Role of Neighbouring Imidazole Groups in the Solvolysis of Hydrazonyl Chlorides

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Cyclization of the *N*-imidazolidin-2-ylidenehydrazonyl chlorides (7; R = H) to the 6,7-dihydro-3-aryl-5*H*-imidazo[2,1-*c*]-*s*-triazoles (12) in 4:1 dioxan–water at 25° proceeds *via* rate-determining ionization (azocarbonium ion formation) over the pH range 3—11. The neighbouring group participates after the rate-determining step. The dimethylated model hydrazonyl chlorides (7; R = Me) which cannot cyclize to (12) show similar kinetic behaviour; in this case water reacts with the azocarbonium ion intermediate to give hydrazides (11; R = Me). Evidence is also presented that (7; R = H) exists as the 2,3-diazabuta-1,3-diene tautomer (7) rather than as the hydrazone (4).

IMIDAZOLE catalysis of acyl transfer in non-enzymatic reactions has been well documented [1,2] and in several cases reactive acylimidazole intermediates have been isolated under appropriate conditions.[3] Such nucleophile catalysis by imidazole occurs only in those cases where the acyl function carries a good leaving group, for example, *p*-nitrophenoxide or acetate. The incorporation of the imidazole and acyl groups in adjacent positions in an organic skeleton brings about a large rate acceleration (relative to the bimolecular case), the origin of which continues to be controversial.[4] Under these conditions, intramolecular nucleophilic participation by imidazole may be favoured to such an extent that breakdown of the acylimidazole intermediate becomes rate determining.[5]

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[1] T. C. Bruice and S. Benkovic, 'Bioorganic Mechanisms,' Benjamin, New York, vol. 1, 1966, p. 125.

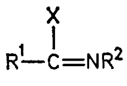
[2] W. P. Jencks, 'Catalysis in Chemistry and Enzymology,' McGraw-Hill, New York, 1969, p. 67.

[3] D. G. Oakenfull, K. Salvesen, and W. P. Jencks, *J. Amer. Chem. Soc.*, 1971, **93**, 188; D. A. Oakenfull and W. P. Jencks, *ibid.*, p. 178; E. Guibe-Jampel, M. Wakselman, and M. Vilkas, *Bull. Soc. chim. France*, 1971, 1308.

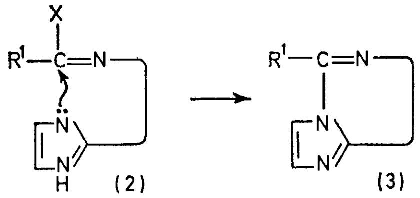
[4] B. Capon, *J. Chem. Soc.* (*B*), 1971, 1207.

[5] T. C. Bruice, *J. Amer. Chem. Soc.*, 1959, **81**, 5444.

Although less well studied than the acyl halides, data for the nitrogen analogues, imidoyl (1; R^1, R^2 = alkyl or aryl groups) and hydrazonyl (1; R^1 = alkyl or aryl; R^2 = NHAr or NRAr) halides, continue to accumulate.



(1)



(2) (3)

In most cases, because of the good leaving groups (X = Cl or Br) involved, and the fact that extra stabilization of a potential carbonium ion can be gained by delocalization of charge onto the group attached to the doubly bonded nitrogen, an ionization mechanism tends to dominate in aqueous solvent mixtures[6,7] (although the mechanism is less clear in, say, benzene where bimolecular reaction of imidoyl halides with amines can occur[8]). In addition, a ready base-catalysed elimination leading to 1,3-dipolar ion formation from hydrazonyl halides (1; R^2 = NHAr) is a possible competing mechanism.[9]

Nucleophilic groups attached to carbon and appropriately placed (*e.g.* R^1 = *o*-$NO_2C_6H_4$) may facilitate substantial displacement of the leaving group X^-.[10] It was concluded, however, from kinetic studies that the observed rate enhancements for such *ortho*-substituents were due to 'internal solvation' of the forming carbonium ion rather than nucleophilic (S_N2) displacement of the leaving group. Examples of halides (1) in which the group attached to nitrogen (R^2) carries a nucleophilic function are far more extensive;[11,12] in most cases, these can be smoothly and quantitatively cyclized under mild conditions (*e.g.* in aqueous solvent mixtures at room temperatures or using base catalysis), providing an important synthetic route to fused triazolyl and oxadiazolyl systems.

