

SOME REACTIONS WITH 3,4-DICHLORO- β -BENZOYL-N-PHENYLACRYLAMIDE AND 3,4-DICHLORO- β -BENZOYL-ACRYLOYL CHLORIDE

E.A. SOLIMAN and GALAL HOSNI

Faculty of Science, Ain Shams University, Cairo, Egypt

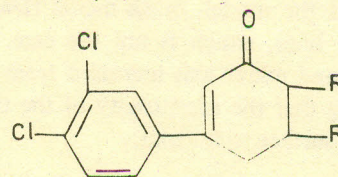
(Received October 28, 1976; revised February 24, 1979)

Abstract. The reaction of 3,4-Dichloro- β -benzoyl-N-phenylacrylamide (I) with active methylene groups under Michael conditions has been investigated. The reactions of I with Grignard reagents, amines, thiourea, hydrazines and hydroxylamine hydrochloride has been described. The Friedel Crafts alkylation of the aromatic hydrocarbons with 3,4-dichloro- β -benzoylacryloyl chloride (XI) and the reaction of it with anthranilic acid have been extended and explored.

Recently^{1,2} it has been reported that addition of active methylene groups to β -acryloylacrylic acids under Michael conditions afforded the formation of cyclic or normal Michael addition products depending on the reaction conditions.

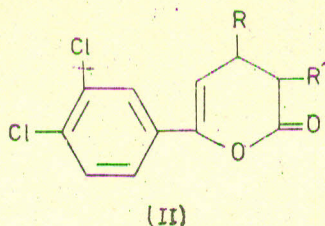
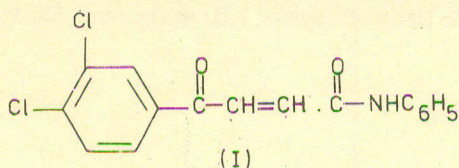
In this work the effect of replacement of carboxyl group by anilide group on the same reaction, has now been extended and explored, the addition of diethylmalonate to amide (I) in sodium methoxide afforded ethyl 3,4-dihydro-6-(3,4-dichlorophenyl)-4-phenylcarbamoyl-2H-pyron-3-carboxylate (IIa). On the other hand, addition of ethylacetoacetate, ethylmethyl ketone and methyl benzyl ketone to (I) under the same Michael conditions afforded the cyclohexenone derivatives IIIa-c respectively. The IR spectrum of IIa showed ν C=O (α -pyrone) at 1720 cm^{-1} (3a), C=O (amide) at 1680 cm^{-1} (3b), C=O (ester) at 1740 cm^{-1} (3c) and NH at 3420 cm^{-1} (3d), while that of IIIb showed ν C=O (ketone) at 1725 cm^{-1} ,

NH at 3340 cm^{-1} , C=O (amide) at 1670 cm^{-1} and C=C at 1610 cm^{-1} (3e).



(III)

R	R'
a, COOC_2H_5	CONHC_6H_5
b, CH_3	CONHC_6H_5
c, C_6H_5	CONHC_6H_5
d, COOC_2H_5	COOH
e, CH_3	COOH
f, C_6H_5	COOH

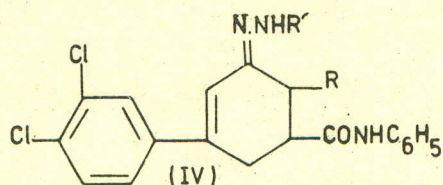


R	R'
a, CONHC_6H_5	COOC_2H_5
b, CONHC_6H_5	COOH
c, COOH	COOC_2H_5

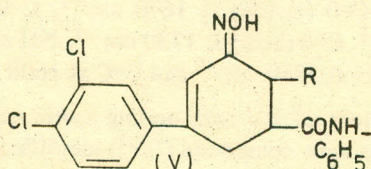
(a) Hydrolysis of IIa with 5% alcoholic KOH and a mixture of boiling HCl and CH_3COOH gave IIb and IIc respectively.

(a) Hydrolysis of IIIa-c with a mixture of boiling HCl and CH_3COOH gave IIId-f, which were prepared authentically via Michael reaction on 3,4-dichloro- β -benzoylacrylic acid.

(a) On the other hand, the condensation of IIIa-c with hydrazines and hydroxylamine hydrochloride afforded the hydrazones IVa-f and the oximes Va-c respectively. The IR spectrum of IVb showed ν NH at 3350 cm^{-1} , C=O (amide) at 1680 cm^{-1} and C=N at 1650 cm^{-1} (3f) while that of Vb showed ν OH at 3500 cm^{-1} (broad) (3g), NH at 3380 cm^{-1} , C=O (amide) at 1685 cm^{-1} and C=N at 1650 cm^{-1} .



