

Thermal 1,3-Aroyl Migration in 1-(α -Aroyloxyarylideneamino)-1,2,3-triazoles (I)

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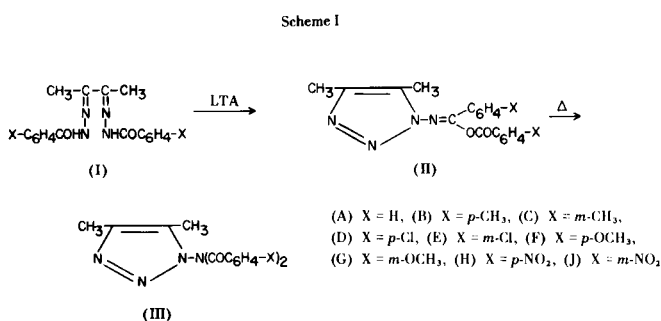
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Kinetic studies on the thermal rearrangement of the 1-(α -aroyloxyarylideneamino)-4,5-dimethyl-1,2,3-triazoles (II) to the corresponding diaroylimides (III) have shown that the 1,3-aroyl migration from oxygen to nitrogen proceeds in a concerted way and the isomerization reaction can be described as an [1,3] sigmatropic aroyl shift.

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The 1-(α -aroyloxyarylideneamino)-4,5-dimethyl-1,2,3-triazoles (II) (1,2,3-triazolyloisoimides), which are obtained (3,4,5) by oxidation of biacetyl bisaroylhydrazones (I) with lead tetraacetate (LTA) undergo uncatalyzed thermal rearrangement to the corresponding 1-(diaroylamino)-4,5-dimethyl-1,2,3-triazoles (III) (Scheme 1).



The chemistry of the isoimides, unknown for a long time, has recently drawn much attention (6) and in connection with our work (3) on the structure of the products (II), we have also undertaken a detailed investigation of the isomerization reaction of these relatively very stable triazolyl-isoimides to III.

The triazolylisoimides by heating at $\sim 150^\circ$ either in the solid state or in solution are almost quantitatively isomerized to imides (III), with a subsequent change in infrared absorption from $\sim 1750\text{ cm}^{-1}$ (ν CO, isoimide) to $\sim 1715\text{ cm}^{-1}$ (ν CO, imide). However, neither the infrared nor the ultraviolet spectra can be followed for kinetic studies, since there is an overlapping of the peaks in mixtures of II and III. Therefore, we have chosen nmr

spectroscopy as the most suitable tool for this kinetic study. The nmr spectra of isoimides (II) in deuteriochloroform solution give two peaks for the methyl protons in the region of 2.3 and 2.4 δ , with the low field peak corresponding (7) to the 5-methyl protons of the triazole ring. During the isomerization this peak (2.4 δ) is progressively reduced, with appearance of a new peak at

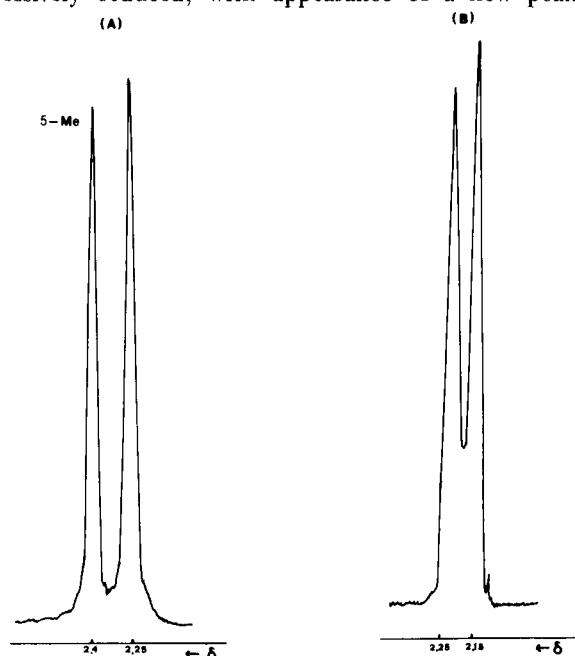


Figure 1. Nmr spectra (region of methyl protons) of the compounds (IIA) (A) and (IIIA) (B) in deuteriochloroform solution (5%).

higher field. The imides (III) have nmr peaks for the methyl protons of the triazole ring in the region of 2.3 and 2.2 δ (Figure 1).

The rearrangement of the isoimides to imides in *sym*-tetrachloroethane solution (5-10%) at 105° was followed measuring the disappearance in the nmr spectra of the 5-CH₃ protons peak in II (peak at ~ 2.4 δ). First-order plots for isoimides were linear to 90% reaction. The reaction rates k_1 (average of two values, with a repeatability of \pm 3%) calculated with a least-squares program, are given in Tables I and II.

