Mononuclear Heterocyclic Rearrangements. Part 14.[1] Rearrangement of Some *Z*-Arylhydrazones of 3-Benzoyl-5-phenylisoxazole to 2-Aryl-4-phenacyl-1,2,3-triazoles in Dioxane–Water

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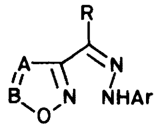
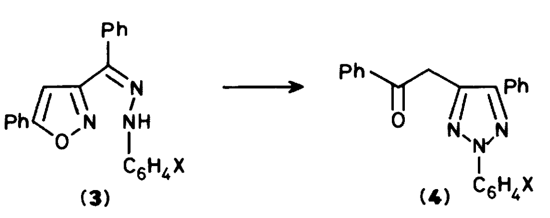
The kinetics of the title reaction have been measured at various pS^+ values. The results show the occurrence of general base catalysis and furnish information about substituent effects on the studied reaction. A reaction mechanism analogous to that proposed for the rearrangement of the arylhydrazones of 3-benzoyl-5-phenyl-1,2,4-oxadiazole is suggested. The reactivity of isoxazole derivatives is much lower than that of 1,2,4-oxadiazole derivatives.

In recent years we have thoroughly investigated the mechanism of mononuclear heterocyclic rearrangements[2] using as model compounds the *Z*-arylhydrazones of some 3-benzoyl-5-substituted 1,2,4-oxadiazoles (**1**).[3] Much information has been gained from our results regarding the structure of the transition state of such a reaction. In addition qualitative results from studies of the influence of structure on the reactivity of the starting heterocycle towards mononuclear heterocyclic rearrangement have indicated[4a] that for a given side chain at C-3 the rate of rearrangement decreases on going from the 1,2,4-oxadiazole (**1**) to the 1,2,5-oxadiazole (**2**),[2b] through the isoxazole (**3**).[4]



(**1**) A = N; B = CAr or CAlk; R = Ph
(**2**) A = CMe; B = N; R = Me
(**3**) A = CH; B = CPh; R = Ph

In order to obtain quantitative data on the ability of isoxazole derivatives to rearrange, we have studied the behaviour of some *Z*-arylhydrazones (**3a**—**c**) of 3-benzoyl-5-phenylisoxazole in dioxane–water, in the presence of borate buffers.



a; X = *p*—MeO
b; X = H
c; X = *p*—NO_2

Scheme.

Results

The *Z*-arylhydrazones of 3-benzoyl-5-phenylisoxazole (**3**) rearrange to 2-aryl-4-phenacyl-1,2,3-triazoles (**4**) in the pS^+ range† 9.8—13.6, at a lower rate than do the previously studied *Z*-arylhydrazones of 3-benzoyl-5-phenyl-1,2,4-oxadiazole. Owing to the expectedly very low reaction rate, the rearrangement has not been studied in the uncatalysed range; however, in the base-catalysed range (pS^+ 9.8—13.6), the reaction could be conveniently studied.

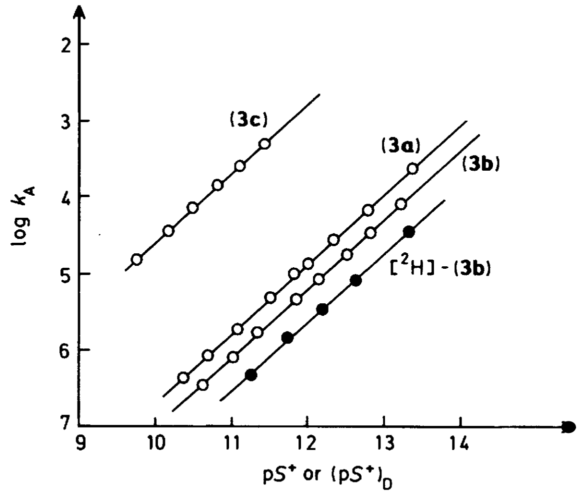


Figure. Plot of log k_A (○) in dioxane–water and of log $(k_A)_D$ (●) in dioxane–D_2O, at 313.15 K, *versus* pS^+ and $(pS^+)_D$, respectively. $(pS^+)_D$ Calculated from the relation $(pS^+)_D = pS^+ + 0.37$ according to A. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1975, 947.