We have recently synthesised a series of *N*-imidazolidin-2-ylidene)hydrazonyl chlorides [of type (2)] and shown that they undergo ready cyclization to the corresponding fused imidazotriazoles [of type (3)].[13] We now report a study of the role of the imidazo-group in promoting cyclization.

RESULTS AND DISCUSSION

The rates of solvolysis of the two series of hydrazonyl chlorides (7; R = Me and R = H) were investigated in 4 : 1 dioxan–water at 25°. Under these conditions the hydrolytic products formed in the two series are different. The sole product from the unmethylated compound (7; R = H) is the fused imidazotriazole (12), none of the corresponding hydrazide (11; R = H) which would be formed by water attack being detected (by t.l.c.).[13] Conversely, the hydrazide (11; R = Me) alone is formed from (7; R = Me) under the same conditions (at high dilution *). Whether this product difference is also reflected in the rates of reaction of the two compounds [*e.g.* by participation of the neighbouring heterocycle in the expulsion of Cl^- from (7; R = H)] was probed.

TABLE 1

Rate constants for the hydrolysis of *N*-1,3-dimethylimidazolidin-2-ylidene-*p*-nitrobenzhydrazonyl chloride (7; R = Me, Ar = *p*-$NO_2C_6H_4$ at 25° in 80% dioxan as a function of pH

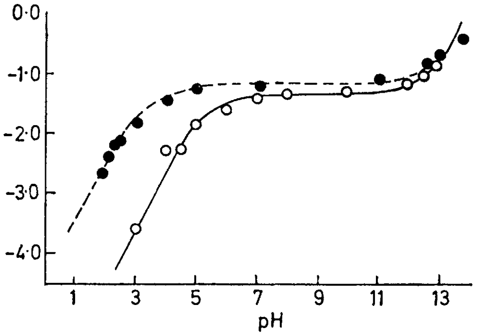
pH	1·9	2·1	2·3	2·5	3·0	4·0	5·0
$10^3 k_{obs}/s^{-1}$	2·08	3·40	5·28	6·86	12·8	38·3	47·3
pH	7·0	11·0	12·5	13·0	13·7		
$10^3 k_{obs}/s^{-1}$	59·0	71·2	148·0	201	351		

TABLE 2

Rate constants for the hydrolysis of *N*-imidazolidin-2-ylidene-*p*-nitrobenzhydrazonyl chloride (7; R = H, Ar = *p*-$NO_2C_6H_4$) in 80% dioxan at 25° as a function of pH

pH	3·0	4·0	4·5	5·0	6·0	7·0
$10^3 k_{obs}/s^{-1}$	0·258	4·43	4·5	13·4	22·4	36·3
pH	8·0	10·0	12·0	12·5	13·0	
$10^3 k_{obs}/s^{-1}$	44·7	50·8	68·5	96·0	169·0	

The rates of solvolysis of (7; R = H, Ar = *p*-$NO_2C_6H_4$) and (7; R = Me, Ar = *p*-$NO_2C_6H_4$) as a function of pH are summarised in Tables 1 and 2. In spite of the different solvolysis products of the two hydrazonyl chlorides, their kinetic behaviour is remarkably similar. In both cases, reaction is slow in



Plot of log k_{obs} *vs.* pH for the solvolysis of the hydrazonyl chlorides (7; Ar = *p*-$NO_2C_6H_4$, R = H) (full line) and (7; R = Me) (broken line) in 4 : 1 dioxan–water at 25°. The curves have been drawn using equation (1) with the values of the constants quoted in the text

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* In much more concentrated solution (*ca.* 0·5M), 2,5-diaryl-1,2,4,5-tetrazines are also formed;[13] this (bimolecular) reaction is suppressed in the dilute solution (<10^{-4}M) used to study the kinetics.

[6] A. F. Hegarty, M. P. Cashman, and F. L. Scott, *J. Chem. Soc.* (*B*), 1971, 1607.

[7] I. Ugi, F. Beck, and U. Fetzer, *Ber.*, 1962, **95**, 126.

[8] Z. Rappoport and R. Ta-Shma, *Tetrahedron Letters*, 1971, 3813.