From Table I it is seen that the influence of substituents on the rearrangement is small enough (mean value of $\rho = + 0.38$) and corresponds to the range of ρ values of other similar reaction (6a). Although in this system there is a cross-correlation for the influence of substituents (8), it is of interest that the rates follow the simple Hammett equation, the recently challenged by Davis and Pryor (9) correlation coefficient r being 0.972. However, the ρ value must be considered as an apparent one.

The data of Table II clearly show that the rates are very little affected by the addition of small amounts of trifluoroacetic acid or triethylamine [0.05M] and by changing the solvent polarity from *sym*-tetrachloroethane to benzonitrile, the relative increase of k_1 (1.2-1.5) being

Table I

Rates of Rearrangement of Isoimides (II) in Imides (III) in 1,1,2,2-Tetrachloroethane Solution at 104.8°

Substituent X	$10^5 k_1, \text{sec}^{-1}$	Substituent X	$10^5 k_1, \text{sec}^{-1}$
H	10.4	<i>p</i> -OCH ₃	7.9
<i>p</i> -CH ₃	7.9	<i>m</i> -OCH ₃	9.7
<i>m</i> -CH ₃	8.75	<i>p</i> -NO ₂	19.5
<i>p</i> -Cl	14.35	<i>m</i> -NO ₂	17.2
<i>m</i> -Cl	15.6		

small enough to suggest a polar transition state. Much more pronounced is the influence of pyridine on the rate of isomerization ($k_{\text{rel.}} = 2.9$). This reagent shows a catalytic effect, especially with *o*-substituted compounds (II), which will be the subject of another communication.

The reaction rate is almost unaffected by the addition of *p*-benzoquinone [0.05M], which reacts as an effective radical trap (10). This, in connection with the facts that: (a) the solvent used was a chlorinated hydrocarbon which interferes with free radicals (11) and (b) there was no line broadening of the nmr spectra during the isomerization process, exclude the aspect of a radical intermediate.

To investigate the possibility of intermolecular rearrangement a mixture of two different isoimides was heated, but no cross-over products could be detected.

The activation parameters of the rearrangement ($\Delta H^* = 29.2$ kcal/mole and $\Delta S^* = -9.2$ cal/mole.deg, for IIA), as well as other factors discussed above, are consistent with a four-centered transition state rather than a polar intermediate (6a,6e).

It has been shown by X-ray (4,12) and dipole moment measurements (13) that the triazolylisoimides in the crystal state and in solution adopt the (*Z*)-configuration in respect to C=N bond and for the formation of the planar transition state (IV) it is only necessary the conformation of the molecule to be changed by a rotation of the aryloxy group by about 70° (Scheme II).

Scheme II

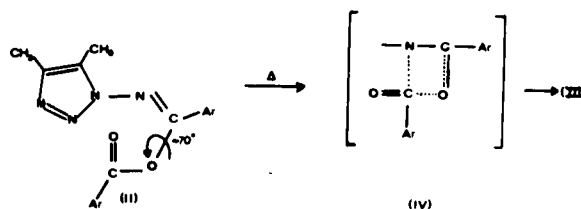


Table II

Rates of Rearrangement of IIA at Various Conditions

Solvent	Temp. °C	$10^5 k_1, \text{sec}^{-1}$	Added reagents (a) [0.05 M]	$\Delta H^* \text{ kcal/mole}$	$\Delta S^* \text{ cal/mole deg}$
1,1,2,2-Tetrachloroethane	95.0	4.7			
1,1,2,2-Tetrachloroethane	100.0	7.7		29.2	-9.2
1,1,2,2-Tetrachloroethane	104.8	10.4			
1,1,2,2-Tetrachloroethane	110.0	20.15			
1,1,2,2-Tetrachloroethane	104.8	16.2	Trifluoroacetic acid		
1,1,2,2-Tetrachloroethane	104.8	12.0	Triethylamine		
1,1,2,2-Tetrachloroethane	104.8	29.9	Pyridine		
1,1,2,2-Tetrachloroethane	104.8	9.4	<i>p</i> -Benzoquinone		
Benzonitrile	104.8	12.6			

(a) The constants are actually referred to pseudo-first-order rates (k_{obsd}).

