

Mononuclear Heterocyclic Rearrangements. Part III (1).
Rearrangement of the *p*-Methoxyphenylhydrazone and the *m*-Nitrophenylhydrazone of 3-Benzoyl-5-phenyl-1,2,4-oxadiazole in
Dioxane/Water in the pS^+ Range 3.8-11.5

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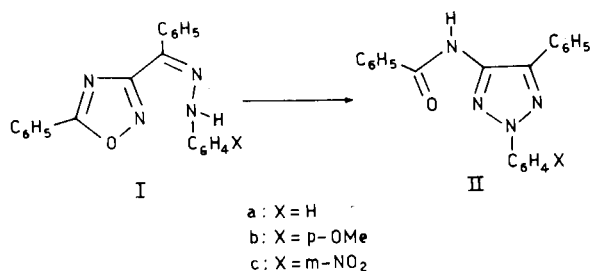
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The rates of the mononuclear heterocyclic rearrangement of the *p*-methoxyphenylhydrazone (Ib) and the *m*-nitrophenylhydrazone (Ic) of 3-benzoyl-5-phenyl-1,2,4-oxadiazole have been measured in the range of pS^+ 3.8-11.5 (solvent: dioxane/water 1:1, v:v) and compared with those of the unsubstituted phenylhydrazone (Ia). The obtained results show that in the base-catalyzed range, electron-repelling as well as electron-withdrawing substituents accelerate the rearrangement rates.

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Studying the mononuclear heterocyclic rearrangements (2) of some arylhydrazones of 3-benzoyl-5-phenyl-1,2,4-oxadiazole into 2-aryl-4-benzoylamino-5-phenyl-1,2,3-triazoles at pS^+ 3.8 we collected data that allowed us to confirm the possible mechanism (internal nucleophilic displacement by nitrogen on nitrogen) of the rearrangement in the pS^+ independent range (1). This mechanism was first formulated by us (3) studying the rearrangement of phenylhydrazone (Ia) in the range 3.8-12.2.

In order to give information about the mechanism in the base-catalyzed range we now report data relative to the rearrangement of the *p*-methoxyphenylhydrazone (Ib) and the *m*-nitrophenylhydrazone (Ic) at high pS^+ values. We give complete kinetic data in the whole range 3.8-11.5 to show that the pS^+ ranges where one of the two possible mechanisms can operate are a function of the substituent which is present.



Results and Discussion.

At each studied pS^+ , compounds Ib and Ic rearrange to the triazoles IIb and IIc in high yields (>98%, as determined by uv-visible spectral analysis at infinity). The kinetic data obtained in the temperature range 10-60° are reported in Tables I-II together with activation parameters. A logarithmic plot of kinetic data *versus* pS^+ is presented in Figure which also contains our previous results on the rearrangement of Ia (3).

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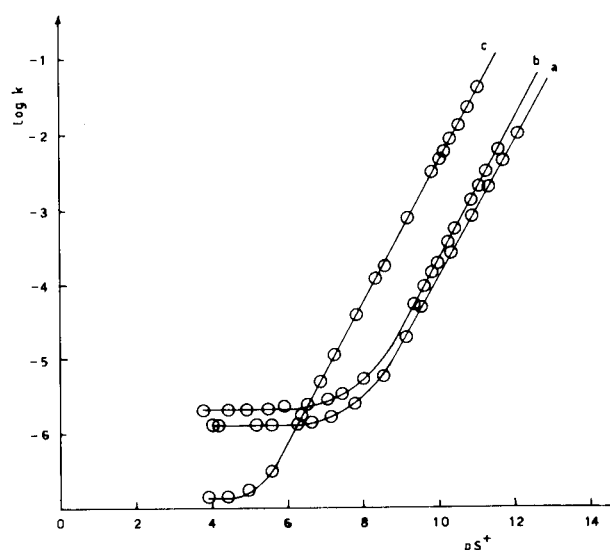


Figure: Plot of $\log k$ at 40° for the rearrangement I-II *versus* pS^+ in dioxane/water (1:1, v:v).
Curve a: X = H; b: X = *p*-OMe; c: X = *m*-NO₂

