Table IV. Results for β-Anilino-α-(*p*-chlorobenzoyl)styrene Derivatives[a] IIIa-g

compd	mp, °C	yield, %	formula[b]
IIIa	159-160	98	$C_{21}H_{16}ClNO$
IIIb	77-78	92	$C_{22}H_{18}ClNO$
IIIc	157-158	78	$C_{22}H_{18}ClNO$
IIId	190-191	85	$C_{21}H_{15}Cl_2NO$
IIIe	188-189	88	$C_{21}H_{15}BrClNO$
IIIf	195-196	87	$C_{21}H_{15}ClINO$
IIIg	127-128	90	$C_{22}H_{18}ClNO$

[a] Elemental analyses (C, H, N, Br, Cl) in agreement with theoretical values were obtained and submitted for review. [b] Compounds III-e, g were crystallized from cyclohexane and IIIf from benzene-cyclohexane.

The Hammett relation may be applied to substituent effects in NMR spectra. The methine proton chemical shift of the substituted aniline derivatives IIIa–g was linearly correlated with the Hammett substituent constant, Figure 2, in which the absolute value of correlation coefficient is 0.9991.

The mass spectra of IIIc,e,g also lend further support for the assigned configurated (Figure 3) since they show peaks at the following *m/e* values: (a) $[M]^+$, (b) $[M - OH]^+$, and (c) $[M - COC_6H_4Cl]^+$, which support the keto structure III, and (d) $[M - C_6H_4Cl]^+$.

Further evidence for structure III was obtained from the reaction of (*p*-chlorobenzoyl)benzoylmethane (IV) and aniline derivatives (IIa–g), which gave a product similar to the corresponding III (Figure 1). Furthermore, compounds IIIa–g were easily hydrolyzed with 30% H_2SO_4 to give (*p*-chlorobenzoyl)benzoylmethane (VI), indicating that they exist in the ketamine form. Other evidence can be adduced in favor of the ketamine III from the fact that the products IIIa–g gave no positive ferric chloride test and showed no propensity to react with diazomethane, even in the presence of methanol. The latter observation cannot be attributable to strong chelation of the enol form, since methanol solvates the enol to break up the chelate ring and permits reaction with the enolic hydrogen (*3*). The structure of (*p*-chlorobenzoyl)methane was established by preparing an authentic sample from the reaction of (*p*-chlorobenzoyl)phenylacetylene with 30% H_2SO_4.

Experimental Section

General Information. IR spectra were recorded by using Pye-Unicam SP 1000 and Beckman IR 12 spectrophotometers (ethanol). NMR spectra were recorded at 100, 500, and 1000 Hz sweep widths on a Varian T60A spectrometer for a 0.1 M chloroform solution of each compound using Me_4Si as internal standard. UV spectra were recorded on Pye-Unicam SP 8000 and Beckman ACTA MVI spectrophotometers. Melting points are uncorrected. Microanalyses were determined by Alfred Bernhardt, West Germany. The purity of the analytical samples was checked by TLC (silica gel).

Reaction of (p-Chlorobenzoyl)phenylacetylene (I) with Aniline Derivatives (IIa–g). General Procedure. A mixture of (*p*-chlorobenzoyl)phenylacetylene (I) (*1*) (1 mol equiv) and aniline derivative II (1 mol equiv) was refluxed in methanol (25 mL/1 g of ketone) for 3 h. The yellow solid separated on concentration and cooling was recrystallized from a suitable solvent to give the corresponding β-ketamine derivative III (Table IV).

The same products were also separated in 75–81% yield when (*p*-chlorobenzoyl)benzoylmethane (V) was used instead of (*p*-chlorobenzoyl)phenylacetylene (I) and the reaction mixture was refluxed for 6 h.

Hydrolysis of β-anilino-α-(*p*-chlorobenzoyl)styrene derivatives (IIIa–g) with 30% H_2SO_4 afforded (*p*-chlorobenzoyl)benzoylmethane mp and mmp 90–91 °C.

