

Kinetics and mechanism of dehydrochlorination of *N*-aryl-*C*-ethoxycarbonylformohydrazidoyl chlorides

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The kinetics of triethylamine (TEA) catalyzed dehydrochlorination of a series of *N*-aryl-*C*-ethoxycarbonylformohydrazidoyl chlorides **1a–m** have been studied under pseudo-first-order conditions in 4:1 (v/v) dioxane–water solution at 30°C. For all compounds studied, the kinetics followed the rate law: $k_{obs} = k_2(\text{TEA})$. The values of the overall second-order rate constants for the studied compounds were correlated by the equation: $\log k_2 = 0.533\sigma^- - 0.218$. The results are compatible with a mechanism involving a fast reversible deprotonation step leading to the anion of **1**, followed by rate-determining step involving the loss of the chloride ion from the anion. The reaction constants of these two steps were estimated to be 0.845 and -0.312 , respectively.

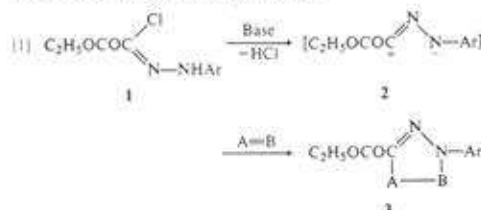
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Opérant à 30°C et dans des solutions 4:1 (v/v) de dioxane/eau, on a étudié les cinétiques du pseudo-premier ordre des réactions de déhydrochloruration catalysées par la triéthylamine (TEA) d'une série (1a–m) de chlorures de *N*-aryl-*C*-éthoxycarbonyl formohydrazidoyles. Dans tous les cas étudiés, l'équation de vitesse de la cinétique est la suivante: $k_{obs} = k_2(\text{TEA})$. Pour tous les composés étudiés, on a établi une corrélation entre les constantes de vitesse globales du deuxième ordre qui est définie par l'équation suivante: $\log k_2 = 0.533\sigma^- - 0.218$. Les résultats sont compatibles avec un mécanisme impliquant une étape de déprotonation réversible rapide conduisant à l'anion de **1** qui serait suivie par une étape déterminante impliquant une perte de l'ion chlorure par l'anion. On a évalué les constantes de vitesses pour ces deux étapes à 0,845 et $-0,312$ respectivement.

[Traduit par la revue]

Introduction

The chemistry of *N*-aryl-*C*-ethoxycarbonylformohydrazidoyl chlorides **1** has been thoroughly investigated during the last decade (1–3). Due to their ease of preparation, such compounds have been extensively used in 1,3-dipolar cycloaddition reactions, where the intermediate nitrilimine **2**, formed *in situ* by the action of a base catalyst, reacts with a dipolarophile $\text{A}=\text{B}$, producing a cycloadduct **3**, eq. (1) (4,5).



However, no attention has yet been given to the mechanism of formation of **2** from **1**. We wish to report here the results of our kinetic study of the triethylamine catalyzed dehydrochlorination of a series of substituted *N*-phenyl-*C*-ethoxycarbonylformohydrazidoyl chlorides **1a–m** in 4:1 (v/v) dioxane–water mixture at 30°C in an attempt to shed some light on the mechanism of this elimination reaction.

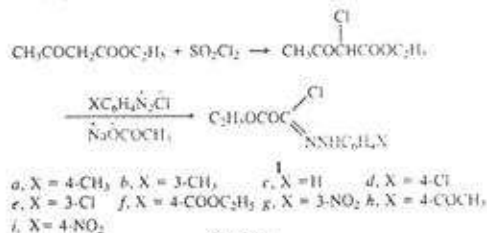
Results and discussion

The sequence followed in the preparation of **1a–m** is outlined in Scheme 1. Some of these hydrazidoyl chlorides were reported and others, namely **1b** and **1e–h**, are new. The structures of these chlorides were evidenced by their elemental and spectral analysis. For example, the infrared spectra of all compounds reveal the presence of characteristic bands near 3280–3220 (hydrazone NH), 1725–1695 (ester, CO), 1665–1600 (C=N), and 1080–1060 (ester C–O–C) cm^{-1} . In their ¹Hmr spectra,

they exhibit a triplet signal at δ 1.3–1.4 (3H, $J = 7$ Hz, $\text{CH}_2\text{CH}_2\text{O}$), a quartet at δ 4.4–4.3 (2H, $J = 7$ Hz, $\text{CH}_2\text{CH}_2\text{O}$), and a singlet near 9.5–8.32 (1H, NH), in addition to the aromatic proton multiplet signal in the region 7.0–8.0 ppm.