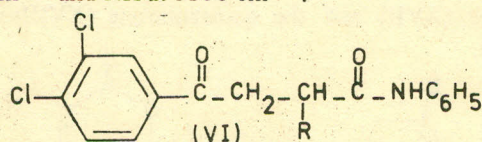
R	R'
a, COOC ₂ H ₅	H
b, CH ₃	H
c, C ₆ H ₅	H
d, COOC ₂ H ₅	C ₆ H ₅
e, CH ₃	C ₆ H ₅
f, C ₆ H ₅	C ₆ H ₅



R	R	R
a, COOC ₂ H ₅	b, CH ₃	c, C ₆ H ₅

The reaction of β -aroyl-N-arylacrylamide with Grignard reagents to give either the 1,4 or the 1,2-addition products have been reported⁴.

In the present investigation, it has been found that (I) consumed only one mole of the Grignard reagents namely, phenyl-magnesium bromide, ethylmagnesium iodide, benzylmagnesium chloride and *p*-methoxyphenylmagnesium bromide to give the 1,4-addition products (VIa-d) as the only crystallisable products. The IR spectrum of VIa showed ν C=O (amide) at 1675 cm⁻¹, C=O (ketone) at 1700 cm⁻¹ and NH at 3350 cm⁻¹.

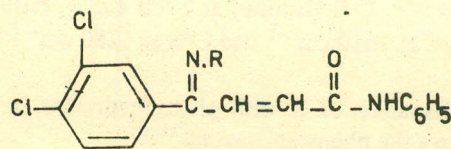


R	R	R
a, C ₆ H ₅	c, CH ₂ C ₆ H ₅	e, NC ₄ H ₈ O
b, CH ₂ CH ₃	d, C ₆ H ₄ OCH ₃ (<i>p</i>)	f, C ₅ H ₁₀ N
		g, NHCH ₂ C ₆ H ₅

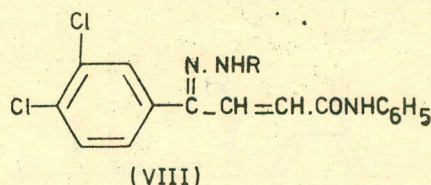
In our previous study⁵ the reactions of β -aroylacrylic acids with hydrazines, hydroxylamine hydrochloride, amines and thiourea have been reported. In the present investigation, these reactions have been applied on the amide (I).

The condensation of (I) with hydrazines and hydroxylamine hydrochloride in cold or boiling alcohol gave the hydrazones VIIa and b and the oxime VIIc respectively. The compounds VIIa and b do not give the colour test for

pyrazolines⁶. The IR spectrum of VIIa showed ν C=O (amide) at 1680 cm⁻¹, C=N at 1640 cm⁻¹, NH at 3380 cm⁻¹ and C=C at 1610 cm⁻¹. As a point of interest, boiling VIIa with formic, acetic, propionic acids, benzoyl chloride or benzenesulphonyl chloride afforded the N-acyl or sulphonyl derivatives VIIa-e respectively.



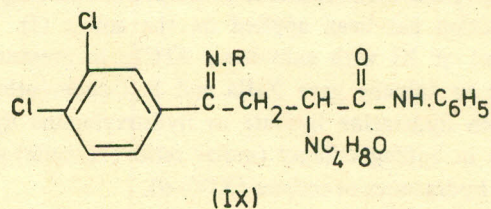
R	R	R
a, NH ₂	b, NHC ₆ H ₅	c, OH



R	R	R
a, CHO	c, CH ₃ CH ₂ CO	d, C ₆ H ₅ CO
b, CH ₃ CO		e, C ₆ H ₅ SO ₂

@ Addition of amines, namely, morpholine, piperidine or benzylamine to (I) in cold benzene gave the addition products (VIe-g). The IR spectrum of VIe showed ν C=O (amide) at 1670 cm⁻¹, C=O (ketone) at 1700 cm⁻¹ and NH at 3330 cm⁻¹.

Condensation of VIe with hydrazines in ethanol afforded the corresponding hydrazones (IXa and b).