Rearrangement of the Isoxazole (**3b**) *in Dioxane–Water*.—The apparent pseudo-first-order kinetic constants, k_A, for the rearrangement (**3b**) $\longrightarrow$ (**4b**) have been measured at various temperatures. Kinetic data at 298.15 K have been calculated from activation parameters (Table 1) and a plot of log k_A at 313.15 K *versus* pS^+ is reported in the Figure.

The rearrangement has been studied at various buffer concentrations in order to determine whether the base catalysis is specific or general. Indeed, the catalysis law (1) would give

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† An operational p*H* scale, pS^+,[5] was established in aqueous dioxane by employing the pK_a values of acids determined by interpolation from the data reported by Harned and Owen.[6] For dioxane–water (1:1 v/v) the meter reading after calibration against buffers was not significantly different from pS^+; in fact it was necessary to apply a correction of +0.16 to the meter reading.

Table 1. Apparent pseudo-first-order kinetic constants calculated at 298.15 K from the activation parameters for the rearrangement of (**3b**)[a] to (**4b**) in dioxane–water at various pS^+ and borate buffer concentrations.

p$S^{+\,b}$	10.60	11.00	11.34	11.85	12.14	12.50	12.80	13.20	13.60
$10^6k_{\rm A}$/s$^{-1\,c}$	0.0458	0.110	0.233	0.684	1.20	2.75	5.21	13.10	30.0
p$S^{+\,d}$	10.50	10.83	11.20	11.59	12.02	12.42	12.85	13.41	
$10^6k_{\rm A}$/s$^{-1\,c}$	0.0461	0.0892	0.197	0.455	1.10	2.44	6.12	19.6	
p$S^{+\,e}$	10.80	11.25	11.75	12.27	12.55	12.95			
$10^6k_{\rm A}$/s$^{-1\,c}$	0.117	0.290	0.856	2.37	4.25	9.29			

[a] [(**3b**)] 6.20 × 10^{-5}M, $\lambda_{\rm max.}$ 362 nm (log ε 4.30 ± 0.02). [b] Total buffer concentration, 0.0125M. [c] Values calculated by activation parameters. The experimental rate constants were measured in the range 303—333 K and were reproducible to within ±3%. [d] Total buffer concentration, 0.025M. [e] Total buffer concentration, 0.050M.

Table 2. Apparent pseudo-first-order kinetic constants measured at 313.15 K for the rearrangement of [^{2}H]-(**3b**) in dioxane–D_2O (1 : 1, v/v) at total buffer concentration 0.0125M

p$S^{+\,a}$	11.25	11.75	12.20	12.62	13.30
$10^6(k_{\rm A})_{\rm D}$/s$^{-1\,b}$	0.480	1.35	3.60	8.81	35.8
$(k_{\rm A})_{\rm H}/(k_{\rm A})_{\rm D}$	2.9	2.9	2.8	2.8	2.8

[a] Buffer: sodium borate–boric acid. [b] The rate constants were measured at constant ionic strength (0.05M) and are accurate to within ±3%.

$$k_{\rm A} = k_u + \Sigma_i k_i [C_i] + \Sigma_{j,k} k_{j,k} [C_j][C_k] \qquad (1)$$

significant values for catalyst present (at least for the terms k_i) only if the catalysis is general. In contrast, if the catalysis is specific, the catalytic kinetic constant should be different from zero only in the case of $k_i = k_{\rm OH}$.

The kinetic data at 298.15 K obtained at constant pS^+ value and at different buffer concentrations indicate an increase of reactivity with increasing buffer concentration (Table 1). The results of multiple linear regression analysis show that the k_i term is different from zero for both the present bases, *i.e.*, $\rm OH^-$ and $\rm H_2BO_3^-$, and that there is no $k_{j,k}$ term contributing to $k_{\rm A}$ [equation (2) with k_u/s^{-1} (−1.68 ± 1.52) ×

$$k_{\rm A} = k_u + k_{\rm OH}\,[{\rm OH^-}] + k_{\rm H_2BO_3}\,[{\rm H_2BO_3^-}] \qquad (2)$$

10^{-7}, $k_{\rm OH}$ l mol^{-1} s^{-1} (0.260 ± 0.003) × 10^{-2}, and $k_{\rm H_2BO_3}$/l mol^{-1} s^{-1} (0.352 ± 0.007) × 10^{-4}; $n = 23$; $R = 0.9985$].

