Mononuclear Heterocyclic Rearrangements. Part 11.[1] Kinetic Study of the Rearrangement of (*Z*)-Phenylhydrazones of Some 5-Alkyl-3-benzoyl-1,2,4-oxadiazoles into 4-Acylamino-2,5-diphenyl-1,2,3-triazoles in Benzene, Dioxane–Water, and Acetonitrile

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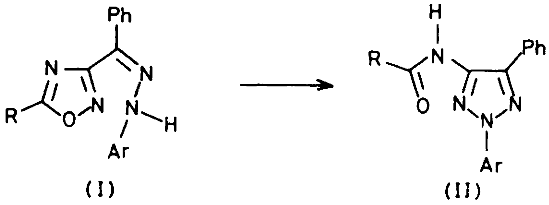
The kinetics of the title reactions have been measured at various catalyst concentrations. The 5-alkyl-substituted phenylhydrazones (alkyl = Me, Et, Pr^i, or Bu^t) rearrange more slowly than the 5-H parent compound; moreover the rearrangement rate is little affected by the structure of the 5-alkyl substituent. These facts are considered as evidence against a rearrangement mechanism involving catalyst addition to the C(5)–N(4) bond of the 1,2,4-oxadiazole ring. The observed reactivity pattern can be related to the influence of the 5-substituent on the leaving group ability of the substituent–C(5)–O system.

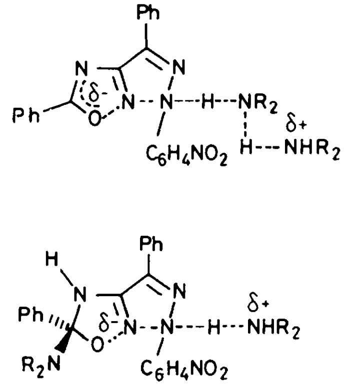
In some of our recent papers [1,2] concerning the mononuclear heterocyclic rearrangements [3,4] of (*Z*)-arylhydrazones of 3-benzoyl-5-phenyl-1,2,4-oxadiazoles (Ia and b) into 2-aryl-4-benzoylamino-5-phenyl-1,2,3-triazoles (IIa and b) in the presence of amines, in different solvents, we have observed different kinetic laws depending on the nature of the solvent, of the catalysing amine, and of the structure of the arylhydrazone studied. For example, the mononuclear heterocyclic rearrangement of (Ia) promoted by piperidine in benzene, dioxane, or ethyl acetate follows two catalysed pathways requiring one or two molecules of piperidine, respectively.[2b] On the other hand (Ib) rearranges in benzene in the presence of tertiary, cyclic secondary, and primary amines with kinetic laws involving one, two, or three molecules of catalyst, respectively.[1,2a] The occurrence of catalytic pathways requiring more than one mole of amine has been ascribed to a catalysis of catalysis; a possible mechanism involving amine addition to the C(5)–N(4) bond of the 1,2,4-oxadiazole ring has been disfavoured.[1,2b] The reaction intermediates involved in the two alternative base-catalysed mechanisms for, for example, the rearrangement of (Ib) promoted by piperidine in benzene, would be as shown in the Scheme.

In order to support the foregoing interpretation, we thought that experiments carried out on a suitable series of phenylhydrazones of 5-substituted 1,2,4-oxadiazoles might allow us to exclude one of the alternative mechanisms. In fact, a substituent present on C(5) of the 1,2,4-oxadiazole ring would affect the two mechanisms in different ways: in the catalysis of catalysis mechanism it would affect the rearrangement rate only by means of its electronic effects, which essentially determine the leaving group ability of the C(5)–O system.[3] In the addition mechanism, the same substituent would affect the rearrangement rate essentially by its steric effect and only in minor part by its electronic effect. Therefore a useful set of substituents would have electronic and steric effects which vary in different ways. A set of alkyl groups (Me, Et, Pr^i, and Bu^t) was chosen with this in mind.



