Mononuclear Heterocyclic Rearrangements. Part 15.[1] Kinetic Study of the Amine-catalysed Rearrangement of Some *Z*-Arylhydrazones of 3-Benzoyl-5-phenylisoxazole into 2-Aryl-4-phenacyl-5-phenyl-1,2,3-triazoles in Acetonitrile and in Benzene

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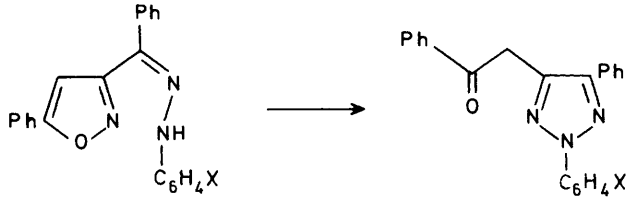
The kinetics of the title reaction have been measured in the presence of n-butylamine, piperidine, triethylamine, and diazabicyclo[2.2.2]octane (DABCO). The reaction has also been studied in the presence of pairs of amines [butylamine (or piperidine) and triethylamine (or DABCO)] in benzene. The results confirmed the lower reactivity of isoxazole derivatives with respect to 1,2,4-oxadiazole derivatives (rate ratios *ca.* 10^{-3}). The kinetic laws observed are accounted for by the 'catalysis of catalysis' mechanism.

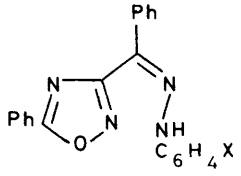
In order to gain information about the effect of the starting ring on mononuclear heterocyclic rearrangements (m.h.r.s)[2] we have studied the rearrangement of some *Z*-arylhydrazones of 3-benzoyl-5-phenylisoxazole (**1a**—**c**) into 2-aryl-4-phenacyl-1,2,3-triazoles (**2a**—**c**) in dioxane–water (DIOX–W)[1] at various pS^+ values. The data obtained (buffer, substituent, and kinetic isotopic effects) parallel those observed for the m.h.r. of *Z*-arylhydrazones of several 5-substituted 3-benzoyl-1,2,4-oxadiazoles (**3**)[3] and indicate that the reactivity of isoxazole derivatives is strongly lower than that of 1,2,4-oxadiazole derivatives.[1,2a]

On the other hand studying the m.h.r. of (**3**) in the presence of some amines (A) and in various solvents, we have observed



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

Scheme. 1



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

Table 1. Kinetic laws observed for some rearrangements of (**1a**—**c**) and (**3a**—**c**)

Equation	Kinetic law[a]	Substrate [solvent, amine, temperature (K)]
(1)	$k_A = k_{II}[A] + k_{III}[A]^2$	(**1a**, **b**) (ACN; PIP; 313); (**1c**) (ACN; BuA; 313); (**3a**, **b**) (PhH; PIP; 313); (**3a**, **b**) (ACN; PIP; 283)
(2)	$k_A = k_{II}[A]$	(**1c**) (ACN; PIP, TEA, and DABCO; 313); (**3c**) (ACN; PIP, BuA, TEA, and DABCO; 283); (**3c**) (PhH; TEA, and DABCO; 313)
(3)	$k_A = k_{III}[A]^2$	(**1c**) (PhH; PIP; 313); (**3c**) (PhH; PIP; 313)
(4)	$k_A = k_{IV}[A]^3$	(**1c**) (PhH; BuA; 313); (**3c**) (PhH; BuA; 313)

[a] k_{II}, k_{III}, and k_{IV} refer to reaction pathways involving one molecule of phenylhydrazone and one, two, and three molecules of amine, respectively.

different kinetic laws depending on the nature of the solvent, the catalysing amine, and the structure of the arylhydrazone[4,5] [a summary of the results previously obtained with (**3a**—**c**) together with the results collected in this work is reported in Table 1]. The results can be confidently accounted for by the occurrence of 'general base-catalysis' and/or 'catalysis of catalysis' depending on how many amine concentration terms appear in the kinetic laws.*

* The kinetic laws observed could be tentatively accounted for by supposing either that large amounts of the added amines (particularly in solvents of low polarity) can significantly modify the solvent properties or that the amines can interact between themselves giving dimers or larger aggregates. Nevertheless it appears difficult to justify the occurrence of different kinetic laws with different amines [primary, secondary, and tertiary: *e.g.*, see the behaviour of (**3c**) in the presence of DABCO, piperidine, and n-butylamine in benzene]. Moreover, the previous hypothesis being correct, one would observe the same effect on the reactivity on increasing amine concentration independently of the nature of the arylhydrazones: in contrast the results obtained in benzene (ε 2.28) and acetonitrile (ε 37.5) [see the behaviour of (**3a** and **c**) in the presence of piperidine] indicate that in both solvents the observed kinetic laws depend on the structure of the used arylhydrazones.