On standing for 3 days at 25°C in 80% (v/v) dioxane–water mixture, these hydrazidoyl chlorides were recovered unchanged. However, addition of triethylamine (TEA) to the solution of **1** in this same solvent mixture liberated the chloride ion. Accordingly, the dehydrochlorination kinetics were followed at 30°C in 80% (v/v) dioxane–water mixture in the presence of a large excess, at least 10-fold, of TEA by determining the chloride ion concentration with an ion selective electrode (see Experimental). In all kinetic runs, the ionic strength in the reaction mixture was maintained at 0.10 by the addition of the appropriate volume of 5 *M* sodium nitrate solution in the same solvent system (80:20 dioxane–water, v/v).

The pseudo-first-order rate constant of the dehydrochlorination of **1** was estimated from the plot of $\log(C_\infty - C_t)$ and C_t are the concentrations of chloride ion liberated at infinite time and at time t , respectively. The values of k_{obs} determined for the series of compounds studied are listed in Table 1. The value of k_{obs} was, in each case, a linear function of the triethylamine concentration as shown in Fig. 1, where k_{obs} is plotted vs. amine concentration. The fact that such plots have zero intercepts indicates that the water-assisted (i.e. the uncatalyzed) reaction is negligible.



SCHEME 1

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TABLE I. Rate constants for dehydrochlorination of *N*-aryl-*C*-ethoxycarbonylformohydrazidoyl chlorides (0.002 M) ($C_2H_5OCCClNNHC_6H_4X$) in 80% dioxane at 30°C and $\mu = 0.1$; $Et_3N = 0.02$ M

X	$\log k_{obs}^a$ S ⁻¹	$\log k_2^a$	σ_x^-
H	1.30	-0.191	0.00
<i>p</i> -CH ₃	0.94	-0.327	-0.17
<i>m</i> -CH ₃	1.15	-0.240	-0.07
<i>p</i> -Cl	1.53	-0.115	0.23
<i>m</i> -Cl	1.86	-0.032	0.37
<i>m</i> -NO ₂	2.72	0.134	0.71
<i>p</i> -C ₂ H ₅ OOC	2.83	0.151	0.68
<i>p</i> -CH ₃ OC	3.50	0.243	0.84
<i>p</i> -NO ₂	5.92	0.471	1.28

^a $k_2 = k_{obs}/[(C_2H_5)_3N]$.

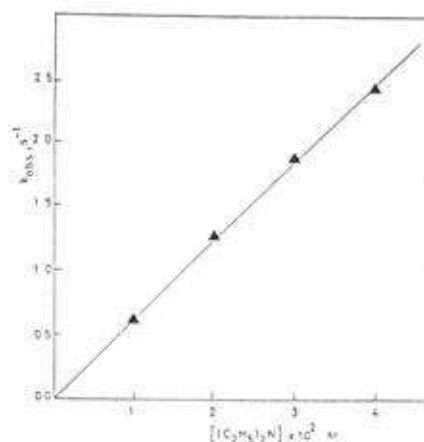


Fig. 1. Plot of the observed pseudo-first-order rate constants against triethylamine concentration for the dehydrochlorination of *N*-phenyl-*C*-ethoxycarbonylhydrazidoyl chloride in 4:1 dioxane-water at 30°C and $\mu = 0.1$.

The plot of the $\log k_2$ (where $k_2 = k_{obs}/[(C_2H_5)_3N]$) vs. the substituent constant σ_x^- is linear (Fig. 2). The equation of the regression line is

$$[\log k_2 = 0.533 \sigma_x^- - 0.218]$$

with correlation coefficient $r = 0.997$ and standard deviation $s = \pm 0.016$.