[9] A. F. Hegarty, M. P. Cashman, and F. L. Scott, *J.C.S. Perkin II*, 1972, 44.

[10] A. F. Hegarty, M. Cashman, and F. L. Scott, *J. Chem. Soc.* (*B*), 1971, 1879.

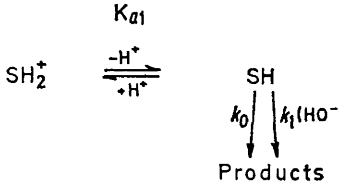
[11] See, for example, (*a*) R. N. Butler and F. L. Scott, *Chem. and Ind.*, 1970, 1261; (*b*) F. L. Scott, T. M. Lambe, and R. N. Butler, *Tetrahedron Letters*, 1971, 2669; (*c*) F. L. Scott, D. A. Cronin, and J. K. O'Halloran, *J. Chem. Soc.* (*C*), 1971, 2769.

[12] A. Pollak and M. Tisler, *Tetrahedron*, 1966, **22**, 2073; L. M. Shegal and I. L. Shegal, *Khim. geterotsikl. Soedinenii*, 1970, 1330.

[13] F. L. Scott, J. K. O'Halloran, J. O'Driscoll, and A. F. Hegarty, *J.C.S. Perkin I*, 1972, 2224.

acidic solution but rises to a ' plateau ' where the rate is essentially independent of pH.

The extent of the plateau (see Figure) is greater for the methylated compound (7; Ar = p-$NO_2C_6H_4$, R = Me), extending from pH 4—11, whereas for the unmethylated analogue it extends from pH 6—11. Both p-nitrophenyl substrates (7; Ar = p-$NO_2C_6H_4$) reacted at about the same rates in this latter region. In more basic solution (pH > 11) the rates of solvolysis of both compounds again increase.



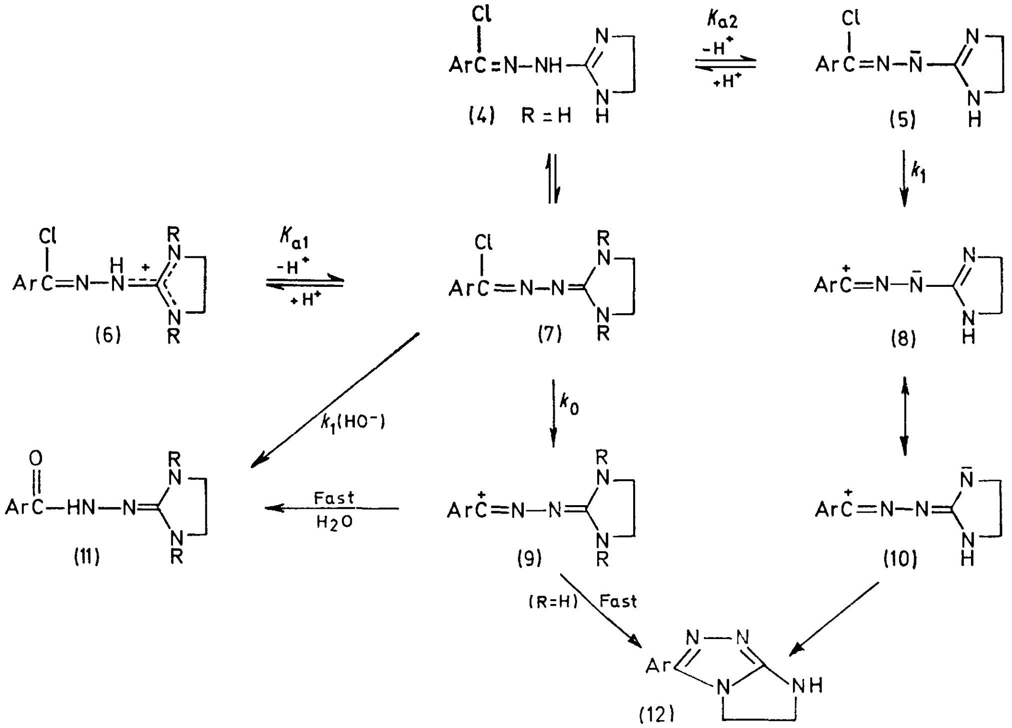
SCHEME 1

This kinetic behaviour can be described in terms of the empirical Scheme 1, where SH is the substrate and K_{a_1} and K_{a_2} are the acidity constants of SH and its conjugate acid SH_2^+. From Scheme 1 the empirical equation (1)

