Independent synthesis of XX was effected by rapidly adding a solution of 2.33 g. (0.01 mole) of 3-anisoylsuccinimide VIII in 70 ml. of hot isopropyl alcohol to a stirred suspension of 1.52 g. (0.04 mole) of sodium borohydride in 50 ml. of warm isopropyl alcohol (98–99%). After stirring for 5 hr. and cooling to room temperature, the solvent was removed to leave a white solid, which was dissolved in dilute sodium hydroxide solution. Acidification of the solution afforded 1.28 g. of an oil, which was dehydrated with sulfuric acid to give 0.04 g. (2%) of XX, m.p. 242–243° and 244–245° after one recrystallization from acetone. The m.p. was not depressed on admixture with a sample of XX obtained as described above. The infrared spectra of the two samples were identical.

[CONTRIBUTION FROM NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILL.]

Effects of Structural Changes on the Interconversion of Stereoisomeric Imines. Isoelectronic Models for Vinyl Anions[1]

BY DAVID Y. CURTIN AND JACK W. HAUSSER[2]

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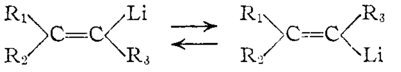
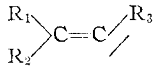
cis-p-Chlorobenzophenone methylimine (*cis*-I) and *trans-p*-nitrobenzophenone methylimine (*trans*-II) have been obtained as crystalline solids and found to rearrange to the equilibrium mixtures of *cis* and *trans* isomers in cyclohexane solution at room temperature and above. The first-order rate constants for the isomerizations have been measured. Examination of available infrared data suggests that the position of the monosubstituted phenyl absorption in the 700 cm.$^{-1}$ region may be used to make configurational assignments to properly constituted olefins, imines, oximes and azo compounds, the absorption frequency of the monosubstituted phenyl ring being as much as 5–9 cm.$^{-1}$ higher when the ring is *cis* to a substituent on the adjacent doubly bound carbon or nitrogen atom. Preliminary evidence indicates that N-arylimines such as *p*-methoxy-*p'*-nitrobenzophenone *p*-tolylimine (*cis*-VI) crystallize as a single stereoisomer but that *cis–trans* isomerization occurs very rapidly in solution even at room temperature and below. Attempts to verify the previous report[29] of the isolation of stable *cis* and *trans* isomers of 2-nitrofluorene *p*-tolylimine have not been successful.

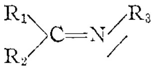
Studies[3,4] of the factors affecting the steric stability of *cis*- and *trans*-vinyllithium compounds of type A and B have suggested[4c] that carbanions C probably in a state of aggregation are prime intermediates. Because of the complexities of these systems it was desired to have model compounds which might be used to obtain information about the effects of structural changes on configurational stability of species related to the carbanions C. For this purpose imines D were of particular interest and a study of their stereochemical behavior was therefore undertaken.



