

Vincenzo Frenna and Nicolò Vivona

Institute of Organic Chemistry, University of Palermo, Via Archirafi 20, Palermo 90123, Italy

Domenico Spinelli and Giovanni Consiglio

Cattedra di Chimica Organica, Faculty of Pharmacy, University of Bologna, Via Zanolini, 3, Bologna 40126, Italy

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The kinetic behaviour of the geometrical isomers I-*E* and I-*Z* of the title compound in the presence of piperidine in benzene has been investigated. The kinetic results suggest that I-*Z* rearranges directly into 2,5-diphenyl-4-benzoylamino-1,2,3-triazole (II), whereas I-*E* probably rearranges only through the intermediate I-*Z* formed by isomerization. All the reactions studied are piperidine-catalyzed.

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Recently we have reported (1) the synthesis and the characterization of the (*E*)-phenylhydrazone of 3-benzoyl-5-phenyl-1,2,4-oxadiazole (I-*E*), and pointed out that it can either isomerize (2) to the *Z*-isomer (I-*Z*) or rearrange (3) into 2,5-diphenyl-4-benzoylamino-1,2,3-triazole. On the other hand, it is well known that I-*Z* rearranges to II (4). Therefore, the following question (see Scheme) arises. Does I-*E* rearrange directly to II, or does it isomerize before to I-*Z*? To answer this question we have started a kinetic study of the rearrangements of I-*E* and I-*Z* in benzene in the presence of piperidine as a catalyst, by uv-visible spectral analysis of the composition of the reaction mixture.

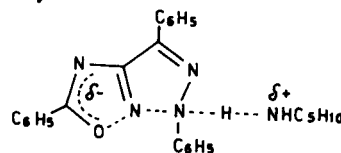
## Results and Discussion.

### Rearrangement of I-*Z*.

The rearrangement of I-*Z* into II has already been studied in dioxane-water (1:1 v/v). A reaction mechanism has been proposed and the effect of the  $pS^+$  on the reaction course has been elucidated (5). Now we report data concerning the reaction in benzene in the presence of piperidine at 40°. Kinetic runs at various piperidine concentrations show that the apparent rate coefficients for the rearrangement  $[(k_A)_R]$  depend on piperidine concentration ([PIP]) (see Table 1). A plot of  $(k_A)_R$  vs. [PIP] (Figure 1) shows a more than linear increase of  $(k_A)_R$  with increas-

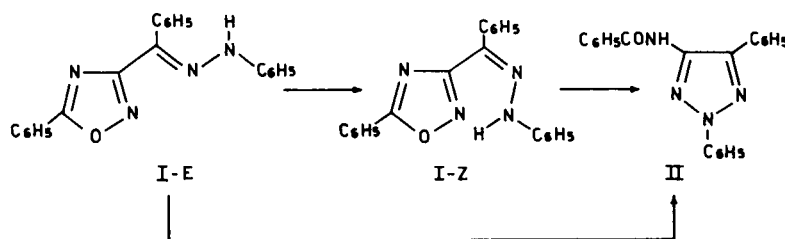
ing [PIP] and the curve crosses the origin, indicating that the reaction is wholly piperidine catalyzed and that no uncatalyzed pathway occurs. On the other hand, a plot of  $(k_A)_R/[PIP]$  vs. [PIP] (Figure 1) is linear over the whole range studied (0.2-1.0M) and this allows a second order kinetic constant (from the intercept) and a third order kinetic constant (from the slope) to be calculated. The experimental data fit the following relation well ( $n = 9$ ,  $r = 0.9999$ ),  $(k_A)_R/[PIP] = (3.21 \pm 0.04) \times 10^{-6} \text{ l. mole}^{-1} \text{ s}^{-1} + (7.65 \pm 0.06) \times 10^{-5} \text{ l.}^2 \text{ mole}^{-2} \text{ s}^{-1} [\text{PIP}]$  pointing out the occurrence of two different catalyzed pathways, thus implying one or two molecules of piperidine, respectively.

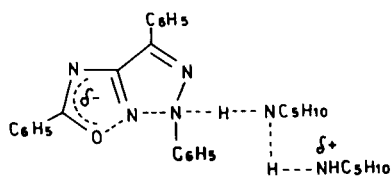
Bearing in mind the mechanism proposed for the rearrangement of I-*Z* in the base catalyzed range (5), one can suggest the following transition state for the second order reaction pathway.