$$k_{obs} = k_0 \cdot \frac{K_{a_1}}{a_{H^+}K_{a_1}} + k_1[HO^-] \qquad (1)$$

may be obtained which relates the observed rate constants (k_{obs}) to the individual rate constants for unimolecular reaction of SH (k_0) and reaction of SH with hydroxide ion (k_1) to give products. The protonated substrate, SH_2^+, is assumed to be unreactive. Use of equation (1) to correlate the observed data in Tables 1 and 2 gave the following constants for (7; R = H, Ar = p-$NO_2C_6H_4$): $k_0 = 5 \times 10^{-2}$ s^{-1}, $K_{a_1} = 4{\cdot}5 \times 10^{-6}$ and $k_1 = 1{\cdot}6$ l mol^{-1} s^{-1}; and for (7; R = Me, Ar = p-$NO_2C_6H_4$): $k_0 = 6{\cdot}3 \times 10^{-2}$ s^{-1}, $K_{a_1} = 6{\cdot}4 \times 10^{-4}$ and $k_1 = 1{\cdot}6$ l mol^{-1} s^{-1}. The curves in the Figure are theoretical and have been drawn using these values. The fit to the observed experimental data points is reasonable, despite the fact that in an aqueous organic solvent mixture the measured pH values do not exactly represent hydrogen ion concentrations (see Experimental section).

A mechanism consistent with this kinetic scheme is presented in Scheme 2. The reactive species over almost the entire pH range is the neutral hydrazonyl chloride (7). This may also exist in a tautomeric form (4) when R = H, but is locked in the diazabutadiene form (7) in the methylated series of compounds (R = Me). Unimolecular C–Cl bond fission [from either or both (4) and (7)] gives the azocarbonium ion intermediate (9). Rapid cyclization of the carbonium ion to the imadazotriazole (12) (when R = H) or reaction with water to form the hydrazide (11) (when R = Me) gives products consistent the observed results.



SCHEME 2

The following observations also support the intermediacy of the azocarbonium ion (7) in this pH region. The effect of variation of the nature of substituents in the aryl ring on the rate of solvolysis of the halides (7; R = Me) is summarised in Table 3. All the measurements were made in the ' plateau ' region (see Figure) and in the presence of a constant concentration of an inert salt. Clearly the rate of formation of (11) decreases with increasing electron-withdrawal in the aromatic group. Correlation of these data with the

Hammett equation, using ordinary σ values,[14] gave a ρ value of $-1{\cdot}31$ ($r = 0{\cdot}999$). The rates of cyclization of the unmethylated analogues (7; R = H) responded similarly to substituent variation in the pH-independent plateau region (Table 3). In this case a Hammett plot of the data gave a ρ value of $-1{\cdot}70$ ($r = 0{\cdot}993$).

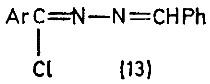
TABLE 3

Rate constants for the hydrolysis of *N*-1,3-dimethylimidazolidin-2-ylidenearylhydrazonyl chlorides (7; R = Me) and *N*-imidazolidin-2-ylidenearylhydrazonyl chlorides (7; R = H) at 25° in 4 : 1 dioxan–water

	$10^2k_{obs}/s^{-1}$	
Ar	(7; R = Me) [a]	(7; R = H) [b]
p-$NO_2C_6H_4$	0·79	1·92
m-$NO_2C_6H_4$	0·96	2·56
m-ClC_6H_4	2·60	7·20
p-BrC_6H_4	4·07	13·3
p-ClC_6H_4	4·16	14·7

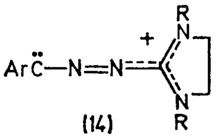
[a] At pH 4. [b] Measured in the plateau region in presence of 0·025M-sodium acetate as buffer (pH = 7·7). Previously reported (J. K. O'Halloran and F. L. Scott, *Tetrahedron Letters*, 1970, 4767) rate constants for these and related chlorides were measured in unbuffered solution and are therefore uncertain; the values reported in Table 3 are therefore to be taken as definitive.

These values are close to that recently reported ($-1{\cdot}7$) for the solvolysis of the related chlorodiazabutadienes (13) in 60% dioxan at 50°, for which a similar intermediate was suggested.[15] This most likely is a reflection of the ability of the carbonium ion (9) in both systems to delocalise part of the charge along the system away from the aromatic group [using structures such as (14)]. The contribution of structures such as (14) must have some importance since, even in absolute terms, (7) is far more reactive than (13) [k_0 for (13; Ar = Ph) is $1{\cdot}36 \times 10^{-2}\ s^{-1}$ in 60% dioxan at 50° whereas k_0 for (7; R = H, Ar = Ph) at 25° in 80% dioxan can be calculated as *ca.* $6 \times 10^{-2}\ s^{-1}$]. Values of ρ indicative of carbonium ion formation of this magnitude have also been reported for other aza-acyl systems.[6,9,11c,16]



$ArC(Cl){=}N{-}N{=}CHPh$

(13)



(14)

The pH-independent reaction, as expected for an ionisation, was sensitive to the presence of ions in solution. The effect of an added salt (sodium nitrate) is to increase remarkably the rate of solvolysis (Table 3); the rate enhancement is unexpectedly large even for an ionization. Even more dramatic is the large rate decrease brought about by the presence of a salt containing a common ion (Cl^-). In this case large rate decreases are observed (Table 4) even though these salts would also tend to increase the rate by a primary salt effect. This is strong evidence that the carbonium ion species is sufficiently long lived to discriminate between the various nucleophiles (water, chloride ion, or the neighbouring imidazolidine ring) reacting with the most powerful nucleophile rather than with the species present in excess.[17]

In acidic solution the overall rate of formation of (11) and (12) decreased due to the presence of decreasing amounts of (7) [which is converted to the unreactive protonated form (6)] in solution. That this is the correct interpretation of the observed rate constants is supported by the fact that there is a distinct difference in the u.v. spectrum of (7) in acidic and neutral solutions [most noticeably, the free hydrazonyl halides (7) have an absorption at *ca.* 320 nm, which is absent in acidic solution]. This difference was used to measure a spectrophotometric pK_a of (7; R = Me; Ar = *p*-$NO_2C_6H_4$). The value obtained (pK_{a1} *ca.* 3·0) is approximately the same as the pK_{a1} value required to fit the kinetic data (see above). The measurement of the pK_a of the unmethylated compound (7; R = H, Ar = *p*-$NO_2C_6H_4$) was more difficult (extrapolations of optical density to 0% reacted being more uncertain), but in this case also the value (pK_{a_1} *ca.* 4·5) was of the same order of magnitude as the kinetic pK_{a_1} for this compound.

TABLE 4

Rate constants for the hydrolysis of *N*-1,3-dimethylimidazolidin-2-ylidene)-*m*-nitrobenzhydrazonyl chloride (7; R = Me, Ar = *m*-$NO_2C_6H_4$ at 25° in 4 : 1 dioxan–water in presence of various added electrolytes

$[NaNO_3]$/M	[KCl]/M	$10^3k/s^{-1}$
		9·59
0·015		32·0
0·030		99·0
0·060		287
0·020	0·010	3·90
0·01	0·020	1·42
	0·030	0·79

In basic solution (or in favourable cases even at pH 3) hydrazonyl halides which possess an amino-hydrogen atom have a ready alternative mechanism of reaction, *via* a 1,3-dipolar ion intermediate [such as (8)].[9] This pathway normally dominates in all the hydrazonyl halides studied at pH 7. Such a mechanism involving 1,3-dipolar ion formation is possible only in the case when R = H (Scheme 2). Loss of chloride ion from the anion (5) would be very rapid to give the 1,3-dipolar ion (8) which can also be written as a 1,5-dipolar ion (10). A ready 1,5-dipolar cyclization then gives the product (12). Such a mechanism would give a kinetic equation indistinguishable from equation (1) when $a_H \gg K_{a_1}$.

Surprisingly, the unmethylated compound (7; R = H, Ar = *p*-$NO_2C_6H_4$) which was studied in detail does not appear to react appreciably by this mechanism. Thus, like the *NN'*-dimethylated analogue it does not show a base-catalysed process until pH *ca.* 13. Moreover both series of compounds show the incursion of base catalysis at approximately the same region (see Figure). Since (7; R = Me) cannot form a 1,3-dipolar ion (except by *N*-demethylation), it seems likely that the observed

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[14] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 1958, **23**, 420.