R	R
a, NH ₂	d, N = C ₆ H ₁₀
b, NHC ₆ H ₅	e, NHCOCH ₂ COCH ₃
c, N = CH ₂	f, NHCOCH ₃

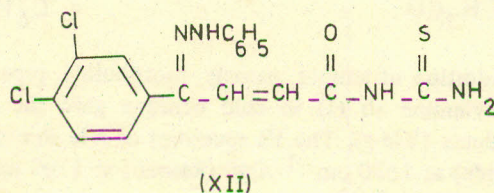
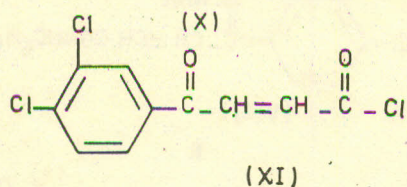
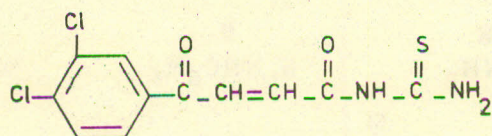
Condensation of IXa with formaldehyde, cyclohexanone and ethylacetoacetate in ethanol afforded the compounds (IXc-e).

On the other hand, acetylation of IXa using acetic anhydride gave the acetyl derivative (IXf).

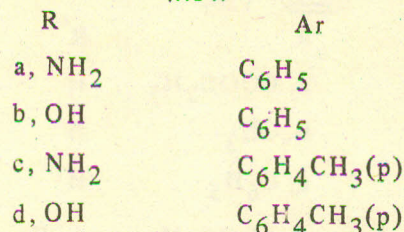
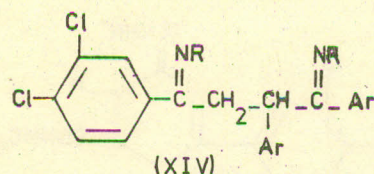
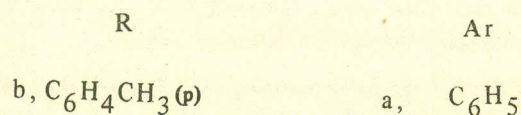
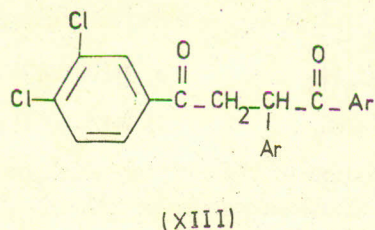
Recently⁵ we have reported that β -aroylacrylic acids react with thiourea to give thiazole derivatives. In the

present investigation reaction of the amide (I) with thiourea did not give the corresponding thiazole but gave 2-thio-1-(3) [3,4-dichloro- β -benzoylacryloyl]-urea (X) with elimination of the aniline. The structure of (X) is established by independent synthesis via reaction of 3,4-dichloro- β -benzoylacryloyl chloride (XI) with thiourea in ether. The IR spectrum of X showed ν C=O (amide) at 1680 cm^{-1} , C=O (ketone) at 1720 cm^{-1} , NH at 3420 cm^{-1} , C=C at 1610 cm^{-1} and C=S at 1280 cm^{-1} (3h).

Condensation of X with phenylhydrazine in boiling alcohol gave the phenylhydrazone (XI).

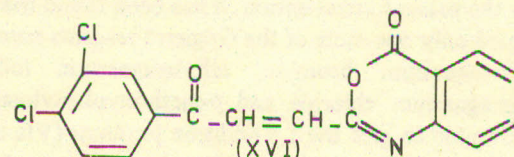
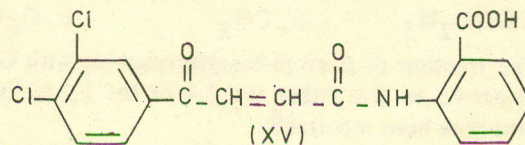


The reaction of β -benzoylacrylic acid with toluene and AlCl_3 has been reported. In the present investigation this reaction has been applied on the amide (I). Thus treatment of XI with anhydrous AlCl_3 in presence of benzene or toluene gave XIIIa and b. Condensation of XIII with hydrazine hydrate or hydroxylamine hydrochloride in boiling ethanol (molar ratio 1:2 mole) afforded the hydrazones or oximes (XIVa-d).