The most compatible mechanism that can account for the foregoing results is outlined in Scheme 2.

According to this sequence, it could be shown that,

$$[\log \frac{k_2}{k_2^0} = (\rho_1 - \rho_2)\sigma_x^- = \rho \sigma_x^-]$$

That is, the observed ρ value is the algebraic sum of the ρ values describing the separate stages.

For the reaction under study, it is expected that opposing effects will be operative in the 1, 2-dichloro transition state. Thus

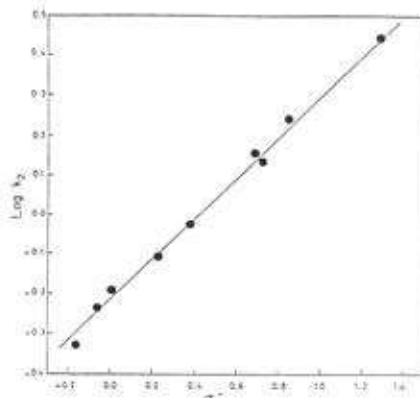


Fig. 2. Hammett plot of $\log k_2$ versus σ^- constant for dehydrochlorination of the hydrazidoyl chlorides, $XC_6H_4NHN(C)COOC_2H_5$, in 4:1 dioxane-water at 30°C and $\mu = 0.1$.

is, ρ_1 and ρ_2 constants will have opposite signs, ρ_1 being negative whereas the value of ρ_2 is positive. The positive sign of the ρ value obtained implies that $\rho_2 < \rho_1$. To confirm this it was necessary to determine the acid dissociation constants K_a of the reaction series studied. However, the very high reactivity shown by these hydrazidoyl chlorides in basic solution made direct measurement of K_a difficult. Therefore, the rate of chloride ion loss from the hydrazidoyl chloride anion (k_2 in Scheme 2) could not be separated from the acidity constant K_a .

To overcome this difficulty, it was thought possible to estimate the value of ρ_2 by determining the pK_a of the hydrazone series 4a-h in 80% (v/v) dioxane-water mixture at 30°C and ionic strength 0.1. The choice of 4 was based on the close similarity of the inductive effects of the CN and Cl groups. For example, the Taft σ constants of these two groups are $\sigma_{CN}^+ = 1.30$ and $\sigma_{Cl}^+ = 1.05$ (6). Also, the values of σ_I of the CN and Cl groups were reported to be 0.60 and 0.47, respectively (6).

The compounds 4a-h required for such study were prepared by coupling ethyl cyanoacetate with diazotized arylamines in ethanol in the presence of sodium acetate. The structures of 4a-n were confirmed by their infrared and ¹Hmr spectra. Thus, the infrared spectra of all compounds reveal the presence of

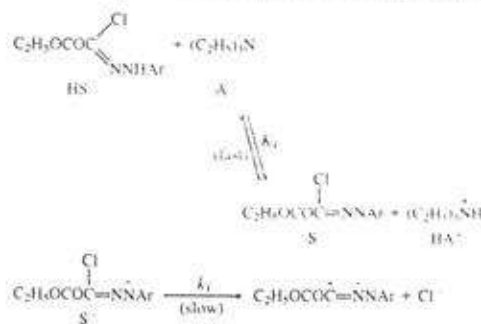
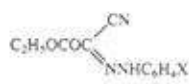


TABLE 2. Acid dissociation constants, pK_a , of ethyl cyanoglyoxalate arylhydrazones ($XC_6H_4NHN=C(CN)COOC_2H_5$) in 80% dioxane-water at 30°C and $\mu = 0.1$