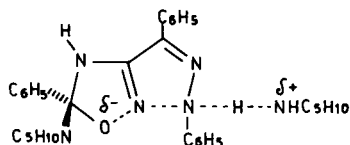
In the case of the third order reaction pathway one can suggest two possible actions for the second molecule of piperidine: (a) it exerts the so called catalysis of catalysis (6), *i.e.*, it helps the first molecule of piperidine to disperse its incipient positive charge as indicated; (b) it favours the

### SCHEME





progress of the reaction *e.g.* through an interaction with the 1,2,4-oxadiazole ring such as the addition at the C<sub>5</sub>-N<sub>4</sub> bond proposed by Harsanyi (7) for rearrangements implying other 1,2,4-oxadiazole derivatives.



It seems unlikely that piperidine acts as a dimer; in fact in several other reactions catalyzed by piperidine or by other similar amines (see also below), this behaviour has not been observed (8,9). At present we are not able to make a choice between these two or other possible pathways.

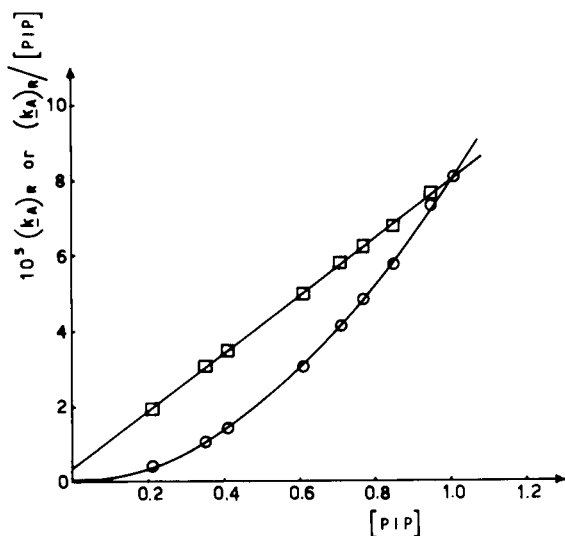


Figure 1. Plot of rearrangement kinetic constants  $(k_A)_R$  (o) or  $(k_A)_R/[PIP]$  (□) at 40°C in benzene. For the linear plot  $n$  9,  $r$  0.9999, C.L. > 99.95%.

#### Isomerization and Rearrangement of (I-E).

As we have pointed out, I-E can either isomerize to I-Z or rearrange into II (1). In order to clarify the course of these reactions we have measured the apparent rate coefficients of rearrangement of I-E into II by treatment with piperidine (1M) at 40°. The rate constant obtained ( $\sim 1 \times 10^{-5} \text{ s}^{-1}$ ), when compared with the analogous data ( $\sim 8 \times 10^{-5} \text{ s}^{-1}$ ) obtained for the rearrangement of I-Z, shows that I-Z rearranges faster than I-E and therefore confirms that

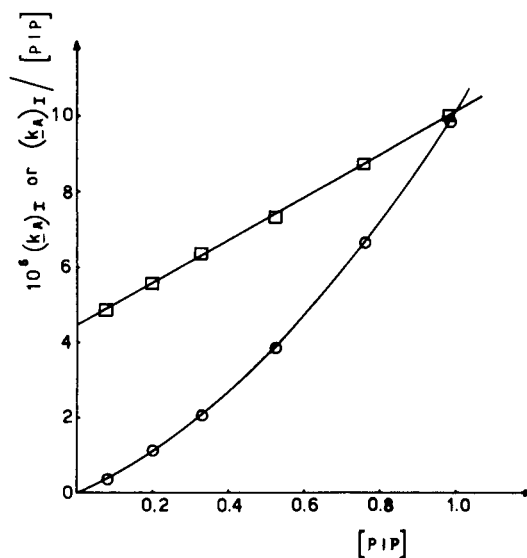


Figure 2. Plot of isomerization kinetic constants  $(k_A)_I$  (o) or  $(k_A)_I/[PIP]$  (□) vs. [PIP] at 40°C in benzene. For the linear plot  $n$  6,  $r$  0.9998, C.L. > 99.95%.