Table III

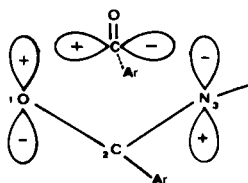
Analytical Data for the 1-(Diaroylamino)-1,2,3-triazoles (III)
Obtained from Isomerization of the Isoimides (II)

Compound	M.p. °C	Ir, ν C=O, cm ⁻¹ (Nujol)	Formula	Analyses %					
				Calcd.		Found		Found	
				C	H	N	C	H	N
(IIIA)	93-94 (a,b)	1715							
(IIIB)	184-186	1705	C ₂₀ H ₂₀ N ₄ O ₂	68.95	5.79	16.08	68.84	5.83	16.31
(IIIC)	172-174	1700	C ₂₀ H ₂₀ N ₄ O ₂				68.45	5.79	15.95
(IIID)	145-147	1715	C ₁₈ H ₁₄ Cl ₂ N ₄ O ₂	55.54	3.62	14.39	55.81	3.70	14.29
(IIIE)	144-146	1715	C ₁₈ H ₁₄ Cl ₂ N ₄ O ₂				55.20	3.59	14.70
(IIIF)	112-114	1700	C ₂₀ H ₂₀ N ₄ O ₄	63.15	5.30	14.73	63.50	5.33	14.68
(IIIG)	110-111	1705	C ₂₀ H ₂₀ N ₄ O ₄				63.27	5.34	15.03
(IIIH)	187-190	1717	C ₁₈ H ₁₄ N ₆ O ₆	52.68	3.44	20.48	52.90	3.37	20.97
(IIIJ)	202-205	1720	C ₁₈ H ₁₄ N ₆ O ₆				52.30	3.37	20.11

(a) Lit. (3) m.p. 94-96°. (b) Crystallized from methanol, whereas all other products from a mixture of methanol-chloroform.

The transition state of this concerted reaction, which can be described as an [1,3] sigmatropic aroyl shift, contains 4 electrons and it is therefore thermally suprafacially allowed, but with inversion of the migrating group (Scheme

Scheme III



III).

The triazolyliisoimides studied are in general much more stable than other isoimides (6) and their stability might be due to the triazolyl ring, which reduces the nucleophilicity of the isoimide nitrogen.

The analytical data of the imides (III) are given in Table III. The triazolylimides show in the mass spectra a fragmentation pattern similar to that of isoimides (14), with the main difference being the fragment corresponding to ArCOO^+ , which appears in the isoimides. The imides (beside the molecular ion M^+) show peaks at $M-28^+$ formed by elimination of nitrogen from the triazole ring and peaks corresponding to ArCO^+ (base peak) and to $\text{CH}_3-\text{C}=\text{C}-\text{CH}_3$ ion.

EXPERIMENTAL

All melting points are uncorrected and they were obtained with a Kofler hot stage apparatus. Ir spectra were obtained with a Perkin-Elmer Model 257 spectrophotometer and nmr spectra re-

ported in δ units with a Varian Associates A-60A spectrometer with TMS as internal reference. The mass spectra were obtained with a Hitachi-Perkin-Elmer Model RMU-6L spectrometer with ionization energy 70 eV. Analyses were performed with a Perkin-Elmer Model 240 CHN analyzer.

Biacetyl bis-aroylhydrazones (I) were prepared by standard procedures (3,15).

1-(α -Aroyloxyarylideneamino)-4,5-dimethyl-1,2,3-triazoles (II) were identical with those previously described (3,7,12); the melting points of the samples used for the kinetic studies were as follows:

(IIA) 138-139°; (IIB) 131-132°; (IIC) 118-120°; (IID) 166-168°; (IIE) 119-121°; (IIF) 124-126°; (IIG) 113-115°; (IIH) 163-164°; (IIJ) 165-167°.

Thermal Rearrangement of Isoimides (II) to 1-(Diaroylamino)-4,5-dimethyl-1,2,3-triazoles (III).

By heating the isoimides (II) at 150° for 90 minutes without solvent gave the corresponding 1-(diaroylamino)-1,2,3-triazoles (III) in 85-90% yield. They were recrystallized from methanol or from a mixture of methanol-chloroform (Table III).

Kinetic Measurements.

A 0.4 ml. aliquot of a standard solution (5-10% or about 0.25M) of an isoimide (II) was placed in a sealed nmr tube (total number of tubes 7-9). The solvent (*sym*-tetrachloroethane, Fluka, Purum) was treated with solid potassium carbonate, dried with molecular sieves and then distilled just before use (b.p. 146°). All other reagents used in this study were "Reagent Grade". The tubes were placed in a bath at 104.8°, the temperature of which was controlled to $\pm 0.05^\circ$. At fixed time intervals each tube was cooled to 0° and then placed in the nmr spectrometer to measure the disappearance of the 5-CH₃ protons peak. It has been checked that at the temperature of the nmr probe (40°) the change in isoimide was practically zero. The accuracy in isoimide concentration was $\pm 1\%$ (mean value of 5 to 7 integration signals). First-order plots were linear to about 90% reaction, with a correlation coefficient r for the line in the range of 0.998. The repeatability in rate constants was $\pm 3\%$; the rates were calculated with a Hewlett-Packard Model 9001 calculator, with a least-squares program.

Acknowledgment.

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