A negative value for k_u has no chemical meaning. On the other hand, the statistical uncertainty is close to the calculated k_u value and this indicates a very low k_u as expected on grounds of the corresponding value[3a] for the rearrangement of the phenylhydrazone of 3-benzoyl-5-phenyl-1,2,4-oxadiazole. The catalytic constant of borate ion is lower than that of hydroxide ion, as expected,[3f] but at each buffer concentration the term $k_{\rm H_2BO_3}[{\rm H_2BO_3^-}]$ gives a significant contribution to the rate of rearrangement, thus indicating the occurrence of general catalysis according to the Hammett criterion.[7]

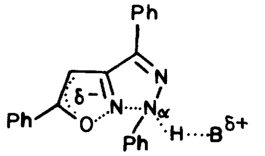
This result has been further supported by evaluating the isotope effect in the rearrangement of the α-*N*-deuteriated *Z*-phenylhydrazone of 3-benzoyl-5-phenylisoxazole [^{2}H]-(**3b**) in dioxane–D_2O.* The relevant kinetic constants at 313.15 K are reported in Table 2; in the Figure the rearrangement rate of compound (**3b**) is compared with that of [^{2}H]-(**3b**), as a function of pS^+. The $(k_{\rm A})_{\rm H}/(k_{\rm A})_{\rm D}$ ratios in the pS^+ range studied (the base-catalysed range) are *ca.* 2.8, thus pointing out that the reaction involves a proton transfer in the rate-determining step.[8]

Table 3. Apparent pseudo-first-order kinetic constants and activation parameters calculated at 313.15 K for the rearrangement of (**3a**)[a] to (**4a**) in dioxane–water at total buffer concentration 0.0125M

pS^+	$10^6k_{\rm A}$/s$^{-1\,b}$	$\Delta H^{\ddagger\,c}$	$\Delta S^{\ddagger\,d}$
10.37	0.430	103	−38
10.70	0.869	98	−48
11.07	1.90	100	−36
11.50	4.95	99	−31
11.82	10.0	95	−36
12.00	14.0	98	−26
12.33	28.6	95	−30
12.77	71.3	95	−23
13.35	245	93	−18

[a] [(**3a**)] 5.40 × 10^{-5}M, $\lambda_{\rm max.}$ 376 nm (log ε 4.25 ± 0.02). [b] Values calculated from activation parameters. The experimental rate constants were measured in the range 303—333 K and are reproducible to within ±3%. [c] kJ mol^{-1}; the maximum error is 3 kJ mol^{-1}. [d] J K^{-1} mol^{-1}; the maximum error is 8 J K^{-1} mol^{-1}.

The whole data, which parallel those observed in the case of the *Z*-phenylhydrazone of 3-benzoyl-5-phenyl-1,2,4-oxadiazole,[3f] agree with the transition state for the rearrangement, which therefore appears as an internal nucleophilic displacement.



Effects of the Substituents Present on the Arylhydrazone Moiety on the Reaction Rate.—The study of the substituent effects has been limited to two substituents, the strongly electron-withdrawing *p*-nitro group and the strongly electron-donating *p*-methoxy group. The relevant apparent first-order kinetic constants, $k_{\rm A}$, for the rearrangement of (**3a**—**c**) calculated at 313.15 K from activation parameters are reported in Tables 3—5; the Figure shows the plot of log $k_{\rm A}$ *versus* pS^+. The most interesting result is that both substituents, although characterized by opposite electronic effects, increase the reaction rate [$(k_{\rm A})_{p\text{-}{\rm NO_2}}/(k_{\rm A})_{\rm H}$ *ca.* 300 and $(k_{\rm A})_{p\text{-}{\rm OMe}}/(k_{\rm A})_{\rm H}$ *ca.* 2]. In the base-catalysed rearrangement of the *Z*-arylhydrazones of 3-benzoyl-5-phenyl-1,2,4-oxadiazole, studied with a large number of substituents, the situation observed was very similar to the present one and the non-linear concave-upward Hammett plot was interpreted as a proof of a changeover of mechanism with changing substituents.[3c,g] The conclusions drawn apply also to isoxazole derivatives: the introduction of a strongly electron-withdrawing substituent causes a large increase in the reactivity, thus indicating that the abstraction of the acidic α-hydrogen atom of the arylhydrazone (favoured by electron-withdrawing

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* The rearrangement could not be carried out in dioxane–water, because [^{2}H]-(**3b**) readily exchanges deuterium with protium and *vice-versa* {see the synthesis of [^{2}H]-(**3b**) in the Experimental section} as expected for a proton bonded to an electronegative atom with a lone pair of electrons.[8]

Table 4. Apparent pseudo-first-order kinetic constants and activation parameters calculated at 313.15 K for the rearrangement of (**3b**)[a] to (**4b**) in dioxane–water at total buffer concentration 0.0125M

pS^+	$10^6k_A/s^{-1}$ [b]	$\Delta H^\ddagger$ [c]	$\Delta S^\ddagger$ [d]
10.60	0.355	103	−39
11.00	0.838	103	−34
11.34	1.71	100	−35
11.85	4.81	98	−33
12.14	8.79	100	−21
12.50	18.5	96	−29
12.80	35.2	96	−23
13.20	85.3	93	−26
13.60	190	95	−20

[a] As in Table 1. [b–d] As in Table 3.

Table 5. Apparent pseudo-first-order kinetic constants and activation parameters calculated at 313.15 K for the rearrangement of (**3c**)[a] to (**4c**) in dioxane–water at total buffer concentration 0.0125M

pS^+	$10^4k_A/s^{-1}$ [b]	$\Delta H^\ddagger$ [c]	$\Delta S^\ddagger$ [d]
9.75	0.155	96	−25
10.17	0.379	96	−23
10.48	0.738	98	−10
10.81	1.48	95	−16
11.09	2.54	97	−3
11.42	5.02	97	+3
11.75	10.1	98	+10
11.95	15.2	98	+13
12.25	28.5	98	+19
12.66	67.1	100	+31
12.93	119	99	+33
13.27	242	99	+41

[a] [(**3c**)] 5.10×10^{-5}M, $\lambda_{max.}$ 402 nm (log ε 4.53 ± 0.02). [b] As in Table 3. The experimental rate constants were measured in the range 293—333 K and are reproducible to within ±3%. [c,d] As in Table 3.

groups) by a base (hydroxide or borate) plays an important role. On the other hand, the introduction of an electron-donating substituent, which should decrease the reactivity by reducing the acidity of the α-hydrogen atom, causes a small increase, instead, because it enhances the nucleophilicity of the α-nitrogen atom. Therefore, the substituent, depending on its electronic effect, can give rise to transition states of different structure.

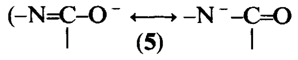
As with other mononuclear heterocyclic rearrangements, the reaction can be regarded as an internal nucleophilic displacement of the α-nitrogen on the 2-nitrogen of the ring, the timing of the breakage and formation of bonds in the nucleophilic attack depending on the nature of the substituents in the aryl moiety. Electron-withdrawing substituents reduce the nucleophilicity of the α-nitrogen whilst increasing the acidity of the bonded hydrogen atom: as a consequence, the loosening of the α-nitrogen–hydrogen bond exerts more effect on the rate than does the nucleophilic attack of the α-nitrogen on the 2-nitrogen. On the other hand, electron-donating substituents enhance the nucleophilicity of the α-nitrogen but lower the acidity of the bonded hydrogen atom: thus the nucleophilic attack of the α-nitrogen on the 2-nitrogen becomes more important than hydrogen abstraction.

Conclusions

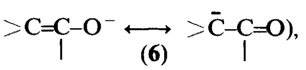
The arylhydrazones of 3-benzoyl-5-phenylisoxazole (**3a**—**c**) rearrange to 2-aryl-4-phenacyl-5-phenyl-1,2,3-triazoles (**4a**—**c**) following the mechanism resulting from our studies of the mononuclear heterocyclic rearrangement of the arylhydrazones of several 5-substituted 3-benzoyl-1,2,4-oxadiazoles. This conclusion is supported by the reactivity pattern in dioxane–water in the pS^+ range 9.8—13.6, at various buffer concentrations; indeed, both substituent and kinetic isotope effects on the isoxazole derivatives reproduce the situation observed for the 1,2,4-oxadiazole derivatives. Moreover, the variation of the reactivity as a function of pS^+ is essentially entropy-controlled as for 1,2,4-oxadiazole derivatives.*

A comparison of the rate of rearrangement of arylhydrazones having a similar structure, *e.g.*, those of 3-benzoyl-5-phenylisoxazole and 3-benzoyl-5-phenyl-1,2,4-oxadiazole, shows that isoxazole derivatives are much less reactive (rate ratio higher than 10^3) in accord with previous qualitative results (see above).[4] The lower reactivity of isoxazoles compared with 1,2,4-oxadiazole derivatives appears to depend on both activation enthalpy and entropy (in the instance of X = H, in the pS^+ range 11.4—12.1, the following average variations of the thermodynamic parameters have been observed: $\Delta\Delta H$ 11 kJ mol^{-1} and $\Delta\Delta S$ −20 J K^{-1} mol^{-1}, respectively).