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Synthesis and Spectroscopic Studies of the Malonohydrazide Derivatives

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3-Aryl-1-phenyl-2-propen-1-ones (IIa–c) reacted with diethyl malonate in the presence of sodium ethoxide to give the corresponding ethyl β-aryl-γ-benzoyl-α-carbethoxybutyrate (III) which upon hydrolysis with 3% methanolic potassium hydroxide yielded the corresponding acid (V). Reaction of III with hydrazine hydrate gave the corresponding 2-(1,3-diaryl-3-hydrazonopropanyl)malonohydrazide (VI). IR, NMR, UV, and mass spectral data of the above compounds were tabulated and discussed.

The reaction of 1,3-diphenyl-2-propen-1-one (IIa) with diethyl malonate has been reported to give the corresponding ethyl γ-benzoyl-α-carbethoxy-β-phenylbutyrate (*1*). The goal of the present investigation was to prepare new nitrogen compounds, to shed more light on the reaction mechanism of α,β-unsaturated ketones with diethyl malonate, and to determine the spectral properties and configuration of the products.

When IIa–c were allowed to react with diethyl malonate in the presence of sodium ethoxide in absolute ethanol, they gave rise to the corresponding ethyl β-aryl-γ-benzoyl-α-carbethoxybutyrates (IIIa–c) (Figure 1).

The structure and the configuration of the reaction products IIIa–c were identified on the basis of the spectroscopic evidence (IR, UV, NMR, and mass spectra) and the chemical reactions.

Spectroscopic Evidence

The IR spectra of the esters (IIIa–c) (Table I) show absorption in the 1730 and 1690–1680-cm^{-1} regions which are correlated to the carbonyl group of ester and ketone, respectively (*2*). The

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Table I. IR, UV, and NMR Spectral Data of IIIa-c, Va-c, and VIa-c

compd	IR bands in Nujol, cm^{-1}	assignt	UV bands (EtOH) λ_{max}, nm	UV bands (EtOH) log ϵ_{max}	NMR values (δ) in $CDCl_3$	assignt
IIIa	1730 s	COOEt	243	4.16	8.03–6.92 m	ArH
	1680 s	COC_6H_5			4.51–3.31 m	$2OCH_2$- + >CHCHCH_2
					1.67–0.90 m	2-CH_3
IIIb	1730 s	COOEt	242	4.20	8.03–6.93 m	ArH
	1685 s	COC_6H_5			4.50–3.33 m	$2OCH_2$- + >CHCHCH_2
					1.90 s	ArCH_3
					1.67–0.83 m	2-CH_3
IIIc	1730 s	COOEt	244	4.27	8.07–7.13 m	ArH
	1690 s	COC_6H_5			4.53–3.33 m	$2OCH_2$- + >CHCHCH_2
					1.37–0.93 m	2-CH_3
Va	3450–2500 br	OH	242	4.11	8.23–6.93 m	ArH
	1710 s	COOH			4.33–3.33 m	>CHCHCH_2
	1690 s	COC_6H_5				
Vb	3450–2500 br	OH	243	4.22	8.01–6.83 m	ArH
	1710 s	COOH			4.25–3.33 m	>CHCHCH_2
	1690 s	COC_6H_5			2.23 s	ArCH_3
Vc	3400–2500 br	OH	243	4.28	8.00–7.15 m	ArH
	1710 s	COOH			4.37–3.90 m	>CHCHCH_2
	1685	COC_6H_5				
VIa	3420 s 3280 br	NH, NH_2	270–252 sh	4.10	7.33–6.83 m	ArH
					4.00–2.33 m	>CHCHCH_2
	1660 s	C=O				
	1620 s	C=N				
VIb	3340 br				7.67–6.67 m	ArH
	3300 s	NH, NH_2	270–248 sh	4.15	4.00–2.50 m	>CHCHCH_2-
	3210 br				2.20 s	ArCH_3
	1660 s	C=O				
	1630 s	C=N				
VIc	3400 s 3320 s 3300 s 3200 m	NH, NH_2	257	4.08	7.50–6.83 m	ArH
					4.00–2.50 m	>CHCHCH_2
	1660 s	C=O				
	1630 s	C=N				