An examination of the Figure allows the following observations to be made. Firstly one can observe that the beginning of the base-catalyzed path is affected by the nature of the present substituent; the change over of mechanism occurs in the pS^+ range 6.5-8.0 for the *p*-methoxyphenylhydrazone (Ib) and the unsubstituted phenylhydrazone (Ia), and in the pS^+ range 4.8-5.3 for the *m*-nitrophenylhydrazone (Ic). This fact together with the observation that the first two curves have quite a similar shape while that of the *m*-nitrophenylhydrazone (Ic) is different, agrees with a different tendency of the substituted substrate to change the mechanism of rearrangement as a function of the present substituent, which affects the acid character of the hydrogen atom linked to the α -nitrogen of the arylhydrazone moiety.

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Table I

Kinetic Data and Activation Parameters for the Rearrangement of Ib
into IIb in Dioxane/Water (1:1, v:v)

pS^+	$10^6 k, s^{-1}$,	at various temperatures	(°C) (a)	$-\log k$ (b)	ΔH^\ddagger (c) kcal mole ⁻¹	ΔS^\ddagger (d) u.e.
3.78 (e)	2.16 (41.0)	7.29 (51.2)	18.7 (60.3)	5.711	22.7	-12.3
4.40 (e)	1.86 (39.9)	6.85 (51.2)	18.8 (60.2)	5.728	23.0	-11.4
4.90 (e)	2.28 (41.3)	6.85 (51.2)	17.9 (60.2)	5.709	22.1	-14.2
5.43 (e)	1.90 (39.9)	7.51 (51.2)	20.7 (60.2)	5.715	23.8	-8.7
5.90 (e)	2.51 (41.3)	8.39 (51.2)	21.6 (60.3)	5.662	23.0	-11.0
6.50 (e)	2.27 (39.9)	8.67 (51.2)	22.5 (60.2)	5.635	22.9	-11.5
7.05 (e)	2.95 (40.6)	9.21 (50.4)	26.6 (60.2)	5.581	23.3	-9.7
7.45 (e)	3.28 (40.0)	11.2 (51.1)	34.2 (60.2)	5.497	23.4	-9.1
8.00 (e)	5.03 (39.9)	20.4 (51.2)	59.0 (60.3)	5.293	24.4	-4.9
9.38 (f)	51.6 (40.1)	189 (51.4)	497 (60.4)	4.294	22.6	-6.1
9.65 (f)	86.8 (40.1)	286 (50.8)	807 (60.5)	4.070	22.2	-6.6
9.85 (f)	134 (40.1)	395 (50.1)	1151 (60.4)	3.877	21.3	-8.3
9.99 (f)	56.8 (30.1)	173 (40.1)	513 (49.9)	3.757	21.0	-8.9
10.29 (f)	106 (30.1)	335 (40.1)	958 (49.8)	3.485	21.6	-5.7
10.47 (f)	49.0 (20.0)	162 (30.1)	498 (39.9)	3.304	20.9	-7.1
10.89 (f)	112 (19.9)	384 (30.1)	1225 (40.0)	2.913	21.2	-4.3
11.10 (f)	185 (20.0)	606 (30.2)	1961 (40.1)	2.721	20.9	-4.5
11.31 (f)	68.9 (10.0)	263 (20.0)	914 (30.0)	2.528	21.5	-1.6
11.62 (f)	137 (10.0)	519 (20.0)	1930 (30.6)	2.242	21.3	-0.8

(a) The rate constants are accurate to better than $\pm 3\%$. (b) At 40°, values calculated from activation parameters. (c) At 40°, the probable error is 0.6 kcal mole⁻¹. (d) At 40°. (e) Buffer, citrate. (f) Buffer, borate.