(I) (II)

a; R = Ar = Ph
b; R = Ph, Ar = $C_6H_4NO_2$-*p*
c; R = Me, Ar = Ph
d; R = Et, Ar = Ph
e; R = Pr^i, Ar = Ph
f; R = Bu^t, Ar = Ph
g; R = H, Ar = Ph



Scheme. R_2NH = piperidine

The nature of the effects exerted by alkyl substituents is complex: indeed, they can influence the reactivity by both electronic and steric effects. Moreover, the electronic effects are composite; they can be both inductive and mesomeric, the first decreasing and the second increasing with the number of 'α-hydrogen bondings' (hyperconjugation). Thus, while the inductive effect increases on going from methyl (Me) to ethyl (Et), isopropyl (Pr^i), and t-butyl (Bu^t), the mesomeric effect decreases in the same order, as first pointed out by Baker and Nathan.[5] Among the various sets of substituent constants,[6] the σ_I values represent a good estimate of the first effect and σ_R of the second, whereas σ values measure the resultant of inductive and resonance effects. However, in each series the range of variation is rather small.

When the reactivity can also be influenced by steric effects, these are superimposed upon the electronic effects and usually predominate. A good measure of steric effects is given by the various sets of E_s and ν values,[6,7] the range of variation being very large, in this case, with values strongly increasing from Me to Et, Pr^i, and Bu^t.

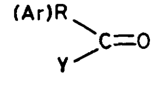
It is well known that many nucleophilic additions to carbon–

Table 1. Apparent first-order rate constants [a] for the rearrangements (Ic—g) $\longrightarrow$ (IIc—g), k_A, in benzene at 313.15 K, in the presence of piperidine

(Ic) [b]											
[PIP]/M	0.104	0.260	0.405	0.541	0.630	0.735	0.820	0.905	1.04		
$10^5k_A/s^{-1}$	0.0127	0.0810	0.196	0.348	0.466	0.639	0.787	0.965	1.26		
(Id) [c]											
[PIP]/M	0.0950	0.140	0.254	0.420	0.510	0.605	0.761	0.905	1.01		
$10^5k_A/s^{-1}$	0.0103	0.0211	0.0733	0.206	0.300	0.417	0.659	0.932	1.16		
(Ie) [d]											
[PIP]/M	0.120	0.206	0.320	0.408	0.510	0.612	0.705	0.810	0.920	1.03	
$10^5k_A/s^{-1}$	0.0173	0.0530	0.123	0.200	0.318	0.447	0.594	0.772	1.01	1.28	
(If) [e]											
[PIP]/M	0.124	0.205	0.310	0.400	0.515	0.618	0.721	0.805	0.927	1.03	
$10^5k_A/s^{-1}$	0.0181	0.0487	0.113	0.184	0.304	0.444	0.596	0.748	0.992	1.21	
(Ig) [f]											
[PIP]/M	0.104	0.208	0.300	0.374	0.541	0.624	0.707	0.800	0.873	0.957	1.04.
$10^5k_A/s^{-1}$	0.467	1.33	2.41	3.51	6.73	8.79	11.1	14.0	16.1	19.1	22.5

[a] The rate constants are accurate to within ±3%. [b] [(Ic)] 1.98×10^{-4}M. At $\lambda_{max.}$ 368 nm, log ε 4.30 ± 0.02. [c] [(Id)] 1.74×10^{-4}M. At $\lambda_{max.}$366 nm, log ε 4.31 ± 0.02. [d] [(Ie)] 1.75×10^{-4}M. At $\lambda_{max.}$ 370 nm, log ε 4.31 ± 0.02. [e] [(If)] 1.45×10^{-4}M. At $\lambda_{max.}$ 366 nm, log ε 4.27 ± 0.02. [f] [(Ig)] 2.10×10^{-4}M. At $\lambda_{max.}$ 370 nm, log ε 4.27 ± 0.02.

oxygen double bonds are very sensitive to steric effects exerted by alkyl or aryl groups linked to the electrophilic carbon atom of (III). Good examples are the alkaline hydrolysis or alcoholysis of esters, the addition of hydrogen sulphite or cyanide ion to aldehydes or ketones, and the reactions of these compounds with ammonia and its derivatives (hydroxylamine, semicarbazide, arylhydrazines, *etc.*).