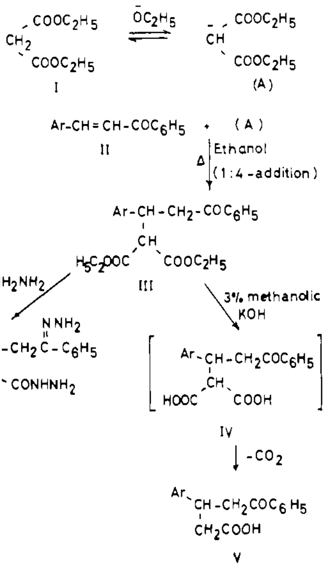

Figure 1. Reaction of 3-aryl-1-phenyl-2-propen-1-one with malonic ester. For compound (a) Ar = C_6H_5, for (b) Ar = p-$CH_3C_6H_4$, and for (c) Ar = p-ClC_6H_4.

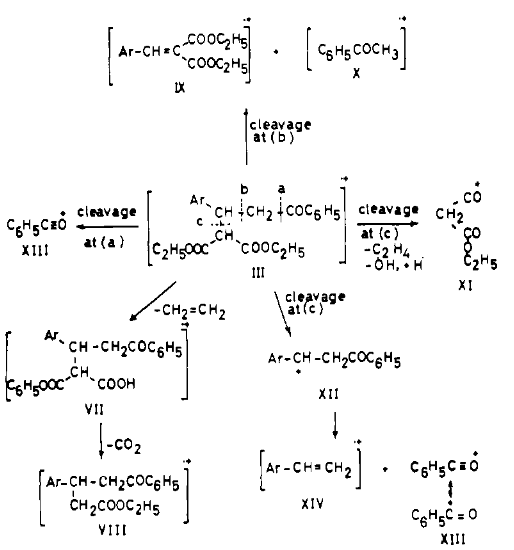

Figure 2. Fragmentation of ethyl β-aryl-γ-benzoyl-α-carbethoxybutyrates (IIIa–c): (a) Ar = C_6H_5, (b) Ar = p-$CH_3C_6H_4$, (c) Ar = p-ClC_6H_4.

NMR spectra of these esters show signals attributed to the ethyl ester, methine, methylene, and aromatic protons (Table I). The UV spectra of these compounds are identical which indicate their structural analogy. They show absorption maxima in the range 244–242 nm (Table I) which are very similar to the spectra of acetophenone (*2*). Accordingly, this absorption band can be attributed to the π–π^* band of the acetophenone moiety. The mass spectra of these compounds also lend further support for the assigned structure, since they show peaks at the following *m/e*: $[M]^{+\cdot}$, $[(CH(CO_2C_2H_5)_2]^+$, $[ArCHCH_2COC_6H_5]^+$, $[MCH_2{=}CH_2]^{+\cdot}$, $[C_6H_5CO]^+$ (cf. Table II and Figure 2).

Chemical Evidence

When the esters IIIa–c were refluxed with 3% methanolic KOH solution, β-aryl-γ-benzoylbutyric acids, Va–c, were obtained in which the ester groups were hydrolyzed to give the acid IV followed by decarboxylation. The structure of these acids was established from their spectral data. Thus, their IR spectra show bands in the regions 1710 and 1690–1685 cm^{-1} which can be correlated to the ν(C=O) of the carboxyl and the benzoyl groups (*2*), respectively, in addition to the broad band at 3450–2500

Table II. Relative Intensity of Major Ions in the Mass Spectra of IIIa-c and VIa-c[a]

compd	m/e	rel intens, %	compd	m/e	rel intens, %	compd	m/e (^{35}Cl, ^{37}Cl)	rel intens, %	fragment ion no.
IIIa	368	0.4	IIIb	382	1	IIIc	402, 404	6.7, 2.3	M
	340	1.1		354	1.5		374, 376	1.7, 0.6	VII
	296	0.15		310	2.1		330, 332	3.3, 1.5	VIII
	248	10.4		262	20.1		282, 284	43.3, 14.4	IX
	120	3.5		120	9.1		120	6.7	X
	115	12.1		115	8.1		115	6.7	XI
	209	41.4		223	15.2		243, 245	70, 22.5	XII
	105	100		105	100		105	100	XIII
	104	3.5		118	5.7		138, 140	6.7, 2.1	XIV
VIa	354	0.2	VIb	368	0.63	VIc	388, 390	1.1, 0.35	M
	336	0.8							$M - H_2O$
	334	0.2		248	14.3		358, 360	11.1, 3.5	XV
	223	7.2		237	32.1		257, 259	28.9, 9.8	XVI
	222	32.1		236	10.7		256, 258	11.6, 6.7	XVII
	221	46.4		235	28.6		255, 257	20, 28.4	XVIII
	145	32.1		159	7.1		179, 181	2.2, 0.7	XIX
	132	12.5		132	14.3		132	6.7	XX
	104	28.6		118	35.8		138, 140	11.1, 6.7	XIV
	119	21.4		119	32.1		119	31.1	XXI
	103	28.6		103	64.3		103	17.8	XXII
	77	100		91	100		111, 113	11.2, 3.5	XXIII
	77	100		77	92.9		77	100	XXIV

[a] See Figures 2 and 3.

cm^{-1} (ν(OH) of ν(COOH)). The UV spectra of these acids are identical, which indicate their structural analogy, and similar to the spectra of the corresponding esters (IIIa-c). They show absorption maxima in the range of 243-242 nm (Table I) which are very similar to the spectra of acetophenone (*2*). Their NMR spectra show chemical shifts which can be assigned to the different protons of these compounds (Table I). The MS spectrum of Vb affords an additional support for the assigned structure, since it shows peaks at the following m/e: 282 (5.1%) $[M]^{+\cdot}$, 264 (2.6%) $[M - H_2O]^{+\cdot}$, 177 (2.6%) $[M - COC_6H_5]^+$, 222 (11.5%) $[M - CH_3COOH]^{+\cdot}$, and 105 (100%) $C_6H_5CO^+$. Adequate evidence for the assigned structure of these esters was supported by their reaction under reflux with hydrazine hydrate to give the corresponding 2-(1,3-diaryl-3-hydrazonopropanyl)malonohydrazide (VI). The structure of these compounds (VIa-c) was confirmed from their spectral data (Tables I and II). Thus, their IR spectra show absorption bands correlated to ν(NH), ν(NH$_2$), and ν(C=O) (Table I). The UV spectra of these compounds are similar to the spectra of the acetophenone hydrazone (*3*). These values confirmed our results that the hydrazine hydrate has reacted with both the carbonyl and the ester groups to give the dihydrazide derivatives (VI). The formation of dihydrazide under our conditions was similar to the reaction of diethyl malonate with hydrazine hydrate. These results show that the diethyl ester group in the compounds IIIa-c has the same malonic ester configuration and in turn does not have any effect on the ketonic group; i.e., the carbonyl group in the esters (III) behaves as a normal ketone in their reactions with hydrazine hydrate. This fact was substantiated from the reaction of ethyl β-aryl-γ-benzoyl-α-phenylbutyrate with hydrazine hydrate in which only the hydrazone derivative was obtained (*2*). The NMR spectra of these compounds are reported in Table I. Further support for the hydrazide derivatives was gained from the mass spectra of these compounds which show peaks reflected their structural configuration (Figure 3, Table II).