A B



C



D

The first substances selected for study were the *p*-chlorobenzophenone methylimines (*cis*- and *trans*-I) and *p*-nitrobenzophenone methylimines (*cis*- and *trans*-II).[5] Reaction of *p*-chlorobenzophenone dichloride with methylamine led to an oil which crystallized on standing at room temperature for a two-week period. The resulting solid could be obtained free from the carbonyl absorption characteristic of the starting ketone, melted sharply and gave correct analytical values for the desired imines I. Absorption at 1620 cm.$^{-1}$ assigned to the carbon–nitrogen double bond[6] and a single sharp absorption at 693 cm.$^{-1}$ attributed to the monosubstituted phenyl group[6] were observed when the infrared spectrum of a freshly prepared solution was measured. On standing, the solution showed no marked change in the absorption at 1620 cm.$^{-1}$, but a lowering of intensity of the absorption at 693 cm.$^{-1}$ and development of a second band at 701 cm.$^{-1}$ were observed. Further, a sharp infrared absorption at 827 cm.$^{-1}$ in the spectrum of the freshly dissolved solid (attributed to the deformation of hydrogens in the *p*-chlorophenyl ring[6]) decreased in intensity when the solution was allowed to stand and a new absorption at 837 cm.$^{-1}$ developed. The n.m.r. spectra of freshly prepared solutions of the imine showed, in addition to absorption due to the protons of the aromatic rings, a single $N-CH_3$ proton resonance at about 6.76τ (in deuteriochloroform) which, however, was unchanged when the solution was allowed to stand. It was concluded from these and other results to be discussed that the crystalline form is a single stereoisomer. Consideration of the infrared absorption in the 700-cm.$^{-1}$ region permits a configurational assignment to be made. Examination of the infrared spectra of a number of olefins suggests that the position of the hydrogen deformation frequency is generally higher in that isomer with another atom or group *cis* to the monosubstituted phenyl ring. The available data are summarized in Table I. It will be seen that the difference between the two isomers is generally 5–9 cm.$^{-1}$, although the α-methyl-β-bromostyrenes did not show an experimentally observable difference. In no case were the relative positions of the monosubstituted phenyl absorptions reversed. A similar difference seems to be present

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(1) Supported in part by the National Science Foundation (G4467). Taken from the Ph.D. Thesis of Jack Walter Hausser, University of Illinois, 1960, available on microfilm from Univ. Microfilms, Ann Arbor, Mich.

(2) Rohm and Haas Fellow, 1958–1959.

(3) A. N. Nesmeyanov, A. E. Borisov and N. A. Vol'kenau, *Izvest. Akad. Nauk. (U.S.S.R.), Otdel. Khim. Nauk*, 992 (1954).

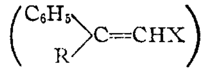
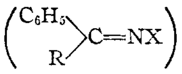
(4) (a) D. Y. Curtin, H. W. Johnson, Jr., and E. G. Steiner, *J. Am. Chem. Soc.*, **77**, 4566 (1955); (b) D. Y. Curtin and J. W. Crump, *ibid.*, **80**, 1922 (1958); (c) W. J. Koehl, Jr., and D. Y. Curtin, Abstracts of 138th Meeting, Amer. Chem. Soc., New York, N. Y., 1960, p. 52P.

(5) Throughout this paper the designations "*cis*" and "*trans*" will be used to describe the relative positions of the *p*-substituted phenyl ring and the methyl or aryl substituent on the imine nitrogen.

(6) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen and Company, London, 2nd Ed., 1958.

TABLE I

USE OF THE AROMATIC HYDROGEN DEFORMATION FREQUENCIES FOR CONFIGURATIONAL ASSIGNMENT

	Frequency, cm.$^{-1}$ Rel. positions of C_6H_5– and X–		Shift, cm.$^{-1}$ (*cis–trans*)
	cis	*trans*	
Olefins  $\left(\begin{matrix}C_6H_5\\R\end{matrix}\!\!>\!C{=}CHX\right)$			
1-Phenylpropenes[a]	702	694	8
	(700)	(692)	(8)
Styrylmethylcarbinols[b]	699	691	8
Stilbenes[c]	696	691	5
p-Methoxystilbenes[d]	693	690	3
α-Methyl-β-bromostyrenes[e]	697	697	0
	(694)	(694)	(0)
Imines  $\left(\begin{matrix}C_6H_5\\R\end{matrix}\!\!>\!C{=}NX\right)$			
p-Chlorobenzophenone methylimines[f]	701	693	8
p-Nitrobenzophenone methylimines[f]	702	694	8
Benzophenone methylimine[f]	698(sh)	692	6
Azo compounds			
Azobenzenes[g]	698	689	9
	(690)		

