

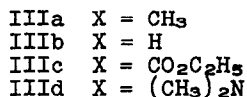
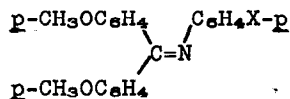
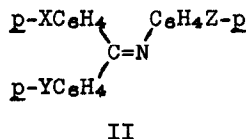
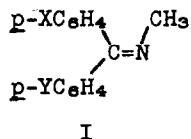
CONFIGURATIONAL STABILITY AT THE CARBON-NITROGEN DOUBLE BOND<sup>1</sup>

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A PREVIOUS study<sup>3</sup> of the cis-trans (or syn-anti) isomerization of imines with the formula I showed that a cis-trans shift of



the methyl group occurred at a rate convenient for measurement in the temperature range from 40 to 60° C. There was evidence<sup>3</sup> that the related N-arylimines II, although crystallizing as a single stereoisomer in each case, isomerized too rapidly in solution for convenient kinetic measurement by the conventional spectral method employed.

It has now been found that the N-phenylimines IIIa-c

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<sup>3</sup> D. Y. Curtin and J. W. Hausser, J. Am. Chem. Soc. **83**, 3474 (1961).

undergo isomerization at a rate convenient for measurement by an n.m.r. method which has been used to follow other rapid reactions.<sup>4</sup> The imines IIIa, m.p. 109-110°; IIIb, m.p. 102-103°; and IIIc, m.p. 85-86°, were prepared from *p,p'*-dimethoxybenzophenone and the appropriate amine in toluene with phosphorus oxychloride as the condensing agent.<sup>5</sup> The n.m.r. spectra were obtained in carbon tetrachloride with the Varian H.R. 60 Spectrophotometer. Sample temperatures from -30 to +75° were measured with a calibrated copper-constantan thermocouple in a dummy sample tube containing carbon tetrachloride. The chemical shifts were determined from audiofrequency side bands of tetramethylsilane generated with a Hewlett-Packard signal generator calibrated with an electronic counter. In each case at the lowest temperature the absorption due to the two methoxyl groups was well separated into two peaks of equal intensity which at higher temperatures coalesced to a single sharp peak. The coalescence temperature was taken as that temperature at which the minimum between the two peaks disappeared and could be measured reproducibly to within about  $\pm 0.5^\circ$ . Because of the possibility of acid catalysis<sup>3</sup> calcium hydride was suspended in some solutions but was without effect on the coalescence temperature. The data are summarized in Table 1. Rate

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<sup>4</sup> J. A. Pople, W. G. Schneider and H. J. Bernstein, High-resolution Nuclear Magnetic Resonance, Chapter 13, McGraw-Hill Book Company, Inc., New York, 1959.

<sup>5</sup> All compounds employed in this work had carbon, hydrogen, and nitrogen microanalyses which were within 0.3 of the calculated values. The infrared spectra showed strong absorption at 1600  $\text{cm}^{-1}$  and in each case the imine was recrystallized until none of the absorption at 1640  $\text{cm}^{-1}$  characteristic of the parent ketone remained.

Table 1  
Isomerization Rates of the Imines III

Substituent (Compound)	Coalescence Temperature (°C.)	Maximum Separation (c.p.s.)	$k_1$ (sec. <sup>-1</sup> )	$k_1$ 62.2° (extra- polated)
p-CH <sub>3</sub> (IIIa)	69.5±0.5	3.92±0.15	8.7±0.3	{4.42} <sup>a</sup> {4.98} <sup>b</sup>
H (IIIb)	62.2	4.90	10.9	10.9
p-COOC <sub>2</sub> H <sub>5</sub> (IIIc)	29.8	5.59	12.4	{177} <sup>a</sup> {110} <sup>b</sup>

<sup>a</sup> Extrapolation assuming  $\Delta S^\ddagger = 0$ .

<sup>b</sup> Extrapolation assuming  $\Delta S^\ddagger = -10$ .