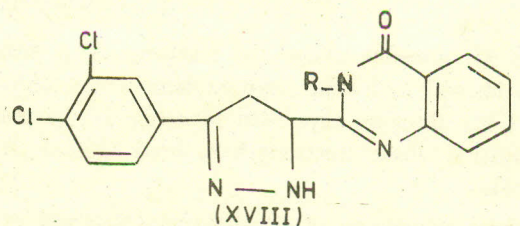
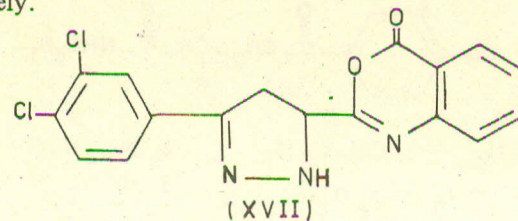


Interestingly, XI reacted with anthranilic acid in ether to give the anthranilic acid derivative (XV), but when the reaction was carried out in pyridine the product was the benzoxazinone (XVI). The IR spectrum of XV showed C=O (amide) at 1670 cm^{-1} , C=O (ketone) at 1720 cm^{-1} , C=O (acid) at 1730 cm^{-1} , NH at 3380 cm^{-1} (broad), OH at 3350 cm^{-1} and C=C at 1600 cm^{-1} .

Treatment of XV with boiling acetic anhydride gave one and the same compound (XVI) identified by m.p. and mixture m.p. experiments.



Condensation of XVI with hydrazine hydrate in boiling alcohol and/or acetic acid afforded the benzoxazinone (XVII) and the quinazolinone (XVIIIa) respectively.



The structure of XVIIIa is established by independent synthesis via reaction of XVII with hydrazine hydrate in boiling acetic acid.

On the other hand, the condensation of XVII with *p*-toluidine in acetic acid gave quinazolinone (XVIIIb).

Experimental

Procedure. The IR spectra were obtained with a Unicam SP 1200 spectro-photometer using the KBr Wafer technique. All melting points are uncorrected.

Base Catalyzed Cycloaddition of Active Methylene Compounds to 3,4-Dichloro- β -benzoyl-N-phenylacrylamide (I). Formation of (II and IIIa-c). A mixture of the amide (I) (0.01 mole), the active methylene compound, (0.01 mole) and sodium methoxide solution (0.015 mole) was heated at 170° for 10 hr. The reaction mixture was poured into water, then extracted with ether to get rid of any unreacted organic materials. The aqueous layer was acidified with ice-cold dilute hydrochloric acid. The residual oil formed was triturated with light petrol (b.p. 80-110°). The solid obtained was crystallized from the proper solvent to give the colourless Michael adducts (II) and (IIIa-c) respectively (cf. Table 1). Yield 90%.

TABLE 1. MICHAEL ADDUCTS (II) and (IIIa-c),

Compd.	m.p. °C	Solvent	Formula (M.Wt.)	Analyses %		
				Required	Found	
II	176	B/E	C ₂₁ H ₁₇ Cl ₂ NO ₅ (434)	C	58.06	58.2
				H	3.91	3.8
				N	3.2	3.2
IIIa	192	E	C ₂₂ H ₁₉ Cl ₂ NO ₄ (432)	C	61.1	59.8
				H	4.4	4.1
				N	3.2	3.2
IIIb	202	E	C ₂₀ H ₁₇ Cl ₂ NO ₂ (374)	C	64.2	63.8
				H	4.5	4.2
IIIc	184	E	C ₂₅ H ₁₉ Cl ₂ NO ₂ (436)	C	68.8	68.4
				H	4.3	4.3

B = benzene; E = ethanol.

Alkaline Hydrolysis of IIa. Formation of IIb. An alcoholic solution of IIa (2g) was treated with aqueous potassium hydroxide solution (5%, 10 ml) and the reaction mixture was refluxed for 8 hr. The cold mixture was acidified with dilute hydrochloric acid. The solid obtained was crystallized from ethanol to give the corresponding acid derivative IIb as colourless crystals melted at 182° Yield 75%.

Analysis. C₁₉H₁₃Cl₂NO₅ Required : C,56.2; H,3.2; N,3.4 Found : C,55.9; H,3.1; N,3.3

Acid Hydrolysis of (IIa) and (IIIa-c). Formation of (IIc) and (III-d-f). A solution of IIa or IIIa-c (2g) in glacial acetic acid (10 ml) and concentrated HCl (10 ml) was refluxed for 4 hr. The reaction mixture was poured into ice, the solid separated was filtered off, and crystallized from proper solvent to give IIa and III-d-f and VI as colourless crystals respectively. Yield 85% (cf. Table 2).

TABLE 2. ACID DERIVATIVES IIc AND III-d-f.