[a] First values those of R. Y. Mixer, R. F. Heck, S. Winstein and W. G. Young, *J. Am. Chem. Soc.*, **75**, 4094 (1953); values in parentheses from Ph.D. Thesis of J. W. Crump, University of Illinois, 1957, corrected from calibration curve. [b] A. R. Philpotts and W. Thain, *Nature*, 166, 1028 (1950). [c] K. Lunde and L. Zechmeister, *Acta Chem. Scand.*, **8**, 1421 (1954). [d] Y. G. Hendrickson, Ph.D. Thesis, University of Illinois, 1955, corrected from calibration curve. [e] Data (corrected from a calibration curve) from spectra in the Ph.D. Thesis of J. W. Crump, University of Illinois, 1957. Data in parentheses from Ph. D. Thesis of E. W. Flynn, University of Illinois, 1956. [f] Present work. [g] R. J. W. LeFevre, *Austral. J. Chem.*, **6**, 341 (1953).

in azo compounds although only one example, the stereoisomeric azobenzenes, is available and it is complicated by the presence of a second maximum in the critical region of the spectrum of the *cis* isomer. A reasonable guess is that the shift in the *cis* isomer is due to steric inhibition of the resonance interaction of the benzene ring with the carbon–carbon double bond but since this is an empirical correlation it must be applied with due caution. Since these spectra were in most cases obtained with other objectives in mind, the absolute values of the maxima in the 700-cm.$^{-1}$ region are not necessarily reliable. It is believed, however, that differences between the *cis* and *trans* isomer measured by the same investigator are less subject to error and it will be noted that in those cases where two sets of results by different investigators are available there is good agreement. It might have been argued that the unshared pair of electrons of the nitrogen atom of the imines could reverse the direction of the shift, but the difference between *cis* and *trans*-azobenzene indicates that this is not the case.[7]

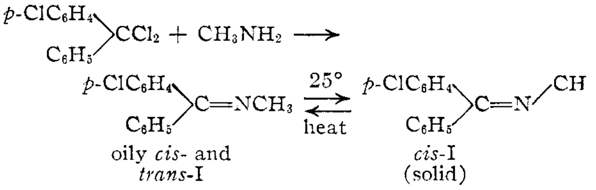
TABLE II

	λ_{max}, mμ	ε
Benzophenone methylimine	246	15,400
cis-Chloro imine, *cis*-I	236	15,100
trans-Chloro imine, *trans*-I	255[a]	18,500
p,p'-Dichlorobenzophenone methylimine	254	18,800
cis-Nitro imine, *cis*-II	245[a]	16,200
trans-Nitro imine, *trans*-II	280	16,700

[a] Calculated.

When the solid isomer, *cis*-I, was heated for 15 min. at 125° or when its solution in cyclohexane was allowed to stand for 2 weeks at room temperature, the infrared spectrum was the same as that of the original oily I. All attempts to isolate the *trans* isomer *trans*-I failed, probably due to the ease of stereoisomerization and to the ready hydrolysis by even traces of moisture of the imines to *p*-chlorobenzophenone and methylamine. The infrared and ultraviolet spectra of *trans*-I were obtained even though it could not be isolated by placing solutions of the equilibrium mixtures in the sample beam of a double beam spectrophotometer and causing the instrument to subtract the contribution of *cis*-I from the spectrum by adding the calculated amount of *cis*-I to the solvent in the reference beam. The ultraviolet spectrum in cyclohexane showed λ_{max} 236 mμ (ε 15,500) while *trans*-I had λ_{max} at 255 mμ (ε 18,500) and the equilibrium mixture λ_{max} 252 mμ (ε 15,700). The ultraviolet data are at least consistent with the configurational assignments. Table II shows the relevent data. It is reasonable that the isomer with the chloro-substituted phenyl ring adjacent to the methyl and therefore tipped out of the planar position required for maximum resonance with the carbon–nitrogen double bond should have a spectrum most nearly resembling the unchlorinated imine as is observed. Similarly, the *trans*-chloro imine *trans*-I with the chlorine substituent on the benzene ring not interfered with by the adjacent methyl group has a maximum which resembles both in position and intensity the dichlorinated imine. In other words, adding or removing a chlorine substituent from that phenyl ring which can assume complete coplanarity required for maximum conjugation has much more effect on the spectrum than adding or removing the substituent from the ring which is interfered with by the adjacent methyl group.