X	acid λ_{max} nm	alkaline λ_{max} nm	pK_a	σ_p^-
<i>m</i> -CH ₃	364	389	8.85	-0.07
H	362	388	8.75	0.00
<i>p</i> -Cl	352	392	8.52	0.23
<i>m</i> -Cl	354	396	8.47	0.37
<i>m</i> -Br	356	395	8.37	0.39
<i>m</i> -NO ₂	340	387	8.09	0.71
<i>p</i> -CH ₃ CO	366	428	8.02	0.84
<i>p</i> -NO ₂	376	472	7.63	1.28

characteristic bands near 3220 (hydrazone NH), 2220 (CN), 1710-1690 (ester CO), 1615 (C=N), and 1250 (ester C—O—C) cm^{-1} . In their ¹Hmr spectra, they exhibit a triplet signal at δ 1.3-1.4 (3H, $J = 7$ Hz, CH_3CH_2O), a quartet at δ 4.4 (2H, $J = 7$ Hz, CH_2CH_2O), and a singlet near 9.6 (1H, NH), in addition to the aromatic proton multiplet in the region 7.0-8.2 ppm.



- 4
 a, X = 3-CH₃; d, X = 3-Cl; g, X = 4-CH₃CO
 b, X = H; e, X = 3-Br; h, X = 4-NO₂
 c, X = 4-Cl; f, X = 3-NO₂

At pH < 8 each of the compounds 4a-h shows an intense $\pi-\pi^*$ absorption band near 360 nm. In alkaline medium, the corresponding anion shows $\pi-\pi^*$ band in the region 380-470 nm (Table 2). Spectra recorded at different pH values show an isobestic point near 380 nm. Typical spectra of an example of the series studied are reproduced in Fig. 3 and the values of λ_{max} of 4a-h in acid (pH < 3) and alkaline (pH > 11) media are summarized in Table 2. The absorbance of a freshly prepared solution measured at the wavelength of the absorption maximum of the anion plotted against pH shows a dependence in the shape of a dissociation curve of a monobasic acid. From the pH-absorbance data, the pK_a values of 4a-h were calculated. The results are summarized in Table 2.

A plot of pK_a vs. the substituent constant σ_p^- was linear (Fig. 4). The equation corresponding to this regression line is

$$\{\log K_a = 0.845 \sigma_p^- - 0.873\}$$

with correction coefficient $r = 0.946$ and standard deviation $s = \pm 0.120$. As shown, the value of the slope (ρ_1) as expected is positive and has a value of 0.845. Since $\rho = \rho_1 - \rho_2$, it follows that $\rho_2 = -0.312$. This ρ_2 value is negative, as expected for a reaction involving the generation of positive charge in the transition state.

These conclusions seem to be in agreement with literature data (7-9). Thus, for the thermolysis of 2,5-diaryltetrazoles 5

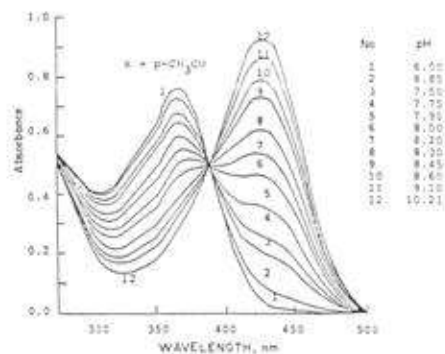
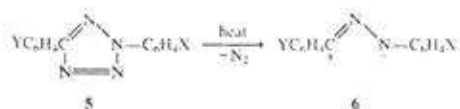


FIG. 3. Absorption spectra of ethyl α -cyanoglyoxalate arylhydrazones, $XC_6H_4NHN=C(CN)COOC_2H_5$, in 4:1 dioxane-water at 30°C and $\mu = 0.1$ at different pH values.

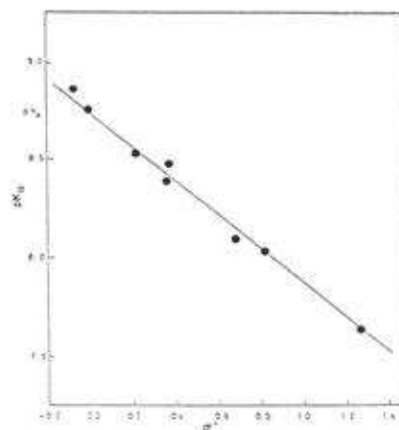


FIG. 4. Hammett plot of acid dissociation constant versus σ_p^- constant for ethyl α -cyanoglyoxalate arylhydrazones, $XC_6H_4NHN=C(CN)COOC_2H_5$, in 4:1 dioxane-water at 30°C and $\mu = 0.1$.

the values of ρ_Y and ρ_X were found to be 1.16 and -0.23, respectively (7). Furthermore, a Hammett ρ value of -0.63 was reported for the formation of the azocarbanion ion 8 from the hydrazidoyl bromides 7 (8,9).