Experimental Section

General Information. Melting points are uncorrected. IR spectra were recorded by using a Perkin-Elmer 577 grating infrared spectrophotometer (Nujol). NMR spectra were measured on a JEOL JNM-PM spectrometer using Me$_4$S as internal standard. UV spectra were measured on a Beckman spectrophotometer ACTA MVI using a scan speed of 0.25 nm/s and chart rate of 10 nm/in. (ethanol). Mass spectra were measured with a Varian MAT 311A mass spectrometer. The purity of the analytical samples was checked by TLC (silica gel). Microanalyses were determined by Dr. Bernhardt, West Germany. Evaporation was performed on rotary evaporators in vacuo.

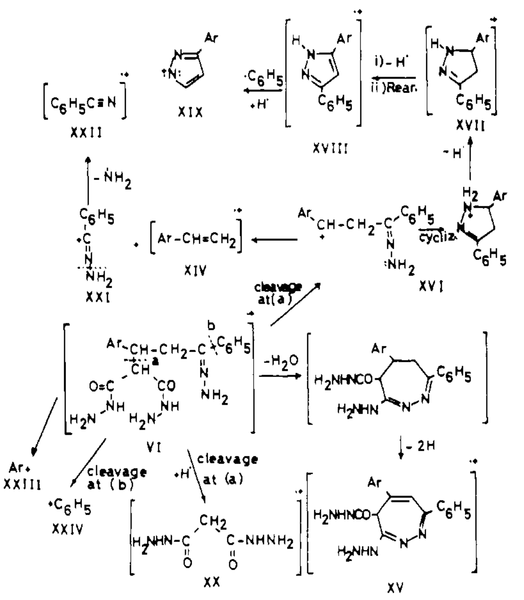

Figure 3. Fragmentation of 2-(1,3-diaryl-3-hydrazonopropanyl)malonohydrazides (VIa-c): (a) Ar = C_6H_5, (b) Ar = p-$CH_3C_6H_4$, (c) Ar = p-ClC_6H_4.

Reaction of 3-Aryl-1-Phenyl-2-propen-1-ones (IIa-c) with Diethyl Malonate. General Procedure. Diethyl malonate (I) (1 mol equiv) and the ketone (II) (1 mol equiv) were added successively to a suspension of sodium ethoxide (1 mol equiv) in absolute ethanol (50 mL/1.0 g of ketone). The reaction mixture, which gradually acquired a deep orange color, was heated on a boiling water bath for 1 h. The solvent was removed by evaporation and the residue dissolved in a dilute hydrochloric acid (10%; 100 mL) and then extracted with benzene. The benzene layer was shaken with sodium hydrogen carbonate solution, dried (Na$_2$SO$_4$), and evaporated. The residue was crystallized from a suitable solvent to give the corresponding ethyl β-aryl-γ-benzoyl-α-carbethoxybutyrate (III) as colorless crystals. The results are reported in Table I.

Table III. Results for IIIa-c,[a] Va-c,[a] and VIa-c[a]

compd	mp, °C	yield, %	formula[b]
IIIa	70-71	93	$C_{22}H_{24}O_5$
IIIb	65-94	92	$C_{23}H_{26}O_5$
IIIc	99-100	88	$C_{22}H_{23}ClO_5$
Va	128-129	76	$C_{17}H_{16}O_3$
Vb	95-96	72	$C_{18}H_{18}O_3$
Vc	125-126	70	$C_{17}H_{15}ClO_3$
VIa	207-208	60	$C_{18}H_{22}N_6O_2$
VIb	174-175	65	$C_{19}H_{24}N_6O_2$
VIc	186-187	68	$C_{18}H_{21}ClN_6O_2$

[a] Elemental analyses (C, H, N, Cl) in agreement with theoretical values were obtained and submitted for review. [b] Compounds IIIa-c were crystallized from cyclohexane, Va-c from methanol-water mixture (3:1), and VIa-c from acetic acid.

The alkaline aqueous layer was acidified with hydrochloric acid solution and extracted with benzene. Evaporation of the solvent left an oily residue.