(III)

Overall, on grounds of the previous hypothesis, we expected very different results, as to the effects of substituents on reactivity, according to which mechanism is operating.

Thus we have studied the mononuclear heterocyclic rearrangement of the phenylhydrazones of some 5-alkyl-3-benzoyl-1,2,4-oxadiazoles (Ic—f; R = Me, Et, Pr^i, or Bu^t) in benzene, dioxane–water, and acetonitrile (respectively, a solvent of low polarity and basicity, a protic polar solvent, and an aprotic dipolar solvent) in the presence of piperidine (PIP) or of buffers.

In order to complete the picture of substituent effects we have also studied the rearrangement of the phenylhydrazone of 3-benzoyl-1,2,4-oxadiazole (Ig; R = H, Ar = Ph) and compared the results with those for the phenylhydrazone of 3-benzoyl-5-phenyl-1,2,4-oxadiazole (Ia; R = Ar = Ph).[2b,8]

Results and Discussion

The apparent first-order kinetic constants, k_A, for the rearrangements of compounds (Ia and c—g) in benzene, at 313 K, in the presence of piperidine, are summarized in Table 1. As usual a more than linear increase of k_A with increasing [PIP] is observed; on the other hand a plot (not shown) of k_A/PIP *versus* PIP is linear. In the case of the phenylhydrazones (Ic—f) the intercepts are not statistically different from zero (Table 2); thus the reactions are of the third order overall (second order in amine). Compounds (Ia) and (Ig) show, on the contrary, intercepts different from zero; a second-order and a third-order catalytic pathway are thus implied (Table 2).

The catalytic pattern observed agrees with expectations based on the electronic effects exerted by the 5-alkyl substituents in that their electron-repelling effect makes the group R–C(5)–O a worse leaving group in the case of (Ic—f) than in the case of (Ia) and (Ig). For the same reason as no second-order catalytic constant is observed for compounds (Ic—f), the corresponding k_{III} values are lower than those relative to (Ia) and (Ig); moreover they are very similar to each other and independent of the steric requirements of the 5-alkyl group.

Table 2. Linear regression analysis [a] of apparent first-order kinetic constants for the rearrangements (Ia and c—g) $\longrightarrow$ (IIa and c—g), at 313.15 K in benzene, in the presence of piperidine according to equation: $k_A/[\text{PIP}] = k_{II} + k_{III}[\text{PIP}]$

Compd.	$10^5(k_{II} \pm s_{II})$ $\text{l mol}^{-1}\ \text{s}^{-1}$	$10^5(k_{III} \pm s_{III})$ $\text{l}^2\ \text{mol}^{-2}\ \text{s}^{-1}$	n	R
(Ia) [b]	0.321 ± 0.004	7.65 ± 0.06	9	0.9999
(Ic)	0.01 ± 0.00	1.17 ± 0.01	9	0.9999
(Id)	0.00 ± 0.00	1.14 ± 0.01	9	0.9999
(Ie)	0.01 ± 0.01	1.19 ± 0.01	10	0.9998
(If)	0.01 ± 0.00	1.14 ± 0.01	10	0.9999
(Ig)	2.58 ± 0.09	18.3 ± 0.1	11	0.9998

[a] s_{II} and s_{III} are the standard deviations of the regression parameters k_{II} and k_{III}, respectively; R is the correlation coefficient. The confidence levels for significance of regression parameters are all better than 99.9%. [b] From ref. 8*b*.

The apparent first-order kinetic constants, k_A, for the rearrangements of compounds (Ic—g) in dioxane–water at 313 K, in the presence of buffers, in the pS^+ range 4.0—12.0, are summarized in Tables A—E; * a plot of log k_A *versus*

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* These Tables are available in Supplementary Publication No. SUP 23793 (7 pp.) (see Instructions for Authors, *J. Chem. Soc., Perkin Trans. 2*, 1984, Issue 1). The kinetic measurements in dioxane–water have been performed at various temperatures in order to recalculate the k_A values from activation parameters. The activation parameters are relevant only in the low pS^+ plateau (uncatalysed reaction pathway); at higher pS^+ they are of doubtful interpretation because the kinetic constants, k_A, are composite values depending upon more reaction processes. As we have already pointed out [8a] the high and constant values observed for activation parameters agree with an S_Ni-type reaction with a highly solvated transition state, the formation of which is associated with a partial loss of stabilization resonance energy of the 1,2,4-oxadiazole ring only in part balanced by the gain derived from incipient formation of the new heterocycle (1,2,3-triazole).