The small value of ρ (-0.312) observed for series 1 undoubtedly results from the compensation of the trivalent anionic nitrogen centre for the positive charge buildup, such that the effect of substitution was reduced.

TABLE 3. *N*-Aryl-*C*-ethoxycarbonylformohydrazidoyl chlorides, $X\text{C}_6\text{H}_4\text{NHN}=\text{C}(\text{Cl})\text{COOC}_2\text{H}_5$

X	Melting point °C (lit.) mp, °C	Yield, %	Molecular formula	Anal., %		
				calcd. C	calcd. H	(found), % N
4-CH ₃	96–97 96–98(10)	80	C ₁₁ H ₁₁ ClN ₂ O ₂			
3-CH ₃	75	69	C ₁₁ H ₁₁ ClN ₂ O ₂	54.88 (54.90)	5.55 (5.43)	11.64 (11.49)
H	80 77–79(10)	70	C ₁₀ H ₁₀ ClN ₂ O ₂			
<i>p</i> -Cl	146 146(10)	83	C ₁₀ H ₉ Cl ₂ N ₂ O ₂	45.98 (46.09)	3.86 (3.72)	10.72 (10.68)
<i>m</i> -Cl	95	70	C ₁₀ H ₉ Cl ₂ N ₂ O ₂	45.98 (46.09)	3.86 (3.72)	10.72 (10.68)
<i>p</i> -COOC ₂ H ₅	149	71	C ₁₃ H ₁₃ ClN ₂ O ₄	52.27 (52.18)	5.06 (4.97)	9.38 (9.37)
<i>m</i> -NO ₂	157	80	C ₁₀ H ₉ ClN ₂ O ₄	44.21 (43.93)	3.71 (3.65)	15.47 (15.60)
<i>p</i> -COCH ₃	157	75	C ₁₂ H ₁₁ ClN ₂ O ₃	53.63 (53.44)	4.88 (4.83)	10.42 (10.39)
<i>p</i> -NO ₂	192 191–193(10)	85	C ₁₀ H ₉ ClN ₂ O ₄	44.21 (44.07)	3.71 (3.68)	15.47 (15.59)

Experimental

All melting points were measured on Bockmonoscop, Karlkolb Scientific Technical Supplies, West Germany, and are uncorrected. The infrared spectra were recorded in potassium bromide on a Zeiss infrared spectrophotometer model IMT16. The electronic absorption spectra were measured on a Pye-Unicam SP8000 spectrophotometer. The proton magnetic resonance spectra were obtained in deuterated chloroform with a Varian EM-390 90-MHz spectrometer. Microanalyses were performed on Perkin Elmer elemental analyzer model 240-B at the microanalytical laboratory of King Abdulaziz University. Ethyl 2-chloroacetate was prepared by chlorination of ethyl acetate with sulfuryl chloride in anhydrous ether as previously described (10).

Preparation of *N*-aryl-*C*-ethoxycarbonylformohydrazidoyl chlorides 1a–i

A solution of ethyl 2-chloroacetate (1.64 g, 0.01 mol) in ethanol (100 mL) was stirred for 15 min with 1.3 g sodium acetate trihydrate. The mixture was then chilled in an ice bath to 0.5°C. While the ester solution was cooling, the desired diazonium salt solution was prepared by diazotizing the appropriate arylamine (0.01 mol) in 6 *M* hydrochloric acid (6 mL) with cold 1 *M* sodium nitrite solution (10 mL) in the usual way. The diazonium salt solution was added to the cold ester solution over a period of 20 min while stirring and keeping the temperature below 5°C. The reaction mixture was then left in a refrigerator for 3 h. The precipitated solid was collected, washed with water, dried, and finally crystallized from ethanol. The compounds prepared, together with their physical constants, are listed in Table 3.