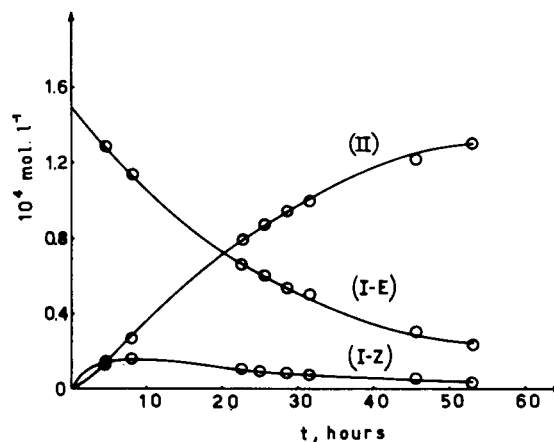


Figure 3. Plot of [(I-E)], [(I-Z)], and [(II)] vs. reaction time at [PIP] 0.985 mole  $\text{l}^{-1}$ .

two reaction pathways are possible for the I-E  $\rightarrow$  II rearrangement (see Scheme).

To select between the three possibilities: *viz.*, (a) I-E  $\rightarrow$  I-Z  $\rightarrow$  II; (b) I-E  $\rightarrow$  II; and (c) a linear combination of (a) and (b), we have measured the concentrations of the disappearing I-E and of the formed I-Z and II during the course of the reaction as a function of the reaction time.

The values of the instantaneous concentrations of the three species present fit well only in pathway a (10) with the rate constant of rearrangement of I-Z into II previously determined; *i.e.*, the rearrangement of I-E into II proceeds only through the intermediate formation of I-Z.

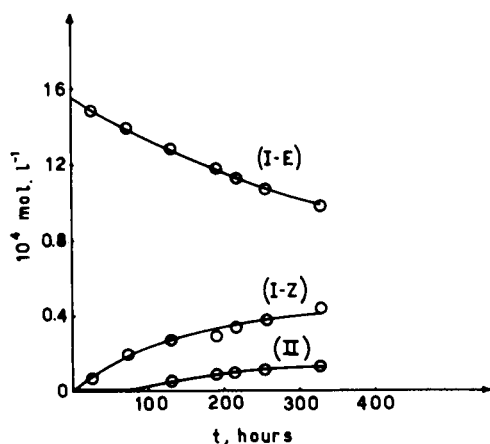


Figure 4. Plot of  $[I-E]$ ,  $[I-Z]$ , and  $[II]$  vs. reaction time at  $[PIP]$   $0.080 \text{ mole l.}^{-1}$

Thus, we have calculated the apparent rate coefficients of isomerization of I-E into I-Z (see Table 2). These values depend only a little more than linearly on piperidine concentration and the obtained curve (Figure 2) crosses the origin, showing that also this reaction is wholly piperidine catalyzed. A plot of  $(k_A)_I/[PIP]$  vs.  $[PIP]$  is linear in the entire range which was studied ( $0.08\text{-}1.0M$ ), see above, and the data fit the following relation well ( $n$  6,  $r$  0.9998),  $(k_A)_I/[PIP] = (4.42 \pm 0.03) \times 10^{-6} \text{ l. mole}^{-1} \text{ s}^{-1} + (5.63 \pm 0.05) \times 10^{-6} \text{ l.}^2 \text{ mole}^{-2} \text{ s}^{-1} [PIP]$ . Because of the low ratio between the third and the second order kinetic constants ( $k_{III}/k_{II} \sim 1.3$ ), we suggest that the trend observed is probably due to a medium effect. Indeed the addition of polar substances (e.g., piperidine) to the solvent (benzene) can affect the reaction rate by changing the reaction medium (9).

Table 1

Apparent First Order Rate Constants for the Rearrangement  $(k_A)_R$  of I-Z (a) into II in Benzene at  $40^\circ$  in the Presence of Piperidine

$[PIP]$ , mole, $\text{l.}^{-1}$	0.21	0.35	0.41	0.61	0.71	0.77	0.85	0.95	1.01
$10^5(k_A)_R$ , $\text{s}^{-1}$	0.40	1.06	1.42	3.04	4.11	4.81	5.76	7.29	8.08

(a)  $[I-Z]$   $1.47 \times 10^{-4} \text{ mole l.}^{-1}$

Table 2

Apparent First Order Rate Constants for the Isomerization  $(k_A)_I$  of I-E (a) into I-Z in Benzene at  $40^\circ$  in the Presence of Piperidine

$[PIP]$ , mole $\text{l.}^{-1}$	0.080	0.200	0.330	0.525	0.760	0.985
$10^6(k_A)_I$ , $\text{s}^{-1}$	0.39	1.12	2.09	3.84	6.62	9.83