Table II

Kinetic Data and Activation Parameters for the Rearrangement of Ic
into IIc in Dioxane/Water (1:1, v:v)

pS^+	$10^6 k, s^{-1}$,	at various temperatures	(°C) (a)	$-\log k$ (b)	ΔH^\ddagger (c) kcal mole ⁻¹	ΔS^\ddagger (d) u.e.
3.85 (e)	0.14 (40.1)	0.51 (50.4)	1.61 (60.2)	6.850	24.4	-12.1
4.40 (e)	0.14 (40.1)	0.52 (50.4)	1.63 (60.2)	6.848	24.4	-11.9
4.93 (e)	0.19 (40.1)	0.74 (51.2)	2.15 (60.2)	6.738	24.7	-10.7
5.56 (e)	0.30 (40.1)	1.13 (51.2)	3.21 (60.2)	6.525	23.7	-12.8
6.36 (e)	1.75 (40.1)	6.90 (51.2)	20.7 (60.2)	5.765	24.8	-5.8
6.82 (e)	4.58 (40.0)	16.4 (50.0)	55.1 (60.2)	5.339	24.8	-3.5
7.22 (c)	10.6 (40.0)	37.6 (50.0)	127 (60.2)	4.975	24.9	-2.0
7.80 (e)	34.7 (40.0)	122 (50.0)	392 (59.7)	4.461	24.9	+0.4
8.30 (e)	110 (40.0)	391 (50.0)	1244 (59.7)	3.957	24.9	+2.6
9.20 (f)	70.8 (20.1)	243 (30.0)	733 (40.0)	3.131	20.7	-6.8
9.57 (f)	44.1 (10.0)	149 (20.0)	537 (30.0)	2.791	20.7	-5.3
9.85 (f)	81.7 (10.0)	293 (20.0)	955 (30.0)	2.536	20.4	-5.2
10.05 (f)	119 (10.0)	441 (20.0)	1412 (30.0)	2.359	20.5	-4.0
10.15 (f)	149 (10.0)	559 (20.0)	1780 (30.0)	2.256	20.6	-3.2
10.35 (f)	219 (10.0)	794 (20.0)	2660 (30.0)	2.085	20.7	-2.1
10.55 (f)	354 (10.0)	1259 (20.0)	4160 (30.0)	1.898	20.4	-2.1
10.80 (f)	562 (10.0)	1994 (20.0)	6910 (30.0)	1.673	20.8	+0.1
11.09 (f)	1047 (10.0)	3802 (20.0)	12880 (30.0)	1.398	20.8	+1.4

(a) The rate constants are accurate to better than $\pm 3\%$. (b) At 40°, values calculated from activation parameters. (c) At 40°, the probable error is 0.6 kcal mole⁻¹. (d) At 40°. (e) Buffer, citrate. (f) Buffer, borate.

A second observation concerns the relative reactivity at each pS^+ . In fact, as already pointed out by us (1) in the range pS^+ -independent, the rearrangement rate is a simple function of the nucleophilicity of α -nitrogen atom of the arylhydrazone moiety (reactivity order: $Ib > Ia \gg Ic$). In the base-catalyzed range one can expect a reactivity order inverted with respect to the above sequence if a unique mechanism is operating independently of the nature of substituents and if the limiting factor is the hydrogen atom acidity. On the contrary, we have observed that both the *m*-nitrophenylhydrazone (Ic) and the *p*-methoxyphenylhydrazone (Ib) rearrange faster than unsubstituted phenylhydrazone (Ia).

This data indicates a situation which is *pro* a nonlinear Hammett (4) plot and probably *pro* a change over of mechanism as a function of the present substituent, in the base-catalyzed range.

EXPERIMENTAL

Synthesis and Purification of Compounds.

Compounds Ib-c (*Z*-isomers), IIb-c, water and dioxane were prepared and/or purified as previously reported (1).

pS^+ and Kinetic Measurements.

pS^+ Measurements were made as previously described (1,3). The kinetics (at constant ionic strength: 0.05 *M*) were followed

spectrophotometrically, as previously reported (1,3), by measuring the disappearance of Ib and Ic respectively at 380 and 348 nm.

The apparent first order kinetic constants are collected in Tables I and II. The concentrations used were about $6 \cdot 10^{-5}$ *M*.

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