Table 3. Apparent first-order rate constants [a] for the rearrangements (Ia and c—g) ⟶ (IIa and c—g), k_A, in acetonitrile in the presence of piperidine

					At 313.15 K							
(Ic) [b]												
10^2[PIP]/M	0.158	0.315	0.630	0.963	1.50	1.98	2.46	3.05	3.50	3.90	4.81	5.50
10^3k_A/s^{-1}	0.125	0.182	0.308	0.439	0.689	0.929	1.17	1.48	1.77	2.00	2.61	3.13
(Id) [c]												
10^2[PIP]/M	0.148	0.297	0.594	0.990	1.48	1.98	2.46	2.97	3.47	3.96	4.45	4.95
10^3k_A/s^{-1}	0.106	0.167	0.272	0.457	0.677	0.945	1.17	1.44	1.75	2.05	2.36	2.72
(Ie) [d]												
10^2[PIP]/M	0.155	0.315	0.720	1.10	1.55	2.05	2.50	3.15	3.50	4.05	4.50	5.25
10^3k_A/s^{-1}	0.0937	0.146	0.259	0.385	0.558	0.752	0.945	1.25	1.42	1.73	1.97	2.43
(If) [e]												
10^2[PIP]/M	0.155	0.309	0.515	1.03	1.55	2.06	2.58	3.09	3.61	4.12	4.64	5.15
10^3k_A/s^{-1}	0.0617	0.101	0.156	0.293	0.461	0.614	0.812	0.992	1.20	1.41	1.62	1.92
(Ig) [f]												
10^2[PIP]/M	0.152	0.303	0.505	0.758	1.01	1.52	2.02	2.53	3.03			
10^3k_A/s^{-1}	1.48	3.00	4.83	7.27	9.80	14.6	19.2	24.0	28.8			
					At 283.15 K							
(Ia) [g]												
10^2[PIP]/M	0.773	1.55	3.10	4.65	6.20	7.75	10.3	12.4	15.5	18.0	20.6	
10^3k_A/s^{-1}	0.270	0.533	1.09	1.66	2.25	2.90	4.06	5.06	6.68	8.05	9.58	
(Ig) [f]												
10^2[PIP]/M	0.750	1.50	3.00	4.50	7.00	10.0	12.0	15.0	18.5	20.0		
10^3k_A/s^{-1}	0.780	1.56	3.15	4.83	7.91	12.0	15.0	19.7	25.6	28.4		

[a] The rate constants are accurate to within ±3%. [b] [(Ic)] 1.81 × 10^{-4}M. At $\lambda_{max.}$ 360 nm, log ε 4.29 ± 0.02. [c] [(Id)] 1.74 × 10^{-4}M. At $\lambda_{max.}$ 360 nm, log ε 4.30 ± 0.02. [d] [(Ie)] 1.80 × 10^{-4}M. At $\lambda_{max.}$ 360 nm, log ε 4.30 ± 0.02. [e] [(If)] 1.55 × 10^{-4}M. At $\lambda_{max.}$ 360 nm, log ε 4.29 ± 0.02. [f] [(Ig)] 2.05 × 10^{-4}M. At $\lambda_{max.}$ 360 nm, log ε 4.22 ± 0.02. [g] [(Ia)] 1.80 × 10^{-4}M. At $\lambda_{max.}$ 364 nm, log ε 4.23 ± 0.02.