It is reasonable that the equilibrium in solution should have nearly equal amounts of the isomers *cis*- and *trans*-I. The fortunate accident that a single isomer is favored in the equilibrium between solid and melt is not without precedent. A number of structurally related oximes seem to show similar behavior.[8]



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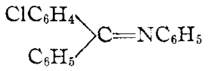
[7] It is of interest in this connection that bar graphs of the absorption maxima of α- and β-benzaldoxime [A. Palm and H. Werbin, *Can. J. Chem.*, **31**, 1004 (1953)] show the absorption in the 700-cm.$^{-1}$ region to be some 10 cm.$^{-1}$ higher in the β-isomer (phenyl and hydroxyl groups *cis*) than in the α, in agreement with the generalization from Table I.

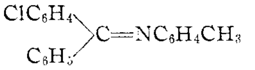
(8) See J. Meisenheimer and W. Theilacker, "Stereochemie," Vol. 3, edited by K. Freudenberg, Franz Deuticke, Leipzig, 1932, p. 1033, for references.

In order to examine the effect of substituents on the rate of isomerization, the *p*-nitrobenzophenone methylimines (II) were also prepared. As with the chloro compounds I, reaction of *p*-nitrobenzophenone dichloride with methylamine led to an oil which crystallized to a single isomer on standing several weeks. In this case, however, the isomer having the more stable crystalline form is the *trans* isomer *trans*-II as shown by infrared and ultraviolet spectral arguments like those employed with the chloro compounds I. Spectral data are included in Tables I and II. Equilibration of the liquid isomers at 100° showed that the slightly more stable isomer under these conditions is the *trans* isomer *trans*-II as was the case with the chloroimines I. The n.m.r. spectra were of particular interest in this case since freshly dissolved *trans*-II in carbon tetrachloride showed a single absorption maximum at 6.73 τ due to the $N-CH_3$ protons whereas the equilibrium mixture showed two peaks partially resolved at 6.72 and at 6.79τ.

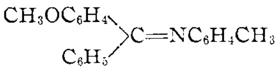
With the hope of observing the same behavior that has been obtained with the N-methylimines, a number of N-arylimines were prepared by treating the appropriate substituted benzophenone with the arylamine and phosphorus oxychloride.[9] *p*-Chlorobenzophenone phenylimine (III), *p*-chlorobenzophenone *p*-tolylimine (IV), *p*-methoxybenzophenone *p*-tolylimine (V) and *p*-methoxy-*p'*-nitrobenzophenone *p*-tolylimine (VI) were obtained as sharply melting solids. [*p*-Nitrobenzophenone *p*-tolylimine (VII) appeared to be a mixture of yellow and orange crystalline forms but was not investigated further.] Examination of the ultraviolet and infrared spectra of solutions showed no change on standing, behavior unlike that of the methylimines I and II described above. The possibility that a single solid stereoisomer was at hand in each case and that it failed to isomerize in solution was ruled out by examination of the n.m.r. spectra of solutions of the two imines V and VI with *p*-methoxy groups. In each case the methoxyl protons appeared as a well-defined doublet with a separation of 0.06 τ (4 c.p.s. at 60 Mc.). In addition, the C-methyl protons of the imine VI appeared as a doublet with a separation of 0.04 τ (2 c.p.s.) It follows that two species must be present with average residence times appreciably greater than 0.1 sec. (k less than 10 sec.$^{-1}$).[10]