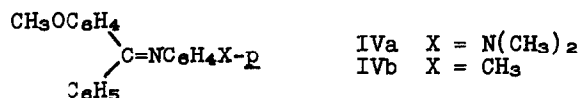
constants calculated<sup>6</sup> at each of the coalescence temperatures are presented together with values extrapolated to 62.2° based on the assumption that  $\Delta S^\ddagger = 0$  and, alternatively, that  $\Delta S^\ddagger = -10$ . Either set of rate constants gives a reasonably linear plot when  $\log k$  is plotted against  $\sigma^-$  with values of  $\rho$  and probable errors of  $+1.85 \pm 0.25$  and  $+1.55 \pm 0.21$ , respectively. It is seen that the value of  $\rho$  is rather insensitive to the choice of  $\Delta S^\ddagger$  and the conclusion that  $\rho$  lies between +1 and +2 seems assured. This result is in harmony with a mechanism involving a linear transition state as was previously proposed<sup>3</sup> with a contribution of resonance structures of the type

$$\text{Ar}_2\text{C}=\text{N}^+=\text{C}_6\text{H}_4\text{X}^-$$

A major danger inherent in this use of n.m.r. arises from the possibility that the origin of the change in the shape of the spectrum arises from some change in molecular structure

<sup>6</sup> Ref. 4, p. 223, equation (10-30).

other than that to which it is attributed. For this reason it was desired to confirm the n.m.r. results by another method. An extrapolation of the data reported here suggested that the use of the *p*-dimethylamino derivative IIIId should have a rate of about  $10^{-4}$  sec.<sup>-1</sup> at 0°, a rate accessible by conventional methods. The rate of isomerization of the closely related unsymmetrically substituted compound IVa should be similar to that of IIIId since the effect of substituents on the non-rearranging benzene rings is small in other cases.<sup>3</sup>



Compounds IVa, m.p. 116-117°, and IVb, m.p. 97-98°, were prepared by the method used for III.<sup>5</sup> There is no evidence concerning the configurations of the solids but by analogy with the methylimines<sup>3</sup> it seems possible that each is a single isomer. When dissolved in carbon tetrachloride at low temperatures they showed a rapid change in the ultraviolet spectrum and this was shown to be associated with a first order process presumed to be the cis-trans-isomerization. The results are summarized in Table 2.<sup>7</sup> As a check on the two sets of results reported here the rate measured at 12° of the imine IVa can be extrapolated to 62° to give a value of 0.9 sec.<sup>-1</sup> which is of the same order of magnitude as the value for the rate of the analogous dimethoxy compound IIIId of 1.3 sec.<sup>-1</sup> calculated

<sup>7</sup> A single run with an initial concentration of  $5 \times 10^{-4}$  M at -7.2° gave a  $k_{\text{obs}}$  of  $23.3 \pm 0.2 \times 10^{-4}$  sec.<sup>-1</sup> for the rate of isomerization of IVb. The reaction was followed by the change in absorption at 280 mμ. It will be noted that  $k_{\text{obs}} = k_1 + k_{-1}$  since this is an approach to equilibrium.<sup>3</sup> The data, although limited, lead to a  $\rho$  of +1.7, similar to the value obtained by the n.m.r. study of the imines III.

Table 2

Rates of Isomerization of Imine IVa  
(ca  $4 \times 10^{-4}$  M in Carbon Tetrachloride)

T (°C.)	$10^4 k_{\text{obs}}$ (sec. <sup>-1</sup> ) <sup>a</sup>	
-7.2 ± 0.2	4.08 ± 0.08 4.37 ± 0.05	$E_a$ 19.7±0.4 (kcal./mole) $\Delta S^\ddagger = -11$ e.u. at -7°
+2.8 ± 0.2	15.0 ± 0.2	
+3.3 ± 0.1	16.0 ± 0.2	
12.2 ± 0.1	53.7 ± 0.5	
12.5 ± 0.2	54.2 ± 0.6	

<sup>a</sup> Followed by the change in absorption at 290 mμ.

from the Hammett equation applied to the rates obtained by the n.m.r. method with the other compounds III.

It is of interest to compare the steric stabilities of the following series of compounds with the structure  $Ar_1Ar_2C=NX$ .

X	$k = k_1 + k_{-1}$ (sec. <sup>-1</sup> )	T
$C_6H_5^8$	20	62°
$CH_3^9$	$10^{-4}$	60°
$Cl^9$	$<10^{-8}$	60°
$OCH_3^{10}$	$<10^{-7}$	200°

The spread of rates of the uncatalyzed isomerizations over more than nine powers of ten is impressive and requires further investigation. It suggests, however, that the bent forms (initial state) of the imino chlorides (X = Cl) and oxime ethers (X = OCH<sub>3</sub>) have special stabilization relative to the

<sup>8</sup> From the present investigation.

<sup>9</sup> Upper limit in degassed cyclohexane. Unpublished work.

<sup>10</sup> Upper limit in degassed decane. Unpublished work of Dr. E. J. Grubbs.

linear species (transition state) which is not present in the alkyl or aryl compounds ( $X = \text{C}_6\text{H}_5$  or  $\text{CH}_3$ ).