are shown in Figure 2. Fitting the data by the least squares method leads to the equation

$$y_S/x_W = 0.0102y_S + 0.0145$$

with a correlation coefficient of 0.9995

To evaluate the extractive effectiveness of a solvent, it is useful to study the distribution coefficient and selectivity. These properties can be obtained from Figures 3 and 4, respectively; as seen from the selectivity[17] and distribution diagrams, the order of solvents is 1,2-dichloroethane, 1,1,2-trichloroethane, trichloroethylene, 1,1,1-trichloroethane, and perchloroethylene.

Glossary

A	solute
S	solvent
W	water
d	density
n_D	refractive index
x_A	weight fraction of solute in aqueous phase
x_W	weight fraction of water in aqueous phase
y_A	weight fraction of solute in organic phase
y_S	weight fraction of solvent in organic phase
y_W	weight fraction of water in organic phase

Greek Letters

$\beta_{A,W}$	solvent selectivity ($\beta_{A,W} = y_A x_W / x_A y_W$)

Literature Cited

(1) Kirk, R. E.; Othmer, D. F. "Encyclopedia of Chemical Technology", 2nd ed.; Interscience: New York, 1966; Vol. X.
(2) Smuk, J. M. Ph.D. Thesis, University of Wisconsin, 1960.
(3) Conway, J. B.; Philip, J. B. *Ind. Eng. Chem.* **1953**, *45*, 1083.
(4) Rigamonti, R.; Spaccamela-Marchetti, E. *Chim. Ind.* (*Milan*) **1955**, *37*, 1039.
(5) Hasegawa, T. *Kogyo Kagaku Tasshi* **1961** *64*, 1239.
(6) Krupatkin, I. L.; Glagoleva, M. F. *Zh. Prikl. Khim.* **1969**, *42*, 1526.
(7) Korenman, I. M.; Klyukvina, T. D. *Tr. Khim. Khim. Tekhnol.* **1970**, *2*, 66.
(8) Ewell, R. H., Harrison, J. M.; Berg. L. *Ind. Eng. Chem.* **1944**, *36*, 871.
(9) Weissberger, A. "Organic Solvents", 2nd ed.; Interscience: London, 1955; Vol. VII.
(10) Weast, R. C. "Handbook of Chemistry and Physics", 52nd ed.; Chemical Rubber Co.: Cleveland, Ohio, 1971.
(11) Othmer, D. F.; White, R. E.; Trueger, E., *Ind. Eng. Chem.* **1941**, *33*, 1240.
(12) Bachman, I. *Ind. Eng. Chem., Anal. Ed.* **1940**, *12*, 38.
(13) Dryden, C. E. *Ind. Eng. Chem.* **1943**, *35*, 492.
(14) Hand, D. B. *J. Phys. Chem.* **1930**, *34*, 1961.
(15) Othmer, D. F.; Tobias, P. E. *Ind. Eng. Chem.* **1942**, *34*, 693.
(16) Brown, T. F. *Ind. Eng. Chem.* **1946**, *40*, 103.
(17) Treybal, R. E. "Liquid Extraction", 2nd ed.; McGraw-Hill: New York, 1963; p 43.

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NEW COMPOUNDS

Synthesis and Spectral Properties of β-Anilino-α-(*p*-chlorobenzoyl)styrene Derivatives

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(*p*-Chlorobenzoyl)phenylacetylene reacted with aniline derivatives to give the corresponding β-anilino-α-(*p*-chlorobenzoyl)styrene derivative. NMR, UV, IR, and mass spectra of these compounds are presented. The Hammett correlation is applied to substituent effects on absorption bands. Chemical shift data for the methine proton in these compounds are reported.

The reactions of acetylenic ketones with amine (*1*) and hydrazine derivatives (*2*, *3*) have been reported.

The present investigation was intended to study the reaction of (*p*-chlorobenzoyl)phenylacetylene with aniline derivatives and to account for the manipulated methods and reasoning in establishing the mechanism of this reaction as well as the structure and configuration of the products.

When (*p*-chlorobenzoyl)phenylacetylene (I) was refluxed with aniline derivatives in methanol, it gave the corresponding β-anilino-α-(*p*-chlorobenzoyl)styrene derivative (III) (cf. Figure 1).

The structure and configuration of the reaction products were established spectroscopically and chemically. Thus, their IR spectra show no absorption in the region around 1700 cm^{-1}, the free carbonyl group, and hence structure V was ruled out. The presence of strong bands at 1597–1591 and 1572–1567 cm^{-1} as well as the absence of any absorption in the region 4000–3100 cm^{-1} (Table I) indicated that these compounds are present in chelated form III in which the ν(NH) or ν(OH) absorption may be lowered by intrahydrogen bonding and lie masked under –CH absorption (*4*). The UV spectra of these compounds in ethanol and cyclohexane (Table II) are very similar and show two absorption bands in the regions 385–380 and 262.5–256 nm indicating their structural analogy. The wavelengths and the intensities of these bands are not changed by the polarity of the solvents showing the presence of a strong intrahydrogen bonding system. The ultraviolet or visible absorption in 1% ethanolic ferric chloride do not show any significant change in the wavelength or intensities of absorption bands. This fact gave further evidence for the structure and the stability of these compounds (III) compared with those previously reported by Weinstein and Wyman (*5*). Confirmation of the above conclusion is forthcoming from the NMR spectra of these compounds (Table I). They show a signal in the region 13.01–12.93 ppm (NH), exchangeable with D_2O. The appearance of NH signal and the absence of any signal which can be attributed to the ($-CH_2-$) group give a further support to the exclusion of structure V. The data in Table III show that the methine proton in this series absorbs in the region 366.2–361.6 Hz and that these shifts depend markedly on the substituent.

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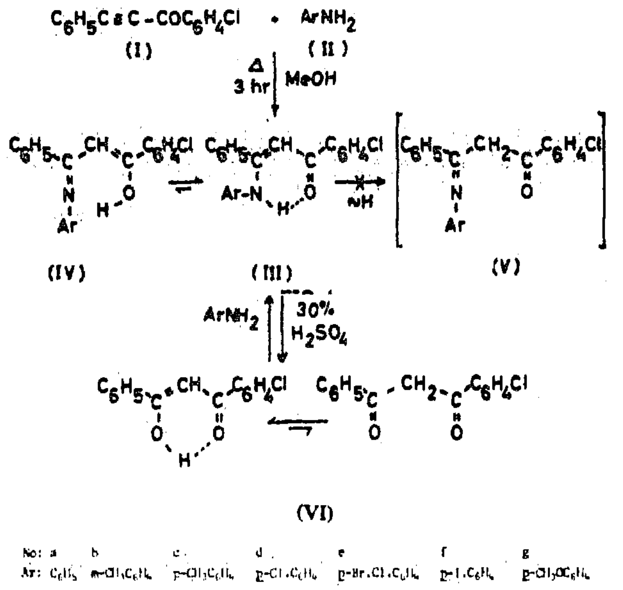

Figure 1. Reaction of (*p*-chlorobenzoyl)phenylacetylene with aniline derivatives.

Table I. IR and NMR Spectral Data of β-Anilino-α-(*p*-chlorobenzoyl)styrene Derivatives IIIa-g

	IR bands in $CHCl_3$		NMR values (δ)	
compd	cm^{-1}	assign	in $CDCl_3$	assign
IIIa	1595 s	C=O···HN	13.01 br	NH
	1572 s	C=C	8.07-6.70 m	ArH
			6.07 s	=CH-
IIIb	1593 s	C=O···HN	12.98 br	NH
	1572 s	C=C	8.07-6.67 m	ArH
			6.06 s	=CH-
			2.20 s	$ArCH_3$
IIIc	1597 s	C=O···HN	12.94 br	NH
	1570 s	C=C	8.02-6.67 m	ArH
			6.04 s	=CH-
			2.23 s	$ArCH_3$
IIId	1591 s	C=O···HN	12.96 br	NH
	1570 s	C=C	8.00-6.67 m	ArH
			6.10 s	=CH-
IIIe	1591 s	C=O···HN	12.92 br	NH
	1570 s	C=C	8.00-6.57 m	ArH
			6.10	=CH-
IIIf	1593 s	C=O···HN	12.93 br	NH
	1567 s	C=C	7.83-6.43 m	ArH
			6.09 s	=CH-
IIIg	1596 s	C=O···HN	12.96 br	NH
	1571 s	C=C	8.00-6.67 m	ArH
			6.03 s	=CH-
			3.72 s	$ArOCH_3$

Table II. UV Absorption Bands of β-Anilino-α-(*p*-chlorobenzoyl)styrene Derivatives IIIa-g