Compd.	m.p. °C	Solvent	Formula (M. Wt.)	Analysis %		
				Required	Found	
IIc	146	B/E	C ₁₅ H ₁₂ Cl ₂ O ₆ (359)	C	50.1	49.8
				H	3.3	3.3
III-d	162	B	C ₁₆ H ₁₄ Cl ₂ O ₅ (357)	C	53.8	53.8
				H	3.9	3.7
IIIe	199	T/E	C ₁₄ H ₁₂ Cl ₂ O ₃ (299)	C	56.2	56.1
				H	4.0	3.8
III-f	123	E	C ₁₉ H ₁₄ Cl ₂ O ₃ (361)	C	63.2	62.9
				H	3.9	3.8

B = benzene; E = ethanol; T = toluene.

Condensation of IIIa-c, I, VIe, XIIIa and b, and XVI with Hydrazines. Formation of IV-d-f, VIIa and b, IXa and b, XII, XIV, XVII and XVIII. A mixture of (0.01 mole) of compound, (0.01 or 0.02 mole) of hydrazine hydrate and/or phenylhydrazine, and (20 ml) ethanol or acetic acid was refluxed for 6 hr. The solid products obtained after evaporation of most of the solvent was crystallized from proper solvent to give the corresponding hydrazone or phenylhydrazone derivatives as pale yellow crystals. Yield 80% (cf. Table 3).

Condensation of IIIa-c, I and XIIIa and b with Hydroxylamine Hydrochloride. Formation of Va-c, VIIc and XIVb and d. A mixture of (0.01 mole) of start, hydroxylamine hydrochloride (0.01 or 0.02 mole), (20 ml) ethanol and (2g) of sodium acetate in few drops of water was added. The mixture was refluxed for 8 hr. The solid products obtained after evaporation of most of the solvent was crystallized from proper solvent to give the corresponding oxime derivatives respectively as pale yellow crystals. Yield 60% (cf. Table 4).

Action of Grignard Reagents on (I). A (0.01 mole) of (I) in 200 ml of dry benzene was added to an ethereal solution of phenylmagnesium bromide, ethylmagnesium iodide, benzylmagnesium chloride and *p*-methoxy phenyl-

TABLE 3. HYDRAZONE AND PHENYLHYDRAZONE DERIVATIVES.

Compd.	m.p. °C	Solvent	Formula (M. Wt.)	Analyses %		
				Required	Found	
IVa	154	E	C ₂₂ H ₂₁ Cl ₂ N ₃ O ₃ (446)	C	59.2	59.0
				H	4.7	4.5
				N	9.4	9.3
IVb	175	E	C ₂₀ H ₁₉ Cl ₂ N ₃ O (388)	C	61.8	61.6
				H	4.9	4.6
				N	10.8	10.7
IVc	146	B/E	C ₂₅ H ₂₁ Cl ₂ N ₃ O (450)	C	66.6	66.4
				H	4.7	4.5
				Cl	15.8	15.7
IVd	183	T	C ₂₈ H ₂₅ Cl ₂ N ₃ O ₃ (522)	C	64.4	64.1
				H	4.7	4.5
				N	8.0	7.7
IVe	192	A	C ₂₆ H ₂₃ Cl ₂ N ₃ O (464)	C	67.2	67.0
				H	4.9	4.8
IVf	187	E	C ₃₁ H ₂₅ Cl ₂ N ₃ O (526)	C	70.7	70.6
				H	4.8	4.6
VIIa	185	E	C ₁₆ H ₁₃ Cl ₂ N ₃ O (334)	C	57.4	57.7
				H	3.8	3.8
				N	12.5	12.6
VIIb	198	E	C ₂₂ H ₁₇ Cl ₂ N ₃ O (410)	C	64.3	64.4
				H	4.1	4.2
				N	10.2	10.4
IXa	181	E	C ₂₀ H ₂₂ Cl ₂ N ₄ O ₂ (421)	C	57.0	57.2
				H	5.2	5.3
IXb	170	E	C ₂₆ H ₂₆ Cl ₂ N ₄ O ₂ (497)	C	62.7	62.9
				H	5.2	5.3
XII	222	E	C ₁₇ H ₁₄ Cl ₂ N ₄ OS (393)	C	51.9	51.6
				H	3.6	3.3
				N	14.2	14.0

(Continued)

XIVa	170	E	C ₂₂ H ₂₀ Cl ₂ N ₄ (411)	C	64.2	64.1
				H	4.9	4.7
XIVc	196	E	C ₂₄ H ₂₄ Cl ₂ N ₄ (439)	C	56.6	56.6
				H	5.4	5.1
				N	12.7	12.4
XVII	172	E	C ₁₇ H ₁₁ Cl ₂ N ₃ O ₂ (360)	C	56.6	56.5
				H	3.0	2.8
XVIII	240	E	C ₁₇ H ₁₃ Cl ₂ N ₅ O (374)	C	54.5	54.3
				H	3.5	3.3
				N	18.7	18.6

A = acetic acid; B = benzene; E = ethanol; T = toluene.