The rationale for the observed trend of reactivities (1,2,4-oxadiazoles much more reactive than isoxazole derivatives) is consistent with the character of the internal nucleophilic displacement suggested for mononuclear heterocyclic rearrangements. In this kind of reaction, which is made possible by the low aromaticity of the heterocycles under consideration, the rates are strongly affected by both the strength of the cleaved bond and the nucleofugacity of the leaving group. In this case on going from a 1,2,4-oxadiazole to the isoxazole derivative (*a*) the aromatic character of the starting ring changes on increasing the strength of the N–O bond,[9] which must be cleaved in the rate-determining step, so disfavouring reaction of the isoxazole derivative and (*b*) the leaving group ABO changes from NCO [in (**1**)] to CCO [in (**3**)] and the varying abilities to carry the incipient negative charge [dependent on the electronegativity of the A atom (nitrogen or carbon) and on the different resonance stabilization of the anions formed (**5**) and (**6**)


(**5**)

$(-N{=}C(-)-O^- \longleftrightarrow -N^- -C(-){=}O$


(**6**)

$>C{=}C(-)-O^- \longleftrightarrow >\bar{C}-C(-){=}O),$

respectively] clearly disfavours isoxazole with respect to 1,2,4-oxadiazole derivatives.

It must be remarked that, with regard to the bond which must be formed, the effects of the substituents present in the arylhydrazone moiety on the rearrangement rates are also in agreement with the proposed mechanism in that they affect the timing of the nucleophilic attack.

Experimental

Synthesis and Purification of Compounds.—Compounds (**3b**) and (**4b**) were prepared according to the method reported[10] previously. 3-Benzoyl-5-phenylisoxazole on treatment with *p*-methoxyphenylhydrazine or *p*-nitrophenylhydrazine in acetic acid gave, predominantly, the corresponding *Z*-phenylhy-

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* Since in the pS^+ range studied the kinetic constants are composite values which depend upon different reaction processes, a discussion on the activation parameters is not meaningful.[1,3a] One can only observe that the reactivity variation is more entropy-dependent than enthalpy-dependent; however, a comparison between activation parameters measured for the rearrangement of isoxazole and 1,2,4-oxadiazole derivatives does seem to be significant.

drazones (**3a,c**), which were purified by crystallization from ethanol. The *Z*-configuration was confirmed by u.v. and n.m.r., spectroscopy [see reports[10] for compound (**3b**)]. The triazoles (**4a,c**) were obtained almost quantitatively through base-induced rearrangement of (**3a,c**) and were purified by crystallization from ethanol.

Compound (**3a**): M.p. 135 °C (Found: C, 74.9; H, 5.3; N, 11.4. $C_{23}H_{19}N_3O_2$ requires C, 74.8; H, 5.2; N, 11.4%); $\nu_{max.}$(Nujol) 3 220 cm^{-1} (NH); $\lambda_{max.}$(dioxane–water) 376 (log ε 4.25 ± 0.02) and 250 nm (4.36 ± 0.02); $\delta(CDCl_3)$ 3.85 (3 H, s, OMe), 6.65 (1 H, s, CH), 6.90—8.10 (14 H, m, ArH), and 11.30 (1 H, s, NH).

Compound (**3c**): M.p. 183–185 °C [lit.,[11,12] m.p. 178—180 °C, 191—192 °C (configuration not stated)]; $\nu_{max.}$ (Nujol) 3 200 cm^{-1} (NH); $\lambda_{max.}$ (dioxane–water) 402 (log ε 4.53 ± 0.02) and 255 nm (4.34 ± 0.02); $\delta(CDCl_3)$ 6.65 (1 H, s, CH), 7.35—8.50 (14 H, m, ArH), and 11.70 (1 H, s, NH).