In order to confirm these conclusions about the mechanism of amine catalysis we have extended the study to some isoxazole derivatives (**1a**—**c**) looking at the following points: the effect of the substituents present in the *Z*-arylhydrazone moiety in the reaction with piperidine (PIP) in acetonitrile (ACN) and that of the structure of the amine in ACN. The reactivity of (**1c**) has also been measured with n-butylamine (BuA), triethylamine (TEA), and diazabicyclo[2.2.2]octane (DABCO): for the sake of comparison the same study has been performed on (**3c**). The effect of the structure of the amines in benzene (PhH) was measured by testing the reactivity of (**1c**) with PIP, BuA, or TEA. The reactivity in PhH with BuA and PIP has also been studied in the presence of two tertiary amines (DABCO or TEA).

Results

Piperidine-catalysed Rearrangement of Compounds (**1a**—**c**) *in ACN: Substituent Effects.*—The study of the substituent effects has been limited to one strongly electron-donating (**1a**) and one strongly electron-withdrawing (**1c**) substituent, together with the unsubstituted phenylhydrazone (**1b**).

The apparent first-order kinetic constants (k_A) for the piperidine-catalysed rearrangement of (**1a**—**c**) at 313 K depend on the amine concentration. They well fit equations (1) and (2), as shown by the results of linear regression analysis (Table 2).

$$k = k_{II}[A] + k_{III}[A]^2 \quad (1)$$

$$k = k_{II}[A] \quad (2)$$

In particular a strongly electron-donating substituent in (**1a**) causes a slight lowering of the reactivity with respect to (**1b**) and at the same time favours a pathway involving two molecules of piperidine [$(k_{III}/k_{II})_{(1a)}$ 2.02 and $(k_{III}/k_{II})_{(1b)}$ 1.47 l mol^{-1}]. In contrast the strongly electron-withdrawing substituent in (**1c**) causes a large increase in reactivity with respect to (**1b**) and the disappearance of the pathway requiring more than one molecule of amine also on account of the solvent used (basic, aprotic, and dipolar).[4] In accord with the previous results for (**3a**—**c**)[6] these observations indicate that the substituents exert an effect both on the acidity of the arylhydrazone hydrogen (N_α–H) and the nucleophilicity of the N_α atom and that the first effect predominates.

The small decrease and the large increase of the reactivity determined by the strong electron-donating (*p*-MeO) and -withdrawing (*p*-NO_2) substituent, respectively, act in such a way that the kinetic data cannot be linearly correlated with Hammett substituent constants, replicating the situation observed with (**3a**—**c**).[6] Considering also the parallel behaviour observed in the rearrangement of (**1a**—**c**)[1] and (**3a**—**c**)[3] in DIOX–W, for which non-linear concave-upward Hammett plots[7] were observed, a changeover of the mechanism with changing substituent can be confidently suggested.

Moreover the uncatalysed pathway could not be detected with isoxazole derivatives and this agrees with the results obtained from studying the reactivity of (**1b**) in DIOX–W at different pS^+ values and/or different buffer concentrations which pointed out the non-significance of the k_u term.[1] On the other hand, this behaviour could have been expected on account of the expectedly low reactivity for the uncatalysed pathway (at 313 K, estimated values in DIOX–W k_u 10^{-8} s^{-1}, in ACN k_u 10^{-7} s^{-1}).

A comparison between isoxazole and 1,2,4-oxadiazole derivatives shows that the behaviour of *Z*-arylhydrazones (**1a**—**c**) at 313 K resembles that of the much more reactive *Z*-arylhydrazones (**3a**—**c**) [at the same temperature the observed reactivity ratios $(k)_{(3a-c)}/(k)_{(1a-c)}$ are *ca.* 10^3] at a lower temperature (283 K),[6] *i.e.* at a temperature where the reactivities in similar ranges of piperidine concentrations could be explored.

Amine-catalysed Rearrangement of (**1c**) *and* (**3c**) *in ACN: Effect of the Amine Structure.*—The study of the effect of structure of the amine used on the reactivity of the title compounds has been enlarged to a primary (BuA) and two tertiary (TEA and DABCO) amines. For the reactivity of (**1c**) with PIP see above. The apparent first-order kinetic constants for the amine-catalysed rearrangement of (**1c**) at 313 K and of (**3c**) at 283 K show that the k_A values increase with increasing amine concentration.

The observed results bring to evidence the following points: (i) in a basic, dipolar, and aprotic solvent, which strongly favours the studied rearrangement, (**1c**) and (**3c**) react with both tertiary (TEA or DABCO) and secondary amines (PIP) according to equation (2), *i.e.* by the catalysed pathway requiring only one molecule of amine (see the results of the linear regression analysis in Table 3). The same behaviour has been observed for the highly reactive (**3c**) also with a primary amine (BuA); in contrast, the less reactive (**1c**) (for which a larger range of BuA concentrations could be explored) also involves the pathway catalysed by two molecules of amine [equation (1)]. (ii) A comparison between the k_{II} values shows that the four amines studied affect the reactivity of the two arylhydrazones (**1c**) and (**3c**) in the same way: in fact a plot of $\log (k_{II})_{(1c)}$ at 313 K *versus* $\log (k_{II})_{(3c)}$ at 283 K is linear (*s* 0.95 ± 0.02, *r* 0.9997, *n* 4) and the intercept (*i* 1.74 ± 0.03) gives the logarithmic average ratio between the reactivity in ACN of (**3c**) at 283 K and of (**1c**) at 313 K. Since there would be no reason to observe a linear free energy relationship if two different mechanisms were operating with the two arylhydrazones, the occurrence of a linear correlation with a slope close to unity for the two arylhydrazones (**1c**) and (**3c**) is a clear piece of evidence for similar mechanisms for the rearrangement of (**1c**) and (**3c**). Further evidence on this point have been collected by studying the rearrangement in PhH and the relevant implications are discussed below.

The results confirmed that aprotic dipolar solvents (ACN, DMSO, DMF, *etc.*) are excellent solvents for m.h.r.s,[4,8] and are much more efficient than apolar solvents {*e.g.* PhH: at [A] 1M $(k_A)_{ACN}/(k_A)_{PhH} > 10^4$}.

Amine-catalysed Rearrangement of (**1c**) *in PhH.*—The reactivity of (**1c**)* in PhH has been tested with a primary amine (BuA), a secondary cyclic amine (PIP), and a tertiary amine (TEA).

Compound (**1c**) appears to have very little reactivity with TEA in PhH (*e.g.* at [TEA] 1M and at 313 K: $k_A < 10^{-9}$ s^{-1}; compare with the extrapolated value in ACN at the same amine concentration: k_A 0.78 × 10^{-2}) and the high uncertainty of the value obtained induced us to abandon this study. Under the same experimental conditions (**1c**) reacts with BuA and PIP and the k_A values measured are amine-concentration dependent. The linear regression analysis of the kinetic data according to equations (3) and (4)† gives respectively [A = PIP: k_{III} (3.85 ± 0.04) × 10^{-6}, *i* 0.01 ± 0.03, *n* 8, *r* 0.9996; A = BuA: k_{IV} (2.29 ± 0.01) × 10^{-6}, *i* 0.02 ± 0.01, *n* = 8, *r* 0.9999].

$$k_A = k_{III}[A]^2 \quad (3)$$

* The reactivities of (**1a**, **b**) in PhH at 313 K with BuA, PIP, and TEA are too low to give reliable kinetic results.

† In both instances we have neglected the intercepts, *i.e.* the possible k_u as well as any other amine-dependent terms, because they are affected by high uncertainty.

Table 2. Linear regression analysis[a] of apparent first-order kinetic constants for the rearrangements (**1a—c**) ⟶ (**2a—c**) at 313.5 K in acetonitrile in the presence of piperidine according to equations $k_A = k_{II}[PIP] + k_{III}[PIP]^2 + i$ or $k_A = k_{II}[PIP] + i$

Compound	$10^4 (k_{II} \pm s_{II})$ / $l\,mol^{-1}\,s^{-1}$	$10^4 (k_{III} \pm s_{III})$ / $l^2\,mol^{-2}\,s^{-1}$	r or R	n	$i \pm s_i$[b]	k_{III}/k_{II} / $l\,mol^{-1}$
(**1a**)	1.13 ± 0.05	2.28 ± 0.05	0.999 96	10	$(-0.102 \pm 0.117)\,10^{-5}$	2.02
(**1b**)	1.65 ± 0.06	2.42 ± 0.05	0.999 96	10	$(-1.74 \times 10^{-3} \pm 0.13)\,10^{-5}$	1.47
(**1c**)	639 ± 4		0.999 99	9	$(-1.47 \pm 4)\,10^{-5}$	

[a] s_{II} and s_{III} are the standard deviations of the regression parameters k_{II} and k_{III}, respectively; r or R are the correlation coefficients; n is the number of experimental points; i is the intercept. The confidence limit values for significance of regression parameters are all better than 99.9%. [b] See text.

Table 3. Linear regression analysis[a] of apparent first-order kinetic constants in acetonitrile for the rearrangements (**1c**) ⟶ (**2c**) and (**3c**) ⟶ (**4c**) in the presence of various amines according to equations $k_A = k_{II}[B] + i$ or $k_A = k_{II}[B] + k_{III}[B]^2 + i$

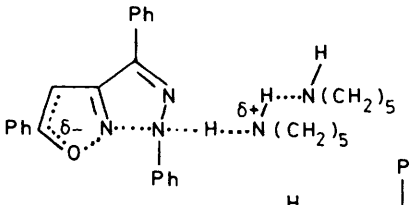
B	$10^2 (k_{II} \pm s_{II})$ / $l\,mol^{-1}\,s^{-1}$	$10 (k_{III} \pm s_{III})$ / $l^2\,mol^{-2}\,s^{-1}$	r or R	n	$i \pm s_i$[b]
Rearrangement (**1c**) ⟶ (**2c**) at 313.15 K					
Piperidine	6.39 ± 0.04		0.999 99	9	$(-1.47 \pm 4)\,10^{-5}$
n-Butylamine	0.724 ± 0.011	2.08 ± 0.02	0.999 95	11	$(-1.9 \pm 8.98)\,10^{-6}$
Triethylamine	0.780 ± 0.006		0.9998	10	$(-0.02 \pm 0.01)\,10^{-3}$
DABCO	0.612 ± 0.003		0.9999	9	$(2.63 \pm 6.89)\,10^{-3}$
Rearrangement (**3c**) ⟶ (**4c**) at 283.15 K					
Piperidine[c]	414 ± 1		0.999 99	7	$(0.005 \pm 0.044)\,10^{-3}$
n-Butylamine	51.3 ± 0.1		0.9999	8	$(-0.04 \pm 0.01)\,10^{-3}$
Triethylamine	55.9 ± 0.2		0.9999	8	$(0.07 \pm 0.01)\,10^{-3}$
DABCO	46.4 ± 0.5		0.9996	8	$(0.02 \pm 0.03)\,10^{-3}$

[a,b] As in Table 2. [c] Data from ref. 6.

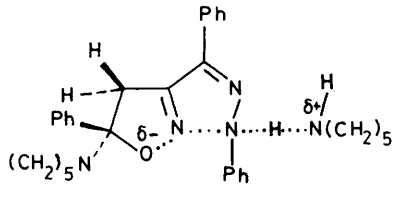
$$k_A = k_{IV}[A]^3 \quad (4)$$

Once more the course of the m.h.r.s in different solvents (polar or apolar), amine being equal, appears to be solvent dependent. Moreover, in the same solvent (benzene) it depends on the structure of the amine (primary or secondary) and in particular on the number of hydrogen atoms bonded to the nitrogen atom.[5b]

Bearing in mind the results previously obtained, this behaviour can be explained by considering two different kinds of transition states:[5b,9] one takes into account the occurrence in apolar solvents of 'catalysis of catalysis,' the other occurrence of an addition to C(5)–C(4) bond as in formulae (**4**) and (**5**), respectively, for the reaction with piperidine.



(**4**)



(**5**)

Comparison between the data for (**1c**) and (**3c**) makes addition to the double bond of the ring most improbable. In fact looking at the reactivities of (**1c**) and (**3c**) one remarks that in ACN the observed reaction pathway in both cases requires only one molecule of PIP, which behaves as a general base favouring the rearrangement by abstraction of the hydrogen of *Z*-arylhydrazone (see also the parallel behaviour observed with various amines and the relevant linear free energy relationship); in this case certainly no addition to the double bond of the ring occurs and the estimated reactivity ratio $(k_{II})_{(3c)}/(k_{II})_{(1c)}$ is *ca.* 10^3. Again, by examining the reactivities of (**1c**) and of (**3c**) in benzene one observes that, amines being equal, similar kinetic laws and therefore similar reaction pathways operate: moreover the reactivity ratios between (**3c**) and (**1c**) are again *ca.* 10^3. All these observations rule out any mechanism involving an addition to the double bond of the ring in the rate-determining step, because for (**1c**) and (**3c**) the addition would occur to the C(5)–C(4) and to the C(5)–N(4) double bond, respectively, and it is very improbable that the additions of the same reagent to two differently polarised double bonds could affect the reactivity ratios in the same way.

Rearrangement of (**1c**) *in Benzene catalysed by Pairs of Amines.*—Another piece of evidence against addition to the double bond of the ring as a rearrangement mechanism is offered by the results obtained in the study of the rearrangement catalysed by pairs of amines (PIP or BuA together with DABCO or TEA). Considering the previous results and the amines present in the reaction mixture the kinetic laws (5) and (6) could be observed. Bearing in mind the behaviour observed with TEA (see above) one can expect no contribution by the term involving this amine (*i.e.*, k_{II} [TA]); moreover, because of the higher steric hindrance of TEA with respect to DABCO, higher effectiveness by DABCO should be expected:[5b] the observed kinetic data agree with these expectations. In fact in the case of the pair PIP and TEA no influence by the TEA

$$k_A = k_{II}[TA] + k_{III}[PIP]^2 + k_{III}[PIP][TA] \quad (5)$$

$$k_A = k_{II}[TA] + k_{IV}[BuA]^3 + k_{IV}[BuA][TA]^2 + k_{IV}[BuA]^2[TA] \quad (6)$$

TA = DABCO or TEA

concentration on the reactivity was observed; in contrast with the pair PIP and DABCO the DABCO concentration affects the reactivity and, moreover, in the presence of BuA, TEA affects the reactivity less than DABCO.

The statistical treatment (stepwise multiple linear regression analysis) of the kinetic data has furnished the following results [equations (7)—(9)] which show k_{III} and k_{IV} values strictly

$$10^6k = (3.84 \pm 0.01)\,[PIP]^2 + (15.4 \pm 0.05)\,[PIP][DABCO] \quad (7)$$
$$(i\ 0.008 \pm 0.005,\ n\ 23,\ R\ 0.9999)$$

$$10^6k = (2.30 \pm 0.01)\,[BuA]^3 + (13.2 \pm 0.3)\,[BuA][DABCO]^2 + (7.07 \pm 0.08)\,[BuA]^2[DABCO] \quad (8)$$
$$(i\ 0.005 \pm 0.003,\ n\ 22,\ R\ 0.9999)$$

$$10^6k = (2.30 \pm 0.03)\,[BuA]^3 + (2.67 \pm 0.05)\,[BuA]^2[TEA] \quad (9)$$
$$(i\ 0.01 \pm 0.01,\ n\ 22,\ R\ 0.9994)$$

comparable with those directly obtained (see above). The absence of routes including catalysis by TEA in the reaction with PIP and the presence only of the term depending on the first power of TEA concentration in the reaction with BuA confirm the influence of steric hindrance on general base catalysis:[10] the structure of DABCO, an amine with low steric requirements, allows a more effective catalysis.

Since there is no contribution from terms depending only on DABCO concentration, all the mixed terms can be easily understood *only* in the light of the 'catalysis of catalysis' mechanism and are not easily reconcilable with the addition of amine to the C(5)–C(4) double bond of the isoxazole ring. In particular the presence of the k_{IV}[BuA][DABCO]^2 term cannot be included in the frame of the addition mechanism.

Experimental

Synthesis and Purification of Compounds.—Compounds (**1b**),[11] (**2b**),[11] (**1a**, **c**),[1] (**2a**, **c**),[1] (**3c**),[3b] (**4c**),[3b] acetonitrile,[12] and benzene[13] were prepared and/or purified according to the methods reported. Piperidine, n-butylamine, and triethylamine (standard reagent) were purified by standing over potassium hydroxide (24 h) and then twice fractionally distilled. DABCO was purified by sublimation.

Kinetic Measurements.—The kinetics were followed spectrophotometrically as previously described[4,5] by measuring the disappearance of (**1a**—**c**) and (**3c**) at the wavelengths of their absorption maxima, where the absorption of (**2a**—**c**) and (**4c**) are very low. The kinetic constants, the wavelengths and the log ε values at the maxima used for spectrophotometric determinations are available in Supplementary Publication No. SUP 56719 (3 pp.).*

* For details of Supplementary Publications see Instructions for Authors, *J. Chem. Soc., Perkin Trans. 2*, 1988, Issue 1.

Acknowledgements

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References

1 Part 14, V. Frenna, N. Vivona, G. Macaluso, D. Spinelli, and G. Consiglio, *J. Chem. Soc., Perkin Trans. 2*, 1987, 537.
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.
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*) V. Frenna, N. Vivona, G. Consiglio, A. Corrao, and D. Spinelli, *ibid.*, 1981, 1325; (*d*) V. Frenna, N. Vivona, A. Corrao, G. Consiglio, and D. Spinelli, *J. Chem. Res.*, 1981, (*S*), 308; (*M*), 3550; (*e*) V. Frenna, N. Vivona, G. Consiglio, and D. Spinelli, *J. Chem. Soc., Perkin Trans. 2*, 1984, 541; (*f*) V. Frenna, N. Vivona, A. Caronia, G. Consiglio, and D. Spinelli, *ibid.*, p. 785.
4 V. Frenna, N. Vivona, G. Consiglio, and D. Spinelli, *J. Chem. Soc., Perkin Trans. 2*, 1983, 1199.
5 (*a*) V. Frenna, N. Vivona, D. Spinelli, and G. Consiglio, *J. Heterocycl. Chem.*, 1981, **18**, 723; (*b*) V. Frenna, N. Vivona, A. Caronia, G. Consiglio, and D. Spinelli, *J. Chem. Soc., Perkin Trans. 2*, 1983, 1203.
6 V. Frenna, N. Vivona, L. Cannella, G. Consiglio, and D. Spinelli, *J. Chem. Soc., Perkin Trans. 2*, 1986, 1183.
7 O. Schreck, *J. Chem. Educ.*, 1971, **48**, 103; O. Exner, *Adv. Linear Free Energy Relationships*, 1972, 12, and references therein.
8 V. Frenna, N. Vivona, G. Consiglio, and D. Spinelli, unpublished results; M. Ruccia, N. Vivona, and G. Cusmano, *Tetrahedron Lett.*, 1972, 4959; *Tetrahedron*, 1974, **30**, 3859; M. Ruccia, N. Vivona, G. Cusmano, and G. Macaluso, *J. Chem. Soc., Perkin Trans. 1*, 1977, 589.
9 J. F. Kirsch and W. P. Jencks, *J. Am. Chem. Soc.*, 1964, **86**, 833; A. Arcoria, E. Maccarone, G. Musumarra, and G. A. Tomaselli, *Tetrahedron*, 1975, **31**, 2522.
10 F. Covitz and F. H. Westheimer, *J. Am. Chem. Soc.*, 1963, **85**, 1773; R. P. Bell, M. H. Rand, and K. M. A. Winne-Jones, *Trans. Faraday Soc.*, 1956, **52**, 1093; W. P. Jencks and M. Gilchrist, *J. Am. Chem. Soc.*, 1966, **88**, 104; T. C. Bruice, A. Donzel, R. W. Huffman, and A. R. Butler, *ibid.*, 1967, **89**, 2106.
11 N. Vivona, G. Macaluso, V. Frenna, and M. Ruccia, *J. Heterocycl. Chem.*, 1983, **20**, 931.
12 A. Weissberger, 'Technique of Organic Chemistry,' Interscience, New York, 1963, 2nd edn., vol. 7, pp. 398 and 435.
13 D. Spinelli, C. Dell'Erba, and G. Guanti, *Ann. Chim. (Italy)*, 1965, **55**, 1260.

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