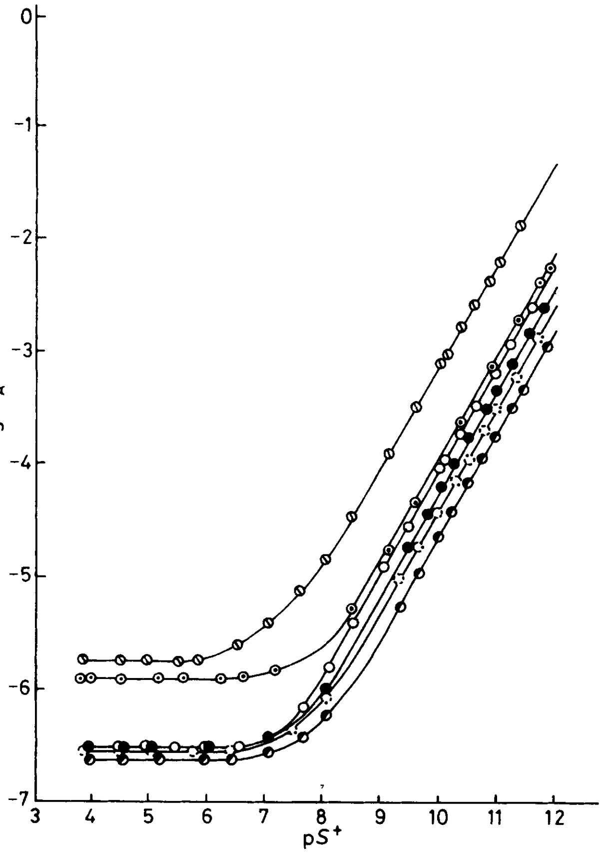

Figure. Plot of log k_A [(◐) (Ig); (○) (Ia); (○) (Ic); (●) (Id); (○) (Ie); (◐) (If)] at 313.15 K in dioxane–water (1 : 1 v/v) *versus* pS^+

pS^+ (Figure) shows the occurrence of the two usual pathways for the rearrangement; the one, at lower pS^+ values, pS^+-independent, the other, at higher pS^+ values, base catalysed.* The rearrangement rate is only moderately affected by the substituent variation, the reactivity ratios $[(k_A)_{Me}/(k_A)_{Bu^t}]$ being 1.3 and 4.0 in the pS^+-independent and pS^+-dependent ranges, respectively. Also in this solvent (Ia and g) react faster than (Ic—f) (see above).

The apparent first-order kinetic constants, k_A, for the rearrangement of compounds (Ia and c—g) in acetonitrile, at 313 K, in the presence of piperidine, are set out in Table 3. The more than linear increase of k_A with increasing [PIP] for compounds (Ic—f) (Figure †) agrees with the general catalysis law described by equation (1).

$$k_A = k_u + k_{II}[\text{PIP}] + k_{III}[\text{PIP}]^2 \qquad (1)$$

Since the uncatalysed pathway, as measured by k_u, makes a significant contribution to the overall rate, we could not use equation (2), as previously,[2b] to calculate the second-order (k_{II}) and third-order (k_{III}) catalytic constants.

$$k_A/[\text{PIP}] = k_{II} + k_{III}[\text{PIP}] \qquad (2)$$

However, we could calculate k_u, k_{II}, and k_{III} by multiple linear regression analysis of kinetic data according to equation (1).

In the case of (Ia) and (Ig) the plot of k_A *versus* [PIP] is linear over the whole range of concentrations and this allows the calculation of k_u and k_{II}. Following the kinetics of

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* As previously shown,[9] in this pS^+ range the mechanism of mononuclear heterocyclic rearrangement would imply a general base catalysis.

† In the Supplementary Publication.

Table 4. Linear regression analysis[a] of apparent first-order kinetic constants for the rearrangements (Ia and c—g) → (IIa and c—g) in acetonitrile, in the presence of piperidine according to the equation: $k_A = k_u + k_{II}[PIP] + k_{III}[PIP]^2$