[15] P. A. Cashell, A. F. Hegarty, and F. L. Scott, *Tetrahedron Letters*, 1971, 4767.

[16] J. B. Aylward and F. L. Scott, *J. Chem. Soc.* (*B*), 1969, 1080.

[17] J. Hine, ' Physical Organic Chemistry, McGraw-Hill, ch. 6.

base-catalysed processes in both cases is the same, *i.e.* direct HO^- attack on the substrates.*

The apparent complete suppression of the 1,3-dipolar ion pathway for (7; R = H) might indicate that the tautomeric form present is the diazabutadiene (7) rather than the alternate hydrazone (4). The existence of (7; R = H) in the same tautomeric form as (7; R = Me) is forced to adopt would be consistent with the similarity in kinetic behaviour of the two systems over the entire pH range. This hypothesis is supported by the fact that the u.v. spectra of both (7; R = H and R = Me) are almost identical in neutral solution (with $\lambda_{max.}$ at 325 and 320 nm respectively for Ar = p-$NO_2C_6H_4$). The spectra of (6; R = H and R = Me) are also similar. Further supporting evidence for the existence of (7; R = H) in the diazabutadiene form is the fact that bromination in glacial acetic acid results in the formation of a perbromide, a reaction characteristic of 2,3-diazabutadienes [18] rather than a hydrazonyl bromide (as would be expected from the bromination of an aldehyde hydrazone).[19]

It thus appears that (7; R = H) [which exists as (7) rather than as the tautomer (4)] and (7; R = Me) are analogous systems in which the major reaction pathway is the unimolecular ionization of the neutral species. Protonation of the neighbouring heterocycle suppresses this reaction (due to the electron-withdrawing ability of the protonated group). As shown above the cyclic product (12) is formed from (7; R = H). We conclude therefore that the neighbouring imidazolidin-2-ylidene ring participates efficiently as a neighbouring group *after* the rate-determining step and does not aid the expulsion of chloride ion.

The formation of the cyclic product (12) from the azocarbonium ion (9; R = H) represents successful competition by the neighbouring ring over the other nucleophiles (*e.g.* water) present in solution. It should be possible therefore under appropriate conditions, *i.e.* in the presence of stronger nucleophiles than water, to trap the azocarbonium ion by an external nucleophile. Thus when (7; R = H, Ar = p-ClC_6H_4) was solvolysed in neat aniline the aniline derivative, phenyl-p-chlorobenzamide imazolidin-2-ylidenehydrazone was isolated in good yield.[13] The intermolecular process can also be enhanced in aqueous solvent mixtures. The solvolysis of (7; R = H, Ar = p-ClC_6H_4) in 1 : 1 dioxan–water containing 0·1M-sulphuric acid gave the corresponding hydrazide (11; R = H, Ar = p-ClC_6H_4) in 78% yield. Under these conditions the neighbouring heterocyclic ring is largely protonated (thus reducing its nucleophilicity) allowing water (which is also present in larger relative concentration) to successfully compete for the intermediate (9).

EXPERIMENTAL

Substrates.—Most of the hydrazonyl chlorides were available from a previous study,[13] which also describes the solvolytic conversion to hydrazides and imidazotriazoles.

N-*Imidazolidin*-2-*ylidene*-m-*nitrobenzhydrazonyl Chloride.*—*N*-Tetrazol-5-yl-*m*-nitrobenzylidenehydrazine was chlorinated in 90% acetic acid to give the corresponding 4-m-*nitrophenyl*-1,1,4-*trichloro*-2,3-*diaza*-2,3-*diene* (Found: C, 34·3; H, 1·6; N, 16·3. $C_8H_4Cl_3N_3O$ requires C, 34·3; H, 1·5; N, 16·6%). This was treated in benzene with ethylene diamine (as previously described [13]) to give the hydrazonyl chloride (7; R = H, Ar = m-$NO_2C_6H_4$), which was solvolysed in 4 : 1 dioxan–water at room temperature to give 6,7-*dihydro*-3-m-*nitrophenyl*-5H-*imidazo*[2,1-c]-s-*triazole hydrochloride hydrate*, m.p. 225° (Found: C, 41·8; H, 3·7; N, 23·6. $C_{10}H_{12}ClNO$ requires C, 41·7; H, 4·2; N, 24·5%). The spectral characteristics for these compounds were similar to those previously reported [13] for the analogous compounds.