	EtOH		cyclohexane	
compd	λ_{max}, nm	log ϵ_{max}	λ_{max}, nm	log ϵ_{max}
IIIa	380	4.47	380	4.42
	257	4.26	259	4.30
IIIb	381	4.45	382	4.37
	256	4.27	256	4.20
IIIc	382	4.44	382	4.42
	254	4.25	256	4.30
IIId	380	4.46	381	4.36
	259.5	4.28	261.5	4.24
IIIe	382	4.53	381	4.51
	261	4.38	262.5	4.41
IIIf	384	4.48	384	4.48
	261	4.33	263	4.37
IIIg	385	4.41	385	4.40
	252	4.26	256	4.28

Table III. Chemical Shift of the Methine Proton in the β-Ketamine Derivatives IIIa-g[a]

compd	chem shift, Hz (=CH-)	σ value
IIIa	364	0.00
IIIb	363.4	-0.069
IIIc	362.4	-0.17
IIId	366.2	+0.227
IIIe	366	+0.232
IIIf	365.6	0.18
IIIg	361.6	-0.268

[a] In Hz from Me_4Si; 0.1 M $CDCl_3$ solution.

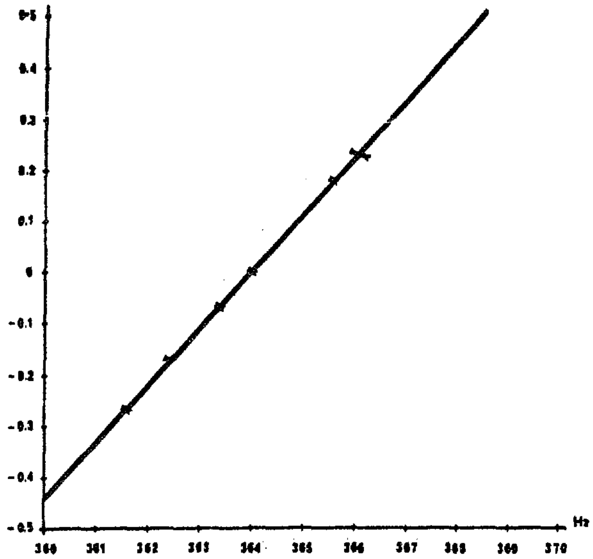

Figure 2. Correlation of the methine proton chemical shifts by Hammett's σ.

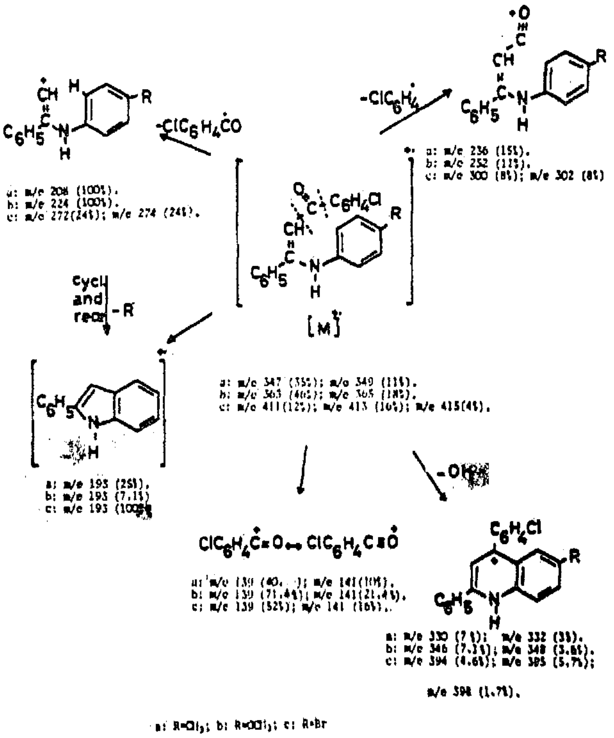

Figure 3. Fragmentation of β-aniline-α-(*p*-chlorobenzoyl)styrene derivatives.

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.

Literature Cited

(1) Bowden, K., Jones, E. R. H., *J. Chem. Soc.*, 953 (1946).
(2) Baddar, F., Al-Hajjar, F., El-Rayyes, N., *J. Heterocyl. Chem.*, **13**, 257 (1976).
(3) Al-Hajjar, F., El-Ezaby, M., El-Rayyes, N., *Chem. Pharm. Bull.*, **25**, 548 (1977).
(4) Cromwell, N., Miller, F., Jonson, A., Frank, R., Wallace, D., *J. Am. Chem. Soc.*, 71, 3337 (1949).
(5) Weinstein, J., Wyman, G., *J. Am. Chem. Soc.*, **23**, 1618 (1958).

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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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