TABLE 4. THE OXIME DERIVATIVES Va-c, VIIc AND XIVb AND XIVd.

Compd.	m.p. °C	Solvent	Formula (M. Wt.)	Analyses %		
				Required	Found	
Va	157	E	C ₂₂ H ₂₀ Cl ₂ N ₂ O ₄ (477)	C	59.1	59.0
				H	4.5	4.4
				N	6.3	6.0
Vb	132	E	C ₂₀ H ₁₈ Cl ₂ N ₂ O ₂ (289)	C	61.7	61.5
				H	4.6	4.4
				N	7.2	7.0
Vc	195	E	C ₂₅ H ₂₀ Cl ₂ N ₂ O ₂ (451)	C	66.5	66.1
				H	4.4	4.2
				N	12.5	12.6
VIIc	155	B	C ₁₆ H ₁₂ Cl ₂ N ₂ O ₂ (335)	C	57.3	57.5
				H	3.5	3.5
XIVb	168	B	C ₂₂ H ₁₈ Cl ₂ N ₂ O ₂ (413)	C	63.9	63.7
				H	4.4	4.2
				N	6.8	6.5
XIVd	193	E	C ₂₄ H ₂₂ Cl ₂ N ₂ O ₂ (441)	C	65.3	65.0
				H	5.0	4.7

B = benzene; E = ethanol.

magnesium bromide (from 2.43g magnesium) in the course of 30 min and an additional 30 ml of dry benzene was added and solution evaporated at its boiling point. After the temperature of the boiling solution reached 78°, the solution was heated under reflux with efficient

stirring for 17 hr. The reaction mixture was decomposed in the usual way with ice-cold saturated ammonium chloride solution. The organic layer was washed and dried and the solvent distilled. The viscous oils obtained were triturated and the products were crystallized from

TABLE 5. GRIGNARD ADDITION PRODUCTS VIa-d.

Compd.	m.p. °C	Solvent	Formula (M. Wt.)	Analyses %		
				Required	Found	
VIa	63	B	C ₂₂ H ₁₇ Cl ₂ NO ₂ (398)	C	66.3	66.1
				H	4.3	4.2
				N	3.5	3.3
VIb	135	M	C ₁₈ H ₁₇ Cl ₂ NO ₂ (350)	C	61.7	61.5
				H	4.9	4.8
VIc	56	P	C ₂₃ H ₁₉ Cl ₂ NO ₂ (410)	C	67.3	67.1
				H	4.1	3.8
				N	3.1	2.9
VIId	168	M	C ₂₃ H ₁₉ Cl ₂ NO ₃ (428)	C	64.5	64.3
				H	4.4	4.1

B = benzene; M = methanol; P = pet. ether.

TABLE 6. N-ACYLE AND SULPHONYL DERIVATIVES VIIa-e.

Compd.	m.p. °C	Solvent	Formula (M. Wt.)	Analyses %		
				Required	Found	
VIIa	218	E	C ₁₇ H ₁₃ Cl ₂ N ₃ O ₂ (362)	C	56.3	56.1
				H	3.6	3.5
				N	19.6	19.4
VIIb	205	E	C ₁₈ H ₁₅ Cl ₂ N ₃ O ₂ (376)	C	57.4	57.2
				H	3.9	3.8
VIIc	160	E	C ₁₉ H ₁₇ Cl ₂ N ₃ O ₂ (390)	C	58.5	58.3
				H	4.4	4.1
				N	10.8	10.5
VIId	220	A	C ₂₃ H ₁₇ Cl ₂ N ₃ O ₂ (438)	C	63.0	63.0
				H	3.9	3.7
VIIe	225	A	C ₂₂ H ₁₇ Cl ₂ N ₃ O ₃ S (474)	C	55.6	55.4
				H	3.6	3.5
				S	6.7	6.6

A = acetic acid; E = ethanol.

the suitable solvent to give VIa-d as colourless crystals. Yield 70% (cf. Table 5).