Preparation of ethyl cyanoglyoxalate arylhydrazones 4a–h

These were prepared by coupling ethyl cyanacetate with diazotized anilines following the same procedure described for 1a–i. The crude product, usually colored, was filtered, washed with water, and dried. Crystallization from acetic acid gave the corresponding ethyl cyanoglyoxalate arylhydrazones 4 in 70–85% yield. The compounds prepared are listed, together with their physical constants, in Table 4.

Kinetic studies

The kinetics of dehydrochlorination of the hydrazidoyl chlorides 1a–i were studied in dioxane–water (4:1, v/v) at 30°C (±0.1°C) and ionic strength $\mu = 0.1$ (NaNO₃). The rates of dehydrochlorination were followed by recording the increase in the chloride ion concentra-

An Orion research microprocessor ion analyzer model 901 (Orion Research Incorporated, Mass., U.S.A.) with double junction reference electrode (90-02) and chloride ion electrode (94-17B) was used to record the chloride ion liberated during the dehydrochlorination of 1.

Stock solutions of hydrazidoyl chlorides 1a–i, usually about 10⁻² *M*, were prepared in 20% aqueous dioxane. A stock solution of triethylamine (1 *M*) was also prepared in the same solvent system. Appropriate concentrations of the amine and the hydrazidoyl chloride were prepared by dilution of the stock solutions and thermostated at 30°C in a constant temperature water bath.

Reactions were followed to 80% completion, with at least 15 readings taken. All kinetic runs were carried out in a double-wall cell, through which water at 30°C was circulated by means of a constant temperature MgW Louda circulating water pump.

In a typical kinetic run, the hydrazidoyl chloride solution (usually 2 × 10⁻³ *M*) was transferred to the cell. Then the appropriate volume of sodium nitrate stock solution (1.0 *M*) was added so that the ionic strength in the test solution was 0.1. The mixture was stirred with a magnetic stirrer. Then the chloride ion and the reference electrodes were introduced. The run was started by injecting the amine solution by means of a syringe and the stop watch was started at the moment of injection. The concentration of the chloride ion liberated was recorded at given intervals. In all kinetic runs, at least a tenfold excess of amine over the hydrazidoyl chloride was used in order to maintain pseudo-first-order kinetics. Duplicate or triplicate runs were performed for each concentration.

Good first-order plots of log (C_∞ - C_t) against time were obtained. The observed pseudo-first-order rate constants were calculated from the slopes of the straight lines obtained by the method of least squares (Table 1). The average deviation from the mean value of the rate constant in duplicate or triplicate experiments was ±3% or less.

Product analysis

A mixture of *N*-*p*-nitrophenyl-*C*-ethoxycarbonylformohydrazidoyl chloride 1i (0.71 g, 0.005 mol), triethylamine (0.71 mL, 0.005 mol), and sodium nitrate solution (5 *M*, 2 mL) in 100 mL 80% dioxane–water mixture was kept at the kinetic temperature 30°C until the chloride 1i disappeared, as evidenced by tlc (thin-layer chromatographic) analysis. The solvent in the mixture was distilled under reduced pressure and the residue was washed with water, dried, and subjected to preparative tlc separation using silica gel as adsorbent and the solvent system:

