ketone (II) were added successively to a suspension of sodium alkoxide (0.15 mol) in dry benzene. The reaction mixture was left at room temperature for 24 hr with occasional stirring, then poured into cold dilute hydrochloric acid solution and worked up as in method (a) to give the corresponding ethyl γ-aroyl-β-aryl-α-phenylbutyrate (IV) as colorless crystals. In the case of methyl α-naphthylacetate (Ib), the reaction mixture gave only the corresponding 3,4,6-triaryl-3-[$\bar{3}$-($\bar{1}$,$\bar{3}$-diarylpropan-$\bar{1}$-one)]-4-hydro-2H-pyran-2-one (IIIa, b). The data are listed in Table I.

γ-Aroyl-α,β-diaryl-butyric Acid (VIII)——General Procedure: A mixture of the ester (IV) (1.0 g) and 3% methanolic KOH (25 ml) was refluxed on a boiling water-bath for one hour. The acid separated from the reaction mixture was crystallized from a suitable solvent to give the corresponding γ-aroyl-α,β-diarylbutyric acid (VIII) as colorless crystals. The results are listed in Table II.

Esterification of γ-*p*-Bromobenzoyl-α,β-diphenyl-butyric Acid (VIIIa)——This was performed by refluxing the acid (VIIIa) (2.5 g) in absolute ethanol (10 ml) containing concentrated H_2SO_4 on a boiling water-bath for 4 hr. The reaction mixture was treated as usual to give the corresponding ester (VIa), which was crystallized from benzene–petroleum-ether (30—60°) as colorless needles; yield, 78%, mp and mixed mp 142—143°.

Reaction of Ethyl γ-Aroyl-β-aryl-α-phenyl-butyrates (IVa, c, d) with Hydrazine Hydrate——General Procedure: A mixture of the ester (IV) (2 g) and hydrazine hydrate (99% w/w; 3 ml) was refluxed in ethanol (25 ml) for 3 hr. The reaction mixture was concentrated, then diluted with water, and the precipitated solid was crystallized from a suitable solvent to give the corresponding hydrazone (IX). The data are listed in Table II.

(3H)-1,2-Diazepin-3-one Derivatives (VIa—d)——General Procedure: A solution of the pyrone (III) (2 g) in ethanol (25 ml) was refluxed with hydrazine hydrate (99% w/w; 3 ml) on a boiling water-bath for 5 hr. Removal of the solvent left a residual oil which solidified upon treatment with petroleum-ether (30—60°). Crystallization of the solid from a suitable solvent gave the corresponding (3H)-1,2-diazepin-3-one derivative (VI) as colorless crystals. The data are listed in Table II.

1-Acetyl-(3H)-1,2-diazepin-3-one Derivative (VIIa)——Acetylation of the (3H)-1,2-diazepin-3-one derivative (VIa) with acetic anhydride gave the corresponding 1-acetyl derivative (VIIa) as colorless crystals, mp 260—261° [(benzene–petroleum-ether (30—60°)]; yield, 75%. *Anal.* Calcd. for $C_{44}H_{34}N_2O_2$: C, 84.86; H, 5.50; N, 4.50. Found: C, 84.62; H, 5.46; N, 4.35.