Acylation and Sulphonation of VIIa. Formation of VIIa-e. A solution of (0.01 mole) of VIIa in (20 ml) formic acid, acetic acid, propionic acid, benzoyl chloride and or benzene sulphonyl chloride (20 ml) was refluxed for 6 hr. The solid products obtained after evaporation of most of the solvent was crystallized from proper solvent to give N-acetyl or sulphonyl derivatives VIIa-e as colourless crystals. Yield 95% (cf. Table 6).

Addition of Amines to (I). Formation of VIe-g. To a solution of (0.01 mole) of (I) in 100 ml of dry benzene, (0.02 mole) of amines, namely, morpholine, piperidine and/or benzylamine was added. The mixture was left overnight. The solid products formed were filtered off washed, dried and crystallized from proper solvent to give the addition products VIe-g. Yield 95% (cf. Table 7).

Condensation of IXa with Formaldehyde and Cyclohexenone. Formation of IXc and d. A mixture of (0.01 mole) of IXa (0.01 mole) of formaldehyde or cyclohexenone and (20 ml) butanol were refluxed for 10 hr. The solid products obtained after evaporation of most of the solvent were crystallized from benzene to give IXc and d as colourless crystals. Yield 60% (cf. Table 8).

TABLE 7. THE ADDITION PRODUCTS VIe-g.

Compd.	m.p. °C	Solvent	Formula (M. Wt.)	Analyses %		
				Required	Found	
VIe	144	P	C ₂₀ H ₂₀ Cl ₂ N ₂ O ₃ (407)	C	58.9	59.1
				H	4.9	4.8
				N	6.8	6.8
VIIf	92	E	C ₂₁ H ₂₂ Cl ₂ N ₂ O ₂ (405)	C	62.2	62.2
				H	5.4	5.3
VIg	221	E	C ₂₃ H ₂₀ Cl ₂ N ₂ O ₂ (427)	C	64.6	64.8
				H	4.6	4.6

E = ethanol; P = Petroleum ether.

TABLE 8. CONDENSATION PRODUCTS IXc AND d.

Compd.	m.p. °C	Solvent	Formula (M. Wt.)	Analyses %		
				Required	Found	
IXc	163	B	C ₂₁ H ₂₂ Cl ₂ N ₄ O ₂ (433)	C	58.1	58.0
				H	5.1	4.8
IXd	203	E	C ₂₆ H ₃₀ Cl ₂ N ₄ O ₂ (501)	C	62.2	62.3
				H	5.9	6.1

B = benzene; E = ethanol.

Reaction of IXa with Ethyl Acetoacetate. Formation of IXe. A mixture of (0.01 mole) of IXa (0.01 mole) of ethylacetoacetate and (20 ml) ethanol was refluxed for 10 hr. The solid product obtained after evaporation of most of the solvent was crystallized from ethanol to give IXe as colourless product melted at 195°. Yield 70%.

Analysis. $C_{24}H_{26}Cl_2N_4O_4$ (505): Required: C,57.0; H,5.1, Found: C,56.6; H,4.8.

Acetylation of IXa. Formation of IXf. A solution of (0.01 mole) of IXa in acetic anhydride (0.01 mole) was refluxed for 10 hr. The solid products obtained after evaporation of most of the solvent was crystallized from ethanol to give the N-acetyl derivative IXf as colourless crystals melted at 207°. Yield 70%.

Analysis. $C_{22}H_{24}Cl_2N_4O_3$ (463): Required: C,57.0; H,5.2; N,12.1, Found: C,56.6; H,4.8; N,12.0.

Reaction of (I) with Thiourea. Formation of X. A mixture of (0.01 mole) of (I), thiourea (0.02 mole) and ethanol (20 ml) was treated with 10 drops of glacial acetic acid and refluxed for 8 hr. The solid product separated after evaporation of most of the solvent and cooling was crystallized from benzene to give the corresponding derivatives X as colourless crystals shared at 205°. Yield 85%.

Analysis %. $C_{11}H_8Cl_2N_2O_2S$ (303): Required: C,43.6; H,2.6; S,9.4, Found: C,43.3; H,2.5; S,9.2.

Synthesis of Authentic Sample of X. A mixture of 3,4-dichloro- β -benzoyl-N-phenylacryloyl chloride (XI) (0.01 mole), thiourea (0.02 mole), and ether (40 ml) was refluxed over a water bath for 6 hr. The solid product obtained after evaporation of ether was crystallized from ethanol to give a product proved to be X by m.p. and mixed m.p. determinations. Yield 90%.

Friedel-Craft's Alkylation of Aromatic Hydrocarbons with (XI). Formation of XIIIa and b. A solution of (0.01 mole) of (XI) in aromatic hydrocarbons; namely, benzene or toluene (50 ml) was treated with dry hydrogen chloride and $AlCl_3$ (0.04 mole) was added. A vigorous evolution of HCl took place and a yellow paste precipitated. The temperature of the reaction mixture was maintained at 20-25°. Stirring was continued for an additional 15 hr at room temperature. The whole was then added to HCl-ice. The organic layer washed with water and the excess solvent removed by steam distillation. The organic materials were extracted by ether. After evaporation of most of the ether, the oil products formed were triturated with petroleum ether (80-100). The solid products obtained were crystallized from proper solvent to give the

TABLE 9. THE ADDITION PRODUCTS XIIIa AND b.

Compd.	m.p. °C	Solvent	Formula (M. Wt.)	Analyses %		
				Required	Found	
XIIIa	102	B	$C_{22}H_{16}Cl_2O_2$ (383)	C	68.9	68.8
				H	4.2	4.0
XIIIb	110	E	$C_{24}H_{20}Cl_2O_2$ (411)	C	70.1	69.7
				H	4.9	4.6

B = benzene; E = ethanol

alkylation products XIIIa and b as colourless crystals. Yield 75% (cf. Table 9).

Reaction of XI with Anthranilic Acid. Formation of XV. An ether of (0.01 mole) of anthranilic acid, was added dropwise to an ether solution of (0.01 mole) of acid chloride XI. The solid product formed was filtered; washed with hot water, then dried and crystallized from ethanol to give XV as colourless product melted at 208°. Yield 60%.

Analysis %. $C_{17}H_{11}Cl_2NO_4$ (356): Required: C,57.3; H,3.1; N,3.9, Found: C,57.0; H,2.9; N,3.6.

Cyclization of XV. Formation of XVI. A solution of XV (2g) in acetic anhydride (10 ml) was refluxed for 6 hr. The solid crystalline product formed after evaporation of most of the solvent and leaving for two days at room temperature was crystallized from ethanol to give the corresponding benzoxazine-4-one derivatives XVI as pale yellow crystals melted at 172°. Yield 80%.

Analysis %. $C_{17}H_9Cl_2NO_3$ (346): Required: C,58.9; H,2.6, Found: C,58.7; H,2.5

Synthesis of Authentic Sample of XVIII:- A mixture of XVII (0.01 mole) hydrazine hydrate (0.02 mole) and (20 ml) glacial acetic acid was refluxed for 6 hr. The solid product obtained after evaporation of most of the solvent and crystallization was proved to be XVIIIa by m.p. and mixture m.p. experiments.

Condensation of XVII with p-Toluidine Formation of XVIIIb. A mixture of (0.01 mole) of XVII (0.01 mole) of p-toluidine and 20 ml of acetic acid was refluxed for 10 hr. The solid product obtained after evaporation of most of the solvent was crystallized from benzene to give XVIIIb as pale yellow crystals melted at 137°.

Analysis %. $C_{24}H_{18}Cl_2N_4O$ (449): Required: C,64.1; H,4.0; N,12.4, Found: C,63.8; H,3.8; N,12.1.

References

1. A. Sammour, A.A. Afify, M.M. Abd Allah and E.A. Soliman, *Acta Chim. (Budapest)*, **85**, 455 (1975).
2. G. Hosni, E.A. Soliman, *Pakistan Association for the Advancement of Science* (1978), vol. XXX. (accepted for publication).
3. L.J. Bellamy, *The Infrared Spectra of Complex Molecules* (London), pp. (a) 132 (b) 204 (c) 179 (d) 249 (e) 34 (f) 277 (g) 95 (h) 355.
4. W.I. Awad, M.F. Islam and M.S. Nour-Eldeen, *Egypt. J. Chem.*, **14**, 153 (1971).
5. A. Sammour, M.I.B. Selim, E.A. Soliman, *Egypt J. Chem.*, **15**, 311 (1972).
6. V. Knorr, *Ann.*, **238**, 200 (1887).
7. A. Sammour, M. Elhashash, *J. Prakt. Cheme.*, **314**, 906 (1972).