Compound	$k_u \pm s_u$ / s^{-1}	$k_{II} \pm s_{II}$ / $l\ mol^{-1}\ s^{-1}$	$k_{III} \pm s_{III}$ / $l^2\ mol^{-2}\ s^{-1}$	n	R	k_{III}/k_{II} / $l\ mol^{-1}$
			At 313.15 K			
(Ia)[b]	$(2.78 \pm 0.88)10^{-4}$	$(4.54 \pm 0.04)10^{-1}$		9	0.9997	
(Ic)	$(6.78 \pm 0.62)10^{-5}$	$(3.58 \pm 0.06)10^{-2}$	$(3.59 \pm 0.10)10^{-1}$	12	1.0000	10
(Id)	$(4.94 \pm 0.77)10^{-5}$	$(3.76 \pm 0.08)10^{-2}$	$(3.26 \pm 0.15)10^{-1}$	12	0.9999	8.7
(Ie)	$(5.09 \pm 0.41)10^{-5}$	$(2.71 \pm 0.04)10^{-2}$	$(3.48 \pm 0.07)10^{-1}$	12	1.0000	13
(If)	$(2.74 \pm 1.01)10^{-5}$	$(2.36 \pm 0.10)10^{-2}$	$(2.46 \pm 0.19)10^{-1}$	12	0.9998	10
(Ig)	$(1.10 \pm 0.43)10^{-4}$	$(9.47 \pm 0.03)10^{-1}$		9	1.0000	
			At 283.15 K			
(Ia)	$(2.06 \pm 0.97)10^{-5}$	$(3.19 \pm 0.02)10^{-2}$	$(7.08 \pm 0.11)10^{-2}$	11	1.0000	2.2
(Ig)	$(1.33 \pm 3.39)10^{-5}$	$(9.81 \pm 0.09)10^{-2}$	$(2.19 \pm 0.04)10^{-1}$	10	1.0000	2.2

[a] s_u, s_{II}, and s_{III} are the standard deviations of the regression parameters k_u, k_{II}, and k_{III}, respectively; R is the correlation coefficient. The confidence levels for significance of regression parameters are all better than 99.9%. [b] From ref. 2*b*.

rearrangement of (Ia) at a lower temperature (283 K) we could extend the reactivity range to [PIP] values as high as 0.08—0.2M. At these concentrations k_A increases more than linearly with [PIP] and this makes possible the calculation of k_{III} for this compound also. The k_u, k_{II}, and k_{III} values calculated for compounds (Ia and c—g) are in Table 4. The k_{III}/k_{II} ratio relative to (Ia) is lower than those calculated for (Ic—g) and recalls the situation observed in benzene.

The variations of the catalytic coefficients as a function of the alkyl substituent are small: $(k_u)_{Me}/(k_u)_{Bu^t} = 2.5$; $(k_{II})_{Me}/(k_{II})_{Bu^t} = 1.5$; $(k_{III})_{Me}/(k_{III})_{Bu^t} = 1.4$, (Ia and g) being, as a whole, more reactive than (Ic—f).

As a whole, the results obtained in benzene, dioxane–water, and acetonitrile show that the nature of the 5-alkyl substituent has only a little influence on the rearrangement rate of the phenylhydrazones (Ic—f). This fact constitutes proof against the mechanism involving an addition at the C(5)–N(4) bond of the 1,2,4-oxadiazole ring for the catalytic pathways requiring more than one molecule of amine. In contrast this addition should be strongly affected by the steric requirements of substituents at C(5) and the relative logarithmic kinetic constants should be linearly correlated with the steric parameters (E_S or ν).[*] The small variations in reactivity observed are to be attributed to the small variations in the electronic effects of the 5-alkyl substituents which control the leaving group ability of the C(5)–O system.[†] This point of view is supported by the behaviour of compounds (Ia and g), which react faster than (Ic—f) by virtue of the electronic effects exerted by hydrogen and phenyl substituents.[‡]

Table 5. Physical data of compounds (Id—f), (IId—f), and (IIId—f)