N-*Imidazolidin*-2-*ylidene*-p-*chlorobenzhydrazide.*— *N*-Imidazolidin-2-ylidene-p-chlorobenzhydrazonyl chloride (7; R = H, Ar = p-ClC_6H_4) (0·26 g) was added to dioxan (10 ml) containing sulphuric acid (0·20 g). The white salt which precipitated was dissolved by the addition of water (10 ml) and the solution was refluxed for 5 h. The solvent was reduced in volume *in vacuo* to 10 ml and aqueous sodium carbonate solution was added until precipitation was complete. Recrystallisation from diethyl ether gave the hydrazide (11; R = H, Ar = p-ClC_6H_4) (0·16 g, 78%), which was identical (m.p., mixed m.p., and i.r. spectrum) with an authentic sample prepared from p-chlorobenzoyl chloride and 2-hydrazino-4,5-dihydroimidazole.[13] In a control experiment it was shown that the cyclic material (12; Ar = p-ClC_6H_4) was stable under these reaction conditions.

Kinetic Measurements.—The solvent used in all cases was 4 : 1 dioxan–water (v/v) and measurements were made at 25°. Dioxan was BDH AnalaR grade (used directly) while the water was deionized and distilled from alkaline permanganate. In all cases the rates of hydrolysis of the hydrazonyl chlorides (7) were measured spectrophotometrically at suitable wavelengths in the u.v. region. A Unicam SP 800 or SP 1800 u.v. spectrometer was used for those solutions which were buffered (*i.e.* in the high or low pH range or in the presence of acetate buffers). For unbuffered solutions a pH-stat mounted in the cell compartment of a Cary 14 u.v. spectrometer (which has been previously described [9]) was used. The cell used was rapidly stirred allowing good mixing and the measurement of reactions with half-lives as small as 2—3 s. In all cases the ' pH values ' quoted are the indicated pH values of the solutions using a glass electrode (Metrohm type EA 125U) which had previously been standardised in aqueous buffers. A Radiometer pH meter model PHM 26 was used both with the pH-stat and for all pH measurements. Before taking measurements in 4 : 1 dioxan–water the electrode was steeped in that solution for 30 min.

The substrates were normally made up in concentrated solution (*ca.* 10^{-2}M) in acetonitrile and reaction was initiated by addition of one drop of this stock solution to 4 : 1 dioxan–water in the cell. In the case of the more insoluble compounds *i.e.* (7; R = H; Ar = p-$NO_2C_6H_4$ and m-$NO_2C_6H_4$) up to 20% dimethyl sulphoxide was added to the acetonitrile to obtain a stock solution of the desired concentration. All the rate constants reported were of good pseudo-first-order and were determined either graphically or using a special least squares programme for an Olivetti Programma 101 computer. Product analyses were carried out in 4 : 1 dioxan–water in necessarily more concentrated

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* Consistent with this interpretation, the hydrazide (11; R = H, Ar = p-$NO_2{\cdot}C_6H_4$) is formed (80%) together with (12; Ar = p-$NO_2{\cdot}C_6H_4$) at pH 13·5.

[18] F. L. Scott and P. A. Cashell, *J. Chem. Soc.* (*C*), 1970, 2674.

[19] A. F. Hegarty and F. L. Scott, *J. Chem. Soc.* (*B*), 1966, 677.

solutions.[13] On completion of hydrolysis of (7) the resulting u.v. spectra were the same as synthetic solutions of the corresponding hydrazides (11; R = Me) [from (7; R = Me)] or the imidazotriazoles (12) [from (7; R = H)] under the same conditions.

The pK_a determinations were carried out in the same dioxan–water solutions, by following the appearance of the absorption band at 320 nm. Since the halides (7) were very reactive at high pH, an optical density *vs.* time curve was determined at each pH and extrapolated back to zero time to give the optical density of unchanged (7). The pK_a of (7) was then determined by comparison of the resultant optical density *vs.* pH curves with theoretical pH-titration curves.

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