(a)  $[I-E]$   $1.55 \times 10^{-4} \text{ mole l.}^{-1}$

Table 3

Experimental and Calculated Values of  $[I-E]$ ,  $[I-Z]$  and  $[II]$  in mole  $\text{l.}^{-1}$  at the Highest Piperidine Concentration ( $0.985 \text{ mole l.}^{-1}$ )

$10^4[I-E]$		$10^4[I-Z]$		$10^4[II]$		Time Hours
Found	Calcd. (a)	Found	Calcd. (a)	Found	Calcd. (a)	
1.49	1.49	0.060	0.057	0.008	0.011	1.25
1.28	1.27	0.145	0.139	0.135	0.146	5.75
1.13	1.12	0.154	0.145	0.272	0.288	9.25
0.663	0.671	0.103	0.097	0.789	0.787	23.75
0.598	0.603	0.093	0.088	0.864	0.864	26.75
0.535	0.542	0.081	0.079	0.939	0.934	29.75
0.497	0.488	0.071	0.071	0.987	0.996	32.75
0.299	0.297	0.048	0.043	1.21	1.21	46.75
0.228	0.228	0.031	0.033	1.30	1.29	54.25

(a) Values calculated applying the kinetic treatment relative to consecutive reactions.

The course of the reaction ( $I-E \rightarrow I-Z$ ) agrees with what is known about the  $E \rightarrow Z$  isomerization which proceeds through an addition-elimination mechanism (11).

### Conclusions.

The kinetic results obtained while investigating the behaviour of  $I-E$  and of  $I-Z$  in benzene in the presence of piperidine show that: (a)  $I-Z$  rearranges into II through two different piperidine-catalyzed pathways; and (b)  $I-E$  isomerizes into  $I-Z$  through a piperidine-catalyzed pathway. The thus formed  $I-Z$  subsequently rearranges into II. It seems reasonable to exclude the direct rearrangement of  $I-E$  into II as a relevant reaction pathway.

## EXPERIMENTAL

### Synthesis and Purification of Compounds.

Compounds  $I-E$  (1),  $I-Z$  (4b), II (4b), benzene (12) and piperidine (13) were prepared and/or purified according to the methods reported.

### Kinetic Measurements.

The kinetics of the rearrangement ( $I-Z \rightarrow II$ ) were followed spectrophotometrically by quenching the samples in benzene/acetic acid and measuring the disappearance of  $I-Z$  at the wavelength of its absorption maximum (376 nm,  $\log \epsilon$  4.24  $\pm$  0.02); compound II does not absorb at this frequency. The apparent first order kinetic constants at various piperidine concentrations with  $[I-Z] \sim 1.5 \times 10^{-4}$  mole  $l^{-1}$  are collected in Table 1.

The chemical behaviour of  $I-E$  at various piperidine concentrations was studied spectrophotometrically using solutions with initial  $[I-E] \sim 1.5 \times 10^{-4}$  mole  $l^{-1}$ . In order to obtain  $[I-E]$ ,  $[I-Z]$ , and  $[II]$  at various time intervals, samples were quenched in benzene and their uv-visible spectra were recorded. Considering the values of molar absorbance of the three compounds present, we used the optical densities in the range of 335-375 nm to calculate  $[I-E]$  and  $[I-Z]$ . In this range, II did not absorb and its concentration was calculated by difference. At each wavelength we had:

$$D = \epsilon_{I-E} [I-E] l + \epsilon_{I-Z} [I-Z] l$$

Therefore, it should be possible to calculate the concentrations of  $I-E$  and  $I-Z$  measuring the optical densities at two wavelengths. To minimize errors we have calculated the concentrations by a least square treatment on eight values of experimental optical densities.

The concentrations so obtained allowed us to calculate the kinetic constants of the  $I-E \rightarrow I-Z$  isomerization (Table 2), which we treated as an irreversible reaction (see below).

The experimental values of  $[I-E]$ ,  $[I-Z]$ , and  $[II]$  agreed well with the values calculated by applying the kinetic treatment relative to consecutive reactions (14), as indicated in Figures 3 and 4 for the highest

and the lowest piperidine concentration, respectively, and in Table 3 where experimental and recalculated concentrations are compared, at the highest piperidine concentration.

### Tlc Analysis.

Tlc analysis confirmed that the  $I-E \rightarrow II$  rearrangement proceeds through the formation of  $I-Z$ . On the other hand we have ascertained that a benzene solution of  $I-Z$  by treatment with piperidine ( $[PIP] 0.1 \div 0.6M$ ) gave II. No evidence was obtained for the formation of  $I-E$ .

### Acknowledgement.

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