$(ClC_6H_4)(C_6H_5)C{=}NC_6H_5$

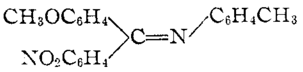
III


$(ClC_6H_4)(C_6H_5)C{=}NC_6H_4CH_3$

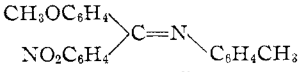
IV


$(CH_3OC_6H_4)(C_6H_5)C{=}NC_6H_4CH_3$

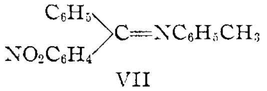
V


$(CH_3OC_6H_4)(NO_2C_6H_4)C{=}N{-}C_6H_4CH_3$

cis-VI


$(CH_3OC_6H_4)(NO_2C_6H_4)C{=}N{-}C_6H_4CH_3$

trans-VI


$(C_6H_5)(NO_2C_6H_4)C{=}NC_6H_4CH_3$

VII

It remained to decide whether the solid imines III–VI were eutectic mixtures of *cis-trans* isomers which failed to isomerize on solution or were single isomers which equilibrated so rapidly when dissolved that the change had not been observed. The infrared spectrum of the imine VI in a potassium bromide disk was examined. When a sample was ground with potassium bromide, pressed, reground and pressed until the spectrum no longer changed, the spectrum differed in many respects from the spectrum obtained in solution. The disk was then ground and the powder heated in a crucible until a characteristic color change from yellow to orange occurred. The sample was again pressed to a disk and the infrared spectrum found now to be very similar to that of the spectrum in chloroform solution. Similar behavior was observed with the imine V with the additional finding that when a sample which gave the correct spectrum for the heated imine was subsequently reground, repressed and maintained at room temperature the spectrum had reverted to that characteristic of the original solid. Since such behavior might involve interconversion of different crystalline forms of the same eutectic mixture and be characteristic of such imines, benzophenone phenylimine, incapable of stereoisomerization, was examined. It was found that no major changes in the infrared spectrum occurred on heating and the spectrum of the (unheated) solid in a potassium bromide disk was identical with a solution spectrum. A second check on the method was obtained by examining the *cis*-chloromethylimine I which had been found to isomerize in solution. In this case a potassium bromide disk heated at the m.p. of the imine for 1 minute showed only changes to be expected for partial isomerization of the compound to the *trans* isomer.

Although the spectral behavior of heated mixtures with potassium bromide described above suggests that stereoisomerism rather than interconversion of different crystalline forms is being observed, it is not compelling proof. The imine VI therefore was dissolved in diethyl ether at 0° and immediately transferred to a quartz cell and the ultraviolet absorbance at 277 mμ measured as a function of time in an effort to detect the stereoisomerization in solution. The absorption was observed to rise to approximately 1.2 times its initial value in about 1 minute and then changed no further. This behavior was reproducible and a control with solvent alone showed no absorbance. This observation taken together with the infrared and n.m.r. results provides rather strong evidence that the N-arylimine VI did crystallize in a single stereoisomeric form but that on solution isomerization occurs too rapidly to be observed except under special conditions.

Rate Measurements.—The rates of isomerization of imines *cis*-I and *trans*-II to their respective equilibrium mixtures were determined in cyclohexane.

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[9] A. W. Weston and R. J. Michaels, Jr., *J. Am. Chem. Soc.*, **73**, 1381 (1951).

[10] J. D. Roberts, "Nuclear Magnetic Resonances," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 63.

TABLE III

RATES OF UNCATALYZED *cis–trans* ISOMERIZATION IN CYCLOHEXANE OF IMINES *cis*-I AND *trans*-II

$$cis \underset{k_2}{\overset{k_1}{\rightleftarrows}} trans$$

T (°C. ± 0.05°)	$K_{eq.}$	$10^5 (k_1 + k_2)$, sec.$^{-1}$	$10^5 k_1$, sec.$^{-1}$	ΔE_a, kcal./mole	ΔS^*, e.u./mole
		cis-I			
40.2	1.4	1.13	0.66	25 ± 0.3	−3.6 ± 1.0
50.2		4.04	2.4		
60.2		12.6	7.3		
		trans-II			
40.2	1.59 ± 0.05 (2.3)	1.16	0.71 (0.81)	27.1 ± 0.5	+3.4 ± