Tetrahedron. Vol. 27, pp 2517 to 2528. Pergamon Press 1971 Printed in Great Britain

SYNTHESIS AND REACTIONS OF PHENYLCARBAMOYLARYLHYDRAZIDIC CHLORIDES

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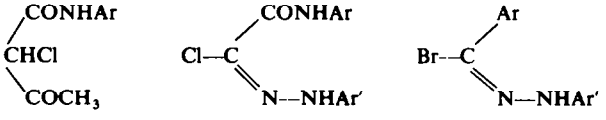
(*Received in the UK* 10 *December* 1970; *Accepted for publication* 23 *December* 1970)

Abstract—The preparation and spectral properties of 18 phenylcarbamoylarylhydrazidic chlorides (IIa–r) derived from coupling of diazotized anilines to α-chloroacetoacetanilide have been investigated. Reaction of these hydrazidic chlorides with various nucleophiles results in ready substitution of the chlorine atom. In particular, reaction of II with primary or secondary amines proved an effective method for the preparation of oxanilamidrazones (IV–VIII). A number of II reacted with NaCN and NaOPh to yield arylazo derivatives of cyanoacetanilide and phenoxyacetanilide, respectively. Treatment of IIa with MeMgI gives pyruvanilide phenylhydrazone. Reaction of IIa with NaOAc gives, XIII through OAc → NAc rearrangement, Structural assignments have been made on the basis of IR and UV spectra and independent synthesis wherever possible.

AMONG the various systems containing active methinyl groups that have been subjected to the Japp–Klingeman reaction,[1] the least studied are α-chloroacetarylamides (I). The products (II) from such amides are hydrazones of unusual structure (Scheme 1). Although such products, formally, are related to hydrazidic bromides (III) which have recently attracted considerable attention in synthetic studies,[2] and particularly as sources of azocarbonium ions,[3] and 1,3-dipolar ions,[4] essentially no information is available in the literature concerning the reactions of C-phenylcarbamoylarylhydrazidic chlorides (II). We wish to report the preparation and reactions of eighteen compounds of type II.



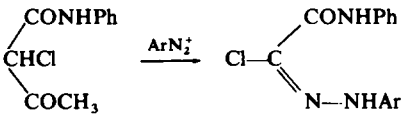
I II III

RESULTS AND DISCUSSION

α-Chloroacetoacetanilide (I, Ar = C_6H_5) couples with diazotized arylamines in NaOAc-buffered solution of EtOH to yield phenylcarbamoylarylhydrazidic chlorides (II, Scheme I). IR and UV spectra of these compounds show that, like other aliphatic azo compounds,[5] they exist as the hydrazones.

In all cases, medium-strong bands in the 3500–3100 cm^{-1} region due to the N—H stretch were observed. Also they showed four other strong bands in the 1700–1400 cm^{-1} region: C=O stretch (1690–1670 cm^{-1}), aromatic C=C stretch (1600 cm^{-1}), C=N stretch (1587 cm^{-1}), and amide N—H deformation band (1538 cm^{-1}). The significant infrared absorption bands of the compounds IIa–r are given in Table 1. A typical spectrum is shown in Fig 1.

SCHEME I



IIa, Ar = C_6H_5
IIb, Ar = 3—$CH_3OC_6H_4$
IIc, Ar = 4—$CH_3C_6H_4$
IId, Ar = 3—$CH_3C_6H_4$
IIe, Ar = 4—ClC_6H_4
IIf, Ar = 3—ClC_6H_4
IIg, Ar = 4—BrC_6H_4
IIh, Ar = 3—BrC_6H_4
IIi, Ar = 4—$HOOCC_6H_4$
IIj, Ar = 3—$HOOCC_6H_4$
IIk, Ar = 4—$O_2NC_6H_4$
IIl, Ar = 3—$O_2NC_6H_4$
IIm, Ar = 4—$HO_3SC_6H_4$
IIn, Ar = 2—$CH_3OC_6H_5$
IIo, Ar = 2—$CH_3C_6H_4$
IIp, Ar = 2—$HOOCC_6H_4$
IIq, Ar = 2—ClC_6H_4
IIr, Ar = 2—$O_2NC_6H_4$

The absorption pattern in the UV region was in each case characterized by the presence of three bands: band A usually is located in the region of 390–320 mμ, band B is located in the 290–250 mμ region, and band C below 240 mμ. Table 2 summarizes the ultraviolet spectral data of the compounds studied, and representative spectra are shown in Fig 2.

Phenylcarbamoylarylhydrazidic chlorides are readily attacked by nucleophilic reagents. Derivatives resulting from the reaction of IIa with nitrogen, oxygen, and

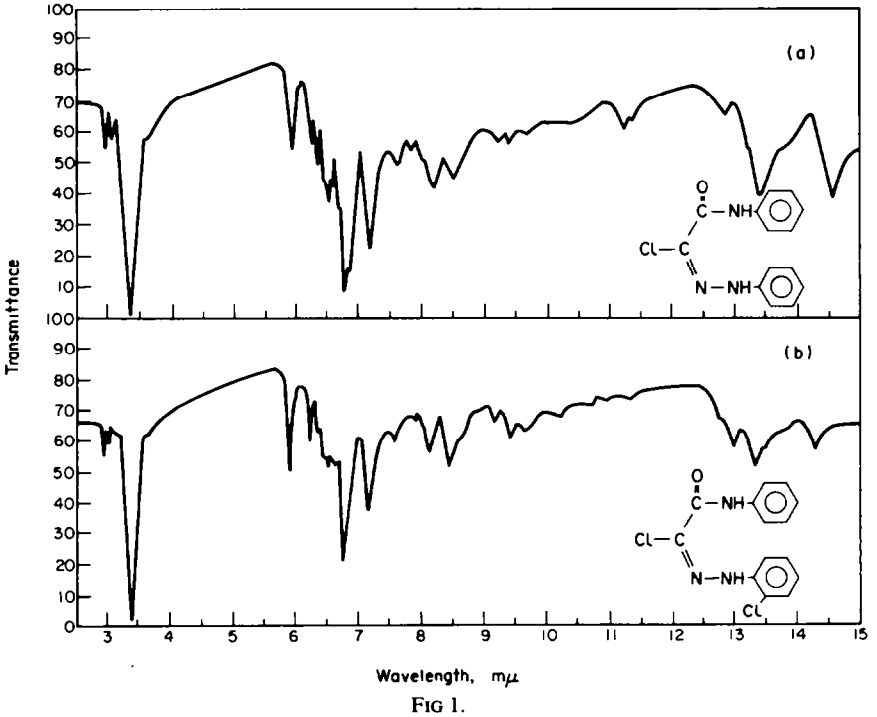


FIG 1.

TABLE 1. CHARACTERISTIC INFRARED ABSORPTION BANDS OF PHENYLCARBAMOYLARYLHYDRAZIDIC CHLORIDES IN NUJOL

Compound No.	ν_{N-H} cm^{-1}	$\nu_{C=O}$ cm^{-1}	$\nu_{C=N}$ cm^{-1}	ν_{C-N-H} cm^{-1}
IIa	3389, 3225	1686	1567	1538
IIb	3278, 3174	1683	1577	1538
IIc	3333, 3225	1689	1579	1538
IId	3378, 3225	1680	1569	1536
IIe	3333, 3225	1694	1584	1538
IIf	3344, 3225	1686	1574	1533
IIg	3355, 3267	1694	1584	1538
IIh	3448, 3246	1694	1582	1538
IIi	3278, —	1666	1587	1517
IIj	3378, 3278	1672	1574	1536
IIk	3333, 3225	1686	1587	1538
IIl	3367, 3246	1689	1587	1538
IIm	3311, 3225	1692	1587	1526
IIn	3367, 3333	1689	1562	1536
IIo	3333	1677	1587	1538
IIp	3389, 3225	1666	1569	1538
IIq	3333, 3278	1694	1569	1536
IIr	3300	1689	1582	1538

TABLE 2. ELECTRONIC ABSORPTION SPECTRA OF PHENYLCARBAMOYLARYLHYDRAZIDIC CHLORIDES IN MeOH

Compound No.	Band A		Band B		Band C	
	λ_{max} mμ	log ε	λ_{max} mμ	log ε	λ_{max} mμ	log ε
IIa	332	4·27	284	4·05	226	4·20
IIb	329	4·16	275	3·89	227	4·16
IIc	336	4·13	294	4·05	232	4·20
IId	326	4·31	284	4·16	222	4·23
IIe	331	4·36	294	4·18	242 (sh)	4·26
IIf	330	4·20	294	4·06	228	4·18
IIg	332	4·26	298	4·10	230	4·16
IIh	329	4·21	294	4·06	226 (sh)	4·22
IIi	338	4·34	260	4·01	226	4·25
IIj	335	4·20	304	4·11	226 (sh)	4·30
IIk	370	4·45	284	3·92	236 (sh)	4·16
IIl	318	4·29	233	4·21	—	—
IIm	335	4·31	257	4·11	226 (sh)	4·06
IIn	338	4·25	278	4·18	221	4·13
IIo	326	4·31	284	4·16	222	4·23
IIp	339	4·36	240 (sh)	3·85	215	4·39
IIq	324	4·25	294	4·06	224	4·15
IIr	392	3·96	263 (sh)	4·18	218	4·27

TABLE 3. ELECTRONIC ABSORPTION SPECTRA OF N-MORPHOLINYLGLYOXALANILIDE ARYLHYDRAZONES IN MeOH

Compound No.	Band A		Band B		Band C	
	λ_{max} mμ	log ε	λ_{max} mμ	log ε	λ_{max} mμ	log ε
IVa	341	4·35	284	4·06	238	4·20
IVb	335	4·23	275 (sh)	3·97	233	4·18
IVc	350	4·32	268	4·07	236	4·25
IVd	338	4·22	225	3·98	221	4·15
IVe	352	4·42	290	4·06	243	4·30
IVf	335	4·28	284	4·06	233	4·23
IVg	365	4·47	290	3·95	233	4·21
IVh	350	4·31	290	4·00	239	4·21
IVi	365	4·51	263	4·25	248	4·20
IVj	350	4·21	257 (sh)	4·08	—	—
IVk	382	4·98	263 (sh)	4·26	—	—
IVl	332	4·19	269	4·39		

(sh) = shoulder

carbon nucleophiles in EtOH are shown in Scheme II. The yields of these derivatives vary with the initial nucleophilic reagent, ranging from 52 to 85 per cent. The identity of the product in each case was established on the basis of elemental and spectral analyses, and m.m.p.s with authentic sample whenever possible (see Experimental Section).

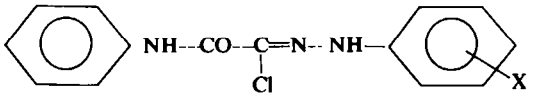
That these substitution reactions are not restricted to Ia, was shown by the conversion of the 3- and 4- substituted phenylhydrazidic chlorides (IIb–l) to oxanilimidrazones derivatives (IVb–l); α-(1-morpholino)glyoxalanilide arylhydrazones. Similarly

TABLE 4. INFRARED DATA OF N-MORPHOLINYLGLYOXALANILIDE ARYLHYDRAZONES IN NUJOL

Compound No.	ν_{N-H} cm^{-1}	$\nu_{C=O}$ cm^{-1}	$\nu_{C=N}$ cm^{-1}	$\nu_{amide\ II}$ cm^{-1}
IVa	3289	1666	1562 (s)	1538 (s)
IVb	3389, 3322	1672	1562	1540
IVc	3401, 3278	1675	1562 (s)	1538 (s)
IVd	3333	1666	1572 (s)	1538
IVe	3278	1666	1562 (s)	1538
IVf	3322	1666	1560 (s)	1538
IVg	3325	1666	1562	1526
IVh	3225	1658	1562	1538
IVi	3401, *3325	1694, †1680	1562 (s)	1526
IVj	3401, *3325	1694, †1680	1562	1520
IVk	3325	1666	1562 (s)	1538
IVl	3333	1666	1562 (s)	1538

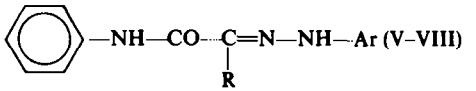
* O—H stretch of carboxyl group
† C=O stretch of carboxyl group.

TABLE 5. PHENYLAMIDOARYLHYDRAZIDIC CHLORIDES (II)



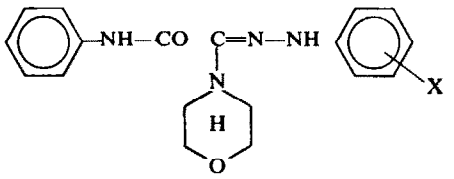
Compound No.	X	m.p.°	Crystals	Yield %		Found (%)				Calcd. (%)			
						C	H	N	Cl (Br)	C	H	N	Cl (Br)
IIa	H	161–162	pale yellow needles	80	$C_{14}H_{12}N_3ClO$								
IIb	3-CH_3O	161–162	yellow needles	70	$C_{15}H_{14}N_3ClO_2$	59·86	4·42	13·73	11·20	59·83	4·61	13·83	11·69
IIc	4-CH_3	175–176	pale yellow needles	80	$C_{15}H_{14}N_3ClO$	—	—	—	—	—	—	—	—
IId	3-CH_3	128–129	pale orange needles	70	$C_{15}H_{14}N_3ClO$	62·3	5·20	14·61	11·80	62·60	4·91	14·60	12·33
IIe	4-Cl	199–200	pale orange needles	75	$C_{14}H_{11}N_3Cl_2O$	54·54	3·52	13·68	23·00	54·54	3·57	13·63	23·03
IIf	3-Cl	191–192	pale orange needles	80	$C_{14}H_{11}N_3Cl_2O$	54·54	3·24	13·30	23·30	54·54	3·57	13·63	23·03
IIg	4-Br	208–209	pale orange needles	75	$C_{14}H_{11}N_3ClBrO$	57·55	3·00	11·89	10·07 (21·95)	57·65	3·12	11·91	10·07 (22·09)
IIh	3-Br	199–200	pale orange needles	80	$C_{14}H_{11}N_3ClBrO$	57·42	2·92	11·92	10·07 (22·00)	57·65	3·12	11·91	10·07 (22·09)
IIi	4-HOOC	284–285	pale orange needles	70	$C_{15}H_{12}N_3ClO_3$	56·72	3·65	13·28	11·13	56·69	3·81	13·29	11·16
IIj	3-HOOC	259–260	pale orange needles	65	$C_{15}H_{12}N_3ClO_3$	56·62	3·72	13·29	10·85	56·69	3·81	13·29	11·16
IIk	4-O_2N	253–254	yellow needles	70	$C_{14}H_{11}N_4ClO_3$	52·68	3·48	18·00	11·13	52·74	3·45	17·89	11·14
IIl	3-O_2N	213–214	pale orange needles	80	$C_{14}H_{11}N_4ClO_3$	52·74	3·52	17·77	11·14	52·74	3·45	17·89	11·14
IIm	3-HO_3S	244–245	orange needles	75	$C_{14}H_{12}N_3ClO_4S$	47·58	3·52	11·85	9·66	47·52	3·39	11·88	10·04
IIn	2-CH_3O	151–152	yellow needles	73	$C_{15}H_{14}N_3ClO_2$	59·88	4·30	13·81	11·47	59·63	4·61	13·83	11·69
IIo	2-CH_3	115–116	yellow needles	80	$C_{15}H_{14}N_3ClO$								
IIp	2-HOOC	216–217	yellow needles	75	$C_{15}H_{12}N_3ClO$								
IIq	2-O_2N	193–195	yellow needles	70	$C_{14}H_{11}N_4ClO_3$	52·81	3·52	17·95	11·11	52·74	3·45	17·89	11·14
IIr	2-Cl	135–136	yellow needles	75	$C_{14}H_{11}N_3Cl_2O$	54·59	3·58	13·75	22·80	54·54	3·57	13·63	23·05

TABLE 6. OXANILAMIDRAZONE DERIVATIVES



Compd. No.	R	Ar	m.p.°	crystals	Yield %	Formula	Found (%)			Calcd. (%)		
							C	H	N	C	H	N
Va	$(C_2H_5)_2N$—	C_6H_5	85	yellow needles	62	$C_{18}H_{22}N_4O$	68·47	6·69	18·03	69·06	7·09	18·06
Vb	$(C_2H_5)_2N$—	2—NO_2—C_6H_4—	130–131	Scarlet red needles	64	$C_{18}H_{21}N_5O_3$	61·12	5·56	16·88	60·84	5·91	16·90
Vi	C_4H_8N—	C_6H_5	118–119	yellow needles	52	$C_{18}H_{20}N_4O$	70·32	6·32	18·12	70·12	6·57	18·14
VII	$C_5H_{10}N$	C_6H_5	138–140	pale yellow needles	85	$C_{19}H_{22}N_4O$	71·60	5·26	17·28	70·89	5·26	17·29
VIIIa	C_7H_8N	C_6H_5	160–161	yellow needles	78	$C_{21}H_{20}N_4O$	72·93	5·98	16·29	73·25	5·81	16·28
VIIIb	C_7H_8N	3—NO_2—C_6H_4—	160–161	Orange needles	77	$C_{21}H_{19}N_5O_3$	64·30	5·19	17·97	64·75	4·88	17·99

TABLE 7. α-MORPHOLINOGLYOXALANILIDE ARYLHYDRAZONES (IV)



Compd. No.	X	m.p.°	Crystals	Yield %	Formula	Found (%)				Calcd. (%)			
						C	H	N	Cl(Br)	C	H	N	Cl(Br)
IVa	H	141–142	yellow needles	80	$C_{18}H_{20}N_4O_2$	66·57	5·64	17·29		66·67	5·91	17·28	
IVb	3—CH_3O	140–141	yellow needles	70	$C_{19}H_{22}N_4O_3$	64·60	6·34	16·82		64·40	6·21	16·81	
IVc	4—CH_3	170–171	pale redish needles	80	$C_{19}H_{22}N_4O_2$	67·33	6·87	16·55		67·42	6·54	16·56	
IVd	3—CH_3	121–122	yellow needles	75	$C_{19}H_{22}N_4O_2$	67·39	6·88	16·57		67·42	6·54	16·56	
IVe	4—Cl	128–130	yellow needles	85	$C_{18}H_{19}N_4O_2Cl$	60·45	5·28	16·81	9·75	60·25	5·29	16·80	9·90
IVf	3—Cl	138–140	yellow needles	80	$C_{18}H_{19}N_4O_2Cl$	60·55	5·20	16·79	9·82	60·25	5·29	16·80	9·90
IVg	4—Br	130–131	yellow needles	85	$C_{18}H_{19}N_4O_2Br$	54·22	4·25	13·54	(19·95)	53·61	4·69	13·55	(19·85)
IVh	3—Br	136–137	yellow needles	81	$C_{18}H_{19}N_4O_2Br$	53·20	4·62	13·56	(19·76)	53·61	4·69	13·55	(19·85)
IVi	4—COOH	273–274	yellow needles	60	$C_{19}H_{20}N_4O_4$	61·70	5·30	17·52		61·95	5·43	17·66	
IVj	3—COOH	200–201	yellow needles	60	$C_{19}H_{20}N_4O_4$	61·60	5·20	17·62		61·95	5·43	17·66	
IVk	4—NO_2	211–212	yellow needles	65	$C_{18}H_{19}N_5O_4$	58·83	4·98	15·12		58·88	5·14	15·15	
IVl	3—NO_2	153–154	orange needles	70	$C_{18}H_{19}N_5O_4$	58·84	5·22	15·14		58·88	5·14	15·15	

treatment of III with benzylamine and IIr with diethylamine gave the corresponding N^1-3-nitrophenyl-N^3-benzyloxanilamidrazone (VIIIb), and N'-2-nitrophenyl-N^3,N^3-diethyloxanilamidrazone (Vb), respectively. 3-Chlorophenylazocyanoacetanilide (IXb) was obtained by the action of NaCN on IIf. Reaction of NaOPh with IIh led to the formation of the corresponding α-phenoxyglyoxalanilide-3-bromophenylhydrazone (Xb), (Scheme III).

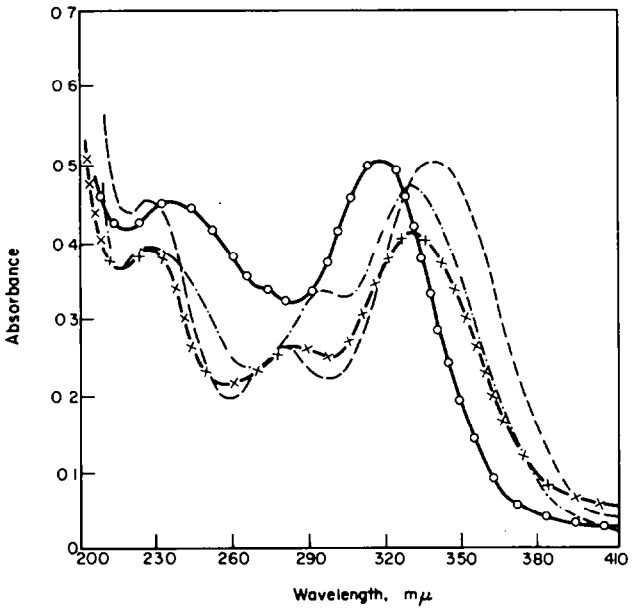


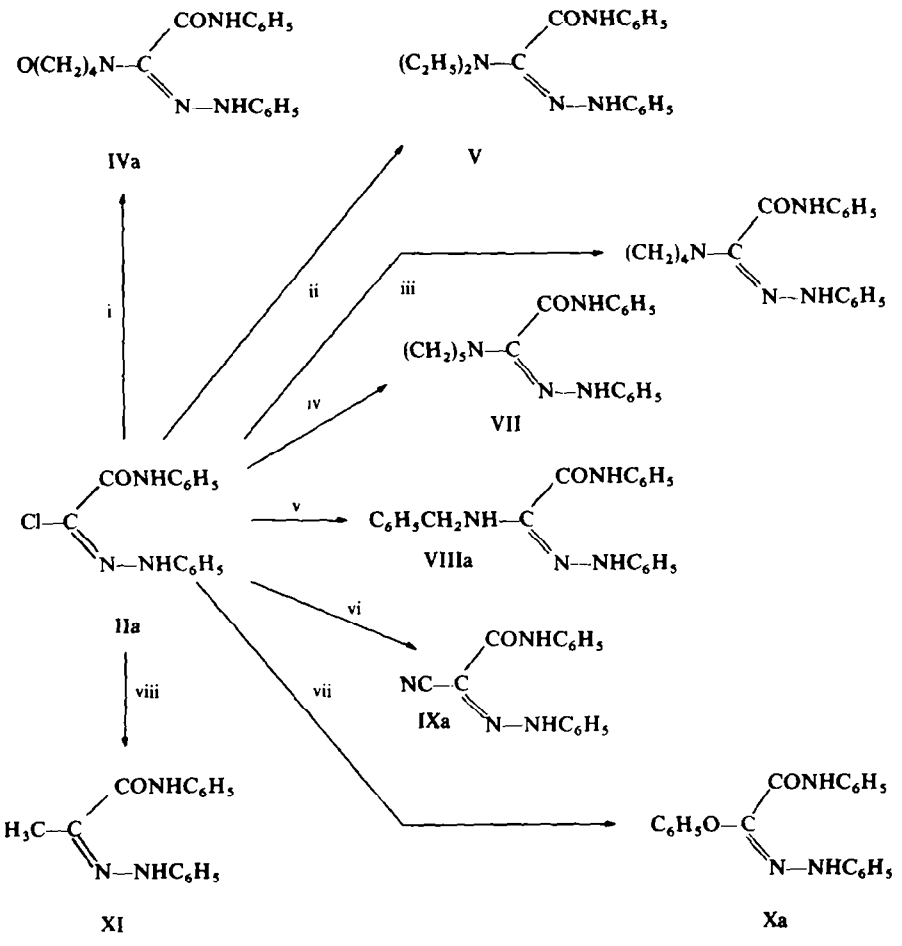
FIG 2. Electronic absorption spectra of phenylazo (— × — × —); p-bromophenylazo (— · — · —); m-nitrophenylazo (— ₒ — ₒ); and o-anisylazo (— — —) derivatives of chloroacetanilide in MeOH

It appeared worthwhile to examine the spectral properties of these new compounds and to relate these to the corresponding phenylcarbamoylarylhydrazidic chlorides. These data are presented in Tables 3 and 4.

In the UV region each oxanilamidrazone derivative exhibits three absorption bands that are located at longer wavelengths than the corresponding bands for the chlorides, II. This is in agreement with the fact that the auxochromic property of the amino nitrogen is greater than that of the chlorine group.[6] The magnitude of the bathochromic shift seems to depend on both the nature and position of the substituent in the hydrazone moiety. The substitution of the chlorine atom by phenoxy-, cyano- or methyl group also exerts a bathochromic effect, which is, however, smaller than that exerted by amino groups.

The infrared absorption in the region around 1560 cm^{-1} agrees with that reported[7] for C=N stretch. Bands around 1665, 1538 and 1600 cm^{-1} are also generally present.

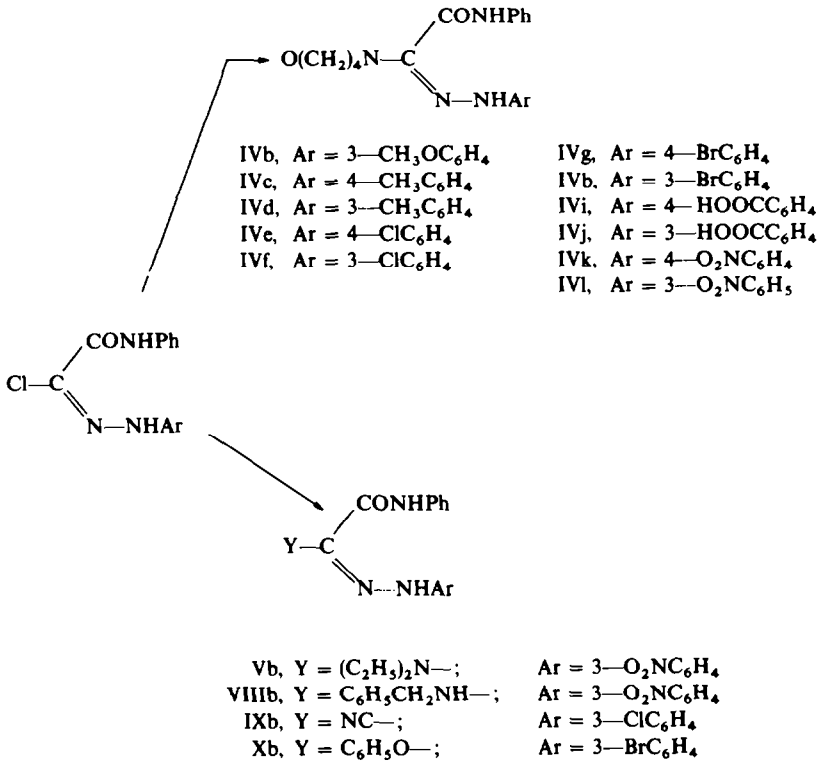
SCHEME II



Reagents: (i) morpholine, (ii) Diethylamine, (iii) Pyrrolidine, (iv) Piperidine, (v) Benzylamine, (vi) NaCN, (vii) NaOPh, (viii) MeMgI.

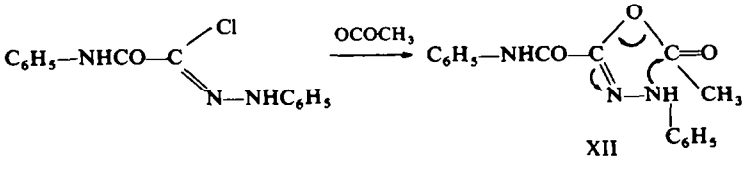
Reaction of Ia with NaOAc in EtOH gave a product which analyzed correctly for $C_{16}H_{15}N_3O_3$. Its electronic absorption spectrum in EtOH was surprisingly different from those of the other substitution products. It had a single absorption maximum near 265 mμ (log e = 4·00) indicating the absence of the hydrazone chromophore. The infrared spectrum (nujol) showed three carbonyl absorption bands at 1709, 1686, and 1666 cm^{-1}, and a strong band due to N—H stretch at 3225 cm^{-1}. These properties are in agreement with structure XIII and not the expected structure XII. In this case, the substitution of the Cl atom of Ia gave XII. This is followed by attack of the nucleophilic amino nitrogen of the hydrazone moiety on the juxtaposed carbonyl

SCHEME III



group leading to the formation of XIII. In a sense, the second step represents an intramolecular O to N acyl migration. Many examples of OAc — NAc rearrangements are known.[8, 9]

The solvolysis of phenylcarbamoylarylhydrazidic chlorides (IIa–s) and oxanilamidrazone derivatives (IVa–l, and V–VIII) will be the subject of a further communication.



XII

C_6H_5—NH—CO—CO—NH—N(COCH$_3$)—C_6H_5

XIII

EXPERIMENTAL

M.ps were determined with a Kofler hot stage apparatus and are uncorrected. The IR spectra were recorded on a Beckman IR 4 spectropnotometer (nujol mulls). UV spectra were measured on a Beckman DK spectrophotometer at room temperature. Elemental analyses were performed by microanalysis laboratory, National Research Center, Dokki, Giza, U.A.R. All yields reported relate to the recrystallized material.

Acetoacetanilide was prepared as previously reported,[10] and α-chloroacetoacetanilide was prepared by the method described by Hodgkinson and Staskun.[11]

Preparation of phenylcarbamoylarylhydrazidic chlorides (IIa–r) General procedure. A solution of α-chloroacetoacetanilide (I) (2·11 g, 0·01 mole) in EtOH 100 ml was stirred for 10 minutes with sodium acetate trihydrate 1·3 g. The mixture was then chilled to 0–5° and treated with a cold (0–5°) solution of diazonium salt prepared by diazotizing an arylamine (0·01 mole) dissolved in 6 M hydrochloric acid (6 ml.) with a solution of sodium nitrite (0·7 g, 0·1 mole) in water 10 ml. The addition of the diazonium salt was carried out with rapid stirring over a period of 20 min. The reaction mixture was kept basic by the addition, when necessary, of more NaOAc. When the addition was complete, then the mixture was stirred for another 15 min and left to stand for three hr in the refrigerator. The resulting yellow solid was removed by filtration and washed thoroughly with H_2O. The crude product was crystallized from EtOH (or HOAc) (charcoal). The compounds prepared are listed in Table 5.

Aminolysis of phenylcarbamoylphenylhydrazidic chloride (IIa). Phenylcarbamoyl phenylhydrazidic chloride (1·4 g. 0·005 mole) was stirred in EtOH (20 ml.). To the resulting suspension, diethylamine (0·44 g., 0·006 mole) dissolved in EtOH 10 ml was added. Immediately, IIa dissolved and a deep red solution was obtained while the temperature of the reaction mixture rose to 45°. After standing for 30 min, the reaction mixture was poured into H_2O. The precipitated solid was separated by filtration. Recrystallization from EtOH gave the amidrazone V (0·96 g., 62%) m.p. 85–86°.[1] Calc. for $C_{18}H_{22}N_4O$, C, 69·06; H, 7·09; N, 18·06. Found: C, 68·47; H, 6·69; N, 18·08%. Characteristics of other derivatives similarly prepared, are given in Table 6.

Morpholinolysis of hydrazidic chlorides (IIa–l). To a suspension of the appropriate hydrazidic chloride (0·005 mole) in EtOH (20 ml.) was added morpholine (0·65 g., 0·007 mole) of the same solvent (10 ml) at room temperature. Immediately a deep coloured solution (usually red) was obtained and the temperature of the reaction mixture rose to 40–45°. After standing for 30 min, the reaction mixture was run into cold water (100 ml). In some cases, the morpholine derivative precipitated before dilution with H_2O. The precipitated solid was recrystallized from EtOH. Table 7 gives analytical data and m.p.'s for crystallized amidrazones.

Preparation of α-phenoxyglyoxalanilidephenylhydrazone (Xa). Phenol (0·47 g., 0·005 mole) was dissolved in dry benzene (20 ml). To the resulting solution metallic sodium (0·12 g., 0·005 mole) was added in small pieces and the mixture left to stand at room temperature. When all sodium metal had reacted and no more gas evolved, phenylcarbamoylphenylhydrazidic chloride (1·4 g., 0·005 mole) was added to the resulting NaOPh suspension. The reaction mixture was then refluxed for 30 min. The solvent was evaporated to near dryness. The crude residue was treated with H_2O and the solid obtained filtered off. Recrystallization from EtOH gave 0·78 g. (65%) of yellow needles, m.p. 196–197°. Calcd. for $C_{20}H_{17}N_3O_2$: C, 72·51; H, 5·13; N, 18·18. Found: C, 72·07; H, 4·91; N, 18·17%.

When this reaction was repeated with phenylcarbamoyl-3-bromophenylhydrazidic chloride (IIh), α-phenoxyglyoxalanilide-3-bromophenylhydrazone (Xb) was obtained in 60% yield. Its melting point was 173–174°. Calcd. for $C_{20}H_{16}BrN_3O_2$: C, 58·53; H, 3·90; Br, 19·51; N, 13·54. Found: C, 58·21; H, 4·20; Br, 19·33; N, 13·53%.

Reaction of IIa with Grignard reagent. To a solution of MeMgI (prepared from 1·0 g. Mg and 8·0 g. MeI in dry ether (125 ml.) was added a suspension of IIa (1·4 g., 0·005 mole) in dry ether (50 ml.). The reaction mixture was refluxed for 2 hr on a water bath at 60° and cooled. The reaction mixture was decomposed with cold NH_4Cl aq. The crude product, obtained upon evaporation of the ethereal layer, was washed several times with H_2O. Recrystallization twice afforded XI (1·0 g. 70%) pale yellow needles, m.p. 174–175°. The product proved to be identical (m.p., IR, and UV) with pyruvanilide phenylhydrazone.[12]

Reaction of IIa with sodium acetate. IIa (1·4 g., 0·005 mole) was dissolved in EtOH (100 ml.) and to the resulting solution NaOAc (1·3 g., 0·001 mole) was added. The mixture was refluxed on a water bath for 2 hr, cooled to room temperature, poured into H_2O, and the white solid precipitated was filtered. Recrystallization from EtOH gave XIII (1·1 g 73%) of colourless needles, melting at 198–200°. UV (EtOH) λ_{max} 265 mμ (log e 4·00); IR (nujol) 3225 (NH), 1709, 1686, 1666 (CO) and 1600 (aromatic C=C) cm^{-1}. Calcd. for $C_{16}H_{15}N_3O_3$: C, 64·64; H, 5·05; N, 14·14. Found: C, 64·50; H, 5·00; N, 14·30%

Reaction of IIa with NaCN. IIa (1·4 g. 0·005 mole) was stirred in EtOH (100 ml.). To the resulting suspension, NaCN (0·23 g. 0·006 mole) was added. The mixture was refluxed on a water bath for one hr, and left overnight at room temperature. The solid precipitated was filtered off, and washed with H_2O. Recrystallization from EtOH gave 1·1 g. (80%) of yellow needles melting at 198–199°. The IR and UV spectra of this material were identical with those of an authentic sample of phenylazocyanoacetanilide[13] (prepared from coupling benzenediazonium chloride to cyanoacetanilide in alcoholic solution of NaOAc.). M.m.p. showed no depression.

When the reaction was repeated with IIh, m-chlorophenylazocyanoacetanilide was obtained in 82% yield, yellow needles, m.p. 229–230° from EtOH. $C_{15}H_{11}ClN_4O$ requires: C, 60·3; H, 3·71; Cl, 11·87; N, 18·7. Found: C, 59·76; H, 4·07; Cl, 11·60; N, 18·52%.

Acknowledgement—The authors are indebted to Prof. Dr. A. Mustafa and Dr. M. Ibrahim for their helpful discussions during the course of this work, and wish to thank Dr. A. Taha who read the manuscript in its original form.

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