Reaction of Ethyl β-Aryl-γ-benzoyl-α-carbethoxybutyrates (IIIa-c) with Hydrazine Hydrate. General Procedure. A mixture of the ester III (2 g) and hydrazine hydrate (99% w/w, 3 mL) was refluxed in ethanol (25 mL) for 2 h. The reaction mixture was concentrated and diluted with water and the precipitated solid was crystallized from a suitable solvent to give the corresponding 2-(1,3-diaryl-3-hydrazonopropanyl)malonohydrazide (VI). The results are reported in Table III.

β-Aryl-γ-benzoylbutyric Acid (V). General Procedure. A mixture of the ester III (1.0 g) and 3% methanolic potassium hydroxide (25 mL) was refluxed on a boiling water bath for 1 h. The acid separated from the reaction mixture was crystallized from a suitable solvent to give the corresponding β-aryl-γ-benzoylbutyric acid IV. The results are reported in Table III.

Reaction of Diethyl Malonate with Hydrazine Hydrate. A mixture of the ester (5 g) and hydrazine hydrate (99% w/w, 3 mL) in methanol was refluxed for 2 h. The colorless needles separated from the reaction mixture on cooling were crystallized from a methanol-water mixture (3:1) to give malonohydrazide as colorless needles: mp 153-154 °C; yield 98%; mol wt (mass spectral) 132.

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Preparation and Properties of the 6-Octadecenamides

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Pure, acid-free petroselinamide (*cis*-6-octadecenamide), fp 75.13 °C, and petroselaidamide (*trans*-6-octadecenamide), fp 96.81 °C, have been prepared and characterized. The binary freezing-point diagram for the two isomers indicate the formation of an incongruently melting 1:1 molecular compound with a peritectic at 73.7 °C (53.8% petroselinamide) and a eutectic at 71.4 °C (78.0%). The X-ray diffraction patterns indicate that petroselinamide has a long-spacing value of 40.8 Å with short spacings at 4.33, 3.86, and 3.45 Å. The corresponding values for the petroselaidamide are 49.3 Å and 4.10, 3.52, and 3.08 Å.

Introduction

Petroselinic acid (*cis*-6-octadecenoic acid) and its derivatives have received considerable attention in the literature because it is the principal monounsaturated C_{18} fatty acid in the oils of the Umbelliferae family and other closely related families, some of which have been considered as possible new oilseed crops.[1] Petroselinic acid and some of its derivatives have shown biological activity which indicates the potential for utility in medical or antimicrobial areas.[2-5] One of the derivatives studied for possible industrial applications is petroselinamide.[6,7] Its trans isomer, petroselaidamide, has apparently never been reported in the literature. This paper reports on the preparation of both these isomeric amides in a highly pure form and describes some of their properties.

Table I. Binary Freezing-Point Data[a] of Petroselaidamide (A)-Petroselinamide (B)

mol % of B	temp, °C	mol % of B	temp, °C
100.00	75.1	(56.03)[c]	(73.7)[c]
89.93	73.5	50.08	76.2
80.44	72.0	40.35	81.2
(76.5)[b]	(71.5)[b]	30.67	85.6
73.70	72.2	20.64	89.8
70.10	72.4	21.15	93.1
59.98	73.4	0.00	96.8

[a] Values in parentheses are obtained by graphical extrapolation. [b] Eutectic. [c] Peritectic.

Experimental Procedures

Pure samples of petroselinic acid (fp 29.6 °C) and petroselaidic acid (fp 52.7 °C), prepared as previously described,[8] were converted to the amides by the formamide procedure of Roe, Scanlon, and Swern.[9] The amides were freed of residual acid by a method previously described,[10] involving the passage of a cyclohexane solution of the crude amide through a gently heated column of Alorco activated alumina, followed by repeated recrystallization of the recovered amide from acetone to a constant freezing point. Anal. Calcd for petroselinamide: N, 4.98. Found: N, 4.94, 4.97; fp 75.13 °C. Calcd for petrose-