Compound (**4a**): M.p. 123—125 °C (Found: C, 75.0; H, 5.2; N, 11.5. $C_{23}H_{19}N_3O_2$ requires C, 74.8; H, 5.2; N, 11.4%); $\nu_{max.}$(Nujol) 1 680 cm^{-1} (C=O); $\lambda_{max.}$(dioxane–water) 295 (log ε 4.41 ± 0.02) and 245 nm (4.29 ± 0.02); δ $(CDCl_3)$ 3.80 (3 H, s, OMe), 4.60 (2 H, s, CH_2), and 6.80—8.20 (14 H, m, ArH).

Compound (**4c**): M.p. 140—42 °C (lit.,[12] 137—138 °C) $\nu_{max.}$(Nujol) 1 680 cm^{-1} (C=O); $\lambda_{max.}$(dioxane–water) 335 (log ε 4.40 ± 0.02) and 245 nm (4.32 ± 0.02); $\delta(CDCl_3)$ 4.60 (2 H, s, CH_2) and 7.20—8.40 (14 H, m, ArH).

Dioxane and water were purified according to the methods reported.[13]

(Z)-α-N-*Deuteriated Phenylhydrazone of* 3-*Benzoyl*-5-*phenylisoxazole* [^{2}H]-(**3b**).—To a solution of (**3b**) (1 g) in dioxane (15 ml) was added slowly an excess of deuterium oxide (*ca.* 8—10 ml) with stirring until the solid separated. The mixture was carefully refluxed for 1—2 min and then left at room temperature. After a time, pure [^{2}H]-(**3b**) crystallized out. An n.m.r. test confirmed complete isotope exchange.

Kinetic Measurements.—The kinetics (at constant ionic strength 0.05M; maintained with KCl) were followed spectrophotometrically by measuring the disappearance of (**3a**—**c**). The wavelengths and log ε values at the maximum used for spectrophotometric determinations of kinetic constants are reported in Tables 1, 3, and 5. The kinetic constants measured at each pS^+ value in the range 293—333 K are available as a Supplementary Publications SUP. No. 56660 (6 pages).* The kinetic measurements were performed at various temperatures in order to recalculate the k_A values reported in Tables 1 and 3—5 by extrapolation or interpolation from activation parameters.

Calculations.—The values of k_A in dioxane–water used in the least-squares treatment were calculated at 298.15 K from activation parameters. The values of hydroxide ion concentration were calculated using 15.80 as the pK_w value in dioxane–water (1:1 v/v)[14] and 0.545 as the mean activity coefficient in the same system.[6] The values $[H_2BO_3^-]$ and $[H_3BO_3]$ were calculated from known total buffer concentrations and using pK_a 11.69 for boric acid.[3f] The values of k_i and $k_{j,k}$ were obtained by using multiple linear regression analysis of the apparent kinetic constants, $(k_A)_R$, at 298.15 K and the equation $k_A = k_u + k_{OH}[OH^-] + k_B[B] + k_A[A] + k_{A,B}[A][B] + k_{B.OH}[B][OH^-]$ (where $A = H_3BO_3$; $B = H_2BO_3^-$). The program used computes a sequence of regression equations in a stepwise manner. At each step one variable is added to the regression equation. The variable added is the one which makes the greatest reduction in the error sum of the squares. Variables with *F* values which are too low are automatically removed.

Acknowledgements

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References

1 First presented at the IV Convegno Nazionale della Divisione di Chimica Farmaceutica (S.C.I.), University of Palermo, 1983; Part 13, V. Frenna, N. Vivona, A. Caronia, G. Consiglio, and D. Spinelli, *J. Chem. Soc., Perkin Trans. 2*, 1986, 1183.

2 (*a*) M. Ruccia, N. Vivona, and D. Spinelli, *Adv. Heterocycl. Chem.*, 1981, **29**, 141; (*b*) A. J. Boulton, A. R. Katritzky, and A. M. Hamid, *J. Chem. Soc. C*, 1967, 2005; A. S. Afridi, A. R. Katritzky, and C. A. Ramsden, *J. Chem. Soc., Perkin Trans. 1*, 1976, 315; A. J. Boulton, 'Lectures in Heterocyclic Chemistry,' Hetero Corporation, Provo, 1973; N. Vivona, G. Macaluso, G. Cusmano, and V. Frenna, *J. Chem. Soc., Perkin Trans. 1*, 1982, 165 and references cited therein.

3 (*a*) D. Spinelli, A. Corrao, V. Frenna, N. Vivona, M. Ruccia, and G. Cusmano, *J. Heterocycl. Chem.*, 1976, **13**, 357; (*b*) D. Spinelli, V. Frenna, A. Corrao, and N. Vivona, *J. Chem. Soc., Perkin Trans. 2*, 1978, 19; (*c*) D. Spinelli, V. Frenna, A. Corrao, N. Vivona, and M. Ruccia, *J. Heterocycl. Chem.*, 1979, **16**, 359; V. Frenna, N. Vivona, D. Spinelli, and G. Consiglio, (*d*) *ibid.*, 1980, **17**, 861; (*e*) *ibid.*, 1981, **18**, 723; (*f*) V. Frenna, N. Vivona, G. Consiglio, A. Corrao, and D. Spinelli, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1325; (*g*) V. Frenna, N. Vivona, A. Corrao, G. Consiglio, and D. Spinelli, *J. Chem. Res.*, 1981, (*S*) 308; (*M*) 3 550; (*h*) V. Frenna, N. Vivona, G. Consiglio, and D. Spinelli, *J. Chem. Soc., Perkin Trans. 2*, 1983, 1199; (*i*) V. Frenna, N. Vivona, A. Caronia, G. Consiglio, and D. Spinelli, *ibid.*, p. 1203; (*j*) V. Frenna, N. Vivona, G. Consiglio, and D. Spinelli, *ibid.*, 1984, 541; (*k*) V. Frenna, N. Vivona, A. Caronia, G. Consiglio, and D. Spinelli, *ibid.*, p. 785.

4 (*a*) Ref. 2*a*, p. 159; (*b*) W. K. Warburton, *J. Chem. Soc. C*, 1966, 1522; M. Ruccia and N. Vivona, *Chem. Commun.*, 1970, 866; M. Ruccia, N. Vivona, and G. Cusmano, *J. Heterocycl. Chem.*, 1971, **8**, 137; H. Kano and E. Yamazaki, *Tetrahedron*, 1964, **20**, 159; M. Ruccia, N. Vivona, G. Cusmano, and G. Macaluso, *J. Chem. Soc., Perkin Trans. 1*, 1977, 589; N. Vivona, G. Cusmano, and G. Macaluso, *ibid.*, p. 1616.

5 R. G. Bates, 'Solute–Solvent Interaction,' eds. J. F. Coetzee and C. D. Ritchie, New York, 1969, p. 46.

6 H. S. Harned and B. B. Owen, 'The Physical Chemistry of Electrolytic Solution,' A.C.S. Monograph. No. 137, Reinhold, New York, 1958, 3rd edn., pp. 716, 755.

7 L. P. Hammett, 'Physical Organic Chemistry,' McGraw-Hill, New York, 1970, 2nd edn., pp. 322—323.

8 A. I. Brodskii, *J. Gen. Chem. USSR* (*Engl. Transl.*), 1954, **24**, 42; see also J. Hine, 'Physical Organic Chemistry,' McGraw-Hill, New York, 1962, 2nd edn., pp. 71—73, 112—114, 120—121.

9 M. Kamiya, *Bull. Chem. Soc. Jpn.*, 1970, **43**, 3344; L. Paoloni and M. Cignitti, *Tetrahedron*, 1968, **24**, 485; W. Adam and A. Grimison, *Theor. Chim. Acta*, 1967, **7**, 342.

10 N. Vivona, G. Macaluso, V. Frenna, and M. Ruccia, *J. Heterocycl. Chem.*, 1983, **20**, 931.

11 S. Cusmano and G. Sigillò, *Gazz. Chim. Ital.*, 1938, **68**, 596.

12 T. Sasaki, T. Yoshioka, and Y. Suzuki, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 185.

13 D. Weissberger, *Tech. Org. Chem.*, Interscience, New York, 1963, II edn., vol. 7, p. 372.

14 E. M. Woolley, D. G. Hurkot, and L. G. Hepler, *J. Phys. Chem.*, 1970, **74**, 3908.

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* For details of the Supplementary Publications Scheme, see 'Instructions for Authors (1987),' *J. Chem. Soc., Perkin Trans. 2*, 1987, Issue 1.