Compd.	M.p. (°C)	$\nu_{max.}$(Nujol)/cm^{-1} NH	$\nu_{max.}$(Nujol)/cm^{-1} C=O	δ($CDCl_3$)
(Id)	53—54[a]	3 250		1.5 (t, 3 H, CH_2CH_3), 3.10 (q, 2 H, CH_2CH_3), 7.0—8.2 (m, 10 H, 2 Ph), 11.50 (s, 1 H, NH)
(Ie)	91—92[a]	3 240		1.45 [d, 6 H, $CH(CH_3)_2$], 3.4 [m, 1 H, $CH(CH_3)_2$], 6.9—8.15 (m, 10 H, 2 Ph), 11.55 (s, 1 H, NH)
(If)	96[a]	3 250		1.50 (s, 9 H, 3 CH_3), 7.0—8.2 (m, 10 H, 2 Ph), 11.65 (s, 1 H, NH)
(IId)	175[b]	3 250	1 670	1.30 (t, 3 H, CH_2CH_3), 2.55 (q, 2 H, CH_2CH_3), 7.4—8.3 (m, 11 H, NH, 2 Ph)
(IIe)	179[b]	3 230	1 665	1.30 [d, 6 H, $CH(CH_3)_2$], 2.7 [m, 1 H, $CH(CH_3)_2$], 7.35—8.30 (m, 11 H, NH, 2 Ph)
(IIf)	192[b]	3 240	1 655	1.28 (s, 9 H, 3 CH_3), 7.5—8.3 (m, 10 H, 2 Ph), 10.05 (s, 1 H, NH)[c]
(IIId)	38[a]		1 660	1.5 (t, 3 H, CH_2CH_3), 3.15 (q, 2 H, CH_2CH_3), 7.5—8.5 (m, 5 H, Ph)
(IIIe)	Oil		1 670	1.5 [d, 6 H, $CH(CH_3)_2$], 3.45 [m, 1 H, $CH(CH_3)_2$], 7.45—8.6 (m, 5 H, Ph)
(IIIf)	Oil		1 680	1.52 (s, 9 H, 3 CH_3), 7.40—8.50 (m, 5 H, Ph)

[a] From light petroleum. [b] From ethanol. [c] In $(CD_3)_2SO$.

Experimental

Synthesis and Purification of Compounds.—Compounds (Ia, c, and g),[11] and (IIa, c, and g),[11] piperidine,[12] benzene,[12] dioxane,[12] and acetonitrile[13] were prepared and/or purified according to the methods reported previously. *Compounds* (Id—f) were prepared from the corresponding 3-benzoyl-5-ethyl- (IIId), 3-benzoyl-5-isopropyl- (IIIe), and 3-benzoyl-5-t-butyl-1,2,4-oxadiazole (IIIf) with phenylhydrazine in ethanol in the presence of acetic acid. Purification was achieved by chromatography and/or crystallization. Thermally induced rearrangement of the phenylhydrazones (Id—f) gave the *triazoles* (IId—f), quantitatively. The *Z*-structure of all phenylhydrazones employed was confirmed by u.v., i.r., and n.m.r. spectra, as described for (Ia).[14] The *oxadiazolyl ketones* (IIId—f) were prepared through the reactions of phenylglyoxyloyl chloride oxime and propionaldehyde oxime, isobutyraldehyde oxime, and pivalaldehyde oxime, respectively, in refluxing toluene, according to the procedure reported,[15] followed by chromatography of the reaction mixture

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[*] Except for the reactions in dioxane–water (base-catalysed range) for which a significant linear correlation does exist between log k_A and E_S or ν (n 5; r 0.940 or 0.947), in all the other cases [reactions in benzene, acetonitrile, and dioxane–water (pS^+-independent range)] there is no correlation between log k_A and the steric parameters.

[†] Accordingly, for all the solvents studied, the k_A values give a satisfactory linear correlation with σ constants.

[‡] The $(k_A)_{Ph}/(k_A)_{Me}$ ratios observed by us are very similar to those measured by Korbonits *et al.* for the rearrangement of some 3-(2-aminoaryl)-1,2,4-oxadiazoles into 3-acylaminoindazoles.[10]

(yields 30%, not optimized). All new compounds gave satisfactory elemental analytical data. Physical data are reported in Table 5.

pS^+ *and Kinetic Measurements.*—The previously reported techniques were used throughout.[8a] The wavelengths and log ε values at the maximum used for spectrophotometric determinations of kinetic constants are reported in Tables 1 and 3, and in the Supplementary Publication.

Acknowledgements

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