TABLE 4. Ethyl cyanoglyoxalate arylhydrazones, $XC_6H_4NHN=C(CN)COOC_2H_5$

X	Melting point °C (lit.) mp, °C	Yield, %	Molecular formula	Anal, %		
				calcd	(found), %	
				C	H	N
H	104 106(14)	75	$C_{11}H_{11}N_3O_2$	60.08 (59.87)	5.10 (4.97)	19.34 (18.97)
m-CH ₃	92	80	$C_{12}H_{13}N_3O_2$	62.33 (62.21)	5.66 (5.51)	18.16 (17.87)
m-Cl	145-146	69	$C_{11}H_{10}ClN_3O_2$	52.49 (51.99)	4.00 (3.84)	16.69 (16.63)
p-Cl	151-152	78	$C_{11}H_{10}ClN_3O_2$	52.49 (52.19)	4.00 (3.92)	16.69 (16.49)
m-Br	155-156	68	$C_{11}H_{10}BrN_3O_2$	44.61 (44.38)	3.40 (3.39)	14.18 (14.07)
p-CH ₃ CO	159	75	$C_{13}H_{13}N_3O_3$	60.22 (60.04)	5.05 (4.83)	16.20 (16.07)
m-NO ₂	135	85	$C_{11}H_{10}N_4O_4$	50.38 (49.98)	3.84 (3.76)	21.36 (20.98)
p-NO ₂	193-194	83	$C_{11}H_{10}N_4O_4$	50.38 (50.58)	3.84 (3.74)	21.36 (21.17)

Two products were separated and identified as 1,4-bis-*p*-nitrophenyl-3,6-dithoxycarbonyl-1,4-dihydro-1,2,4,5-tetrazine **8** and ethyl oxalate mono-*p*-nitrophenylhydrazide **9**, by comparison with authentic samples prepared by literature methods (11).

The tetrazine derivative **8** was obtained in 35% yield, mp 237°C (AcOH) (lit. (11) mp 236-237.5°C); ir (KBr) $\bar{\nu}$: 1746 (ester CO), 1580 (C=N), 1520, 1330 (NO₂), 1290 (C=N), 1175 (C—O—C) cm^{-1} ; ¹Hmr (CDCl₃) δ : 1.2 (t, 6H, $J = 7$ Hz, 2CH₃—CH₂), 4.3 (q, 4H, $J = 7$ Hz, 2CH₂—CH₂O), 7.3 (d, 2H, $J = 9$ Hz, 2 *p*-NO₂—ArH), 8.3 (d, 2H, $J = 9$ Hz, 2 *p*-NO₂—ArH) ppm.

The hydrazide **9** was obtained in 60% yield, mp 170°C (ethanol); ir (KBr) $\bar{\nu}$: 3320 (NH), 1738 (ester CO), 1690 (amide CO), 1505, 1320 (NO₂) cm^{-1} ; ¹Hmr (CDCl₃) δ : 1.43 (t, 3H, $J = 7$ Hz, CH₃—CH₂O), 4.52 (q, 2H, $J = 7$ Hz, CH₂—CH₂O), 7.06 (d, 2H, $J = 9$ Hz, *p*-NO₂—ArH), 8.26 (d, 2H, $J = 9$ Hz, *p*-NO₂—ArH), 8.7 (s, 1H, CONH), 10.90 (s, 1H, HNC₆H₄—NO₂-*p*) ppm. Anal. calcd for C₁₀H₁₁N₃O₅: C 47.43, H 4.38, N 16.59; found: C 47.10, H 4.13, N 16.30%.

Determination of acid dissociation constants of 4a-h

The acid dissociation constants of the compounds 4a-h were determined spectrophotometrically in 80% dioxane-water at 30 ± 0.1°C and an ionic strength of 0.1.

A Tacussel digital pH meter PHN 78 fitted with a glass electrode type C-285-725 and a reference electrode type TB/HS 286-506 was employed for the determination of pH. The instrument was accurate to ±0.01 pH unit. It was calibrated using two standard Beckman buffer solutions of pH 4.01 and 7.00. The pH meter readings (*B*) recorded in dioxane-water solutions were converted to hydrogen ion concentration [H⁺] by means of the widely used relation of van Uitert and Hass (12), namely:

$$-\log [H^+] = B + \log U_{11}$$

where $\log U_{11}$ is the correction factor for the solvent composition and

ionic strength used, for which *B* is read. For this purpose, readings were made on a series of solutions containing known amounts of hydrochloric acid and sodium chloride, such that the ionic strength was equal to 0.1 in 80% dioxane-water at 30.0 ± 0.1°C. The value of $\log U_{11}$ was found to be -0.55.

The experimental procedure in the determination of *pK_a* constants and their calculations from the absorbance-pH data were as described earlier (13). The *pK_a* values obtained were reproducible to within ±0.01 *pK_a* unit. The results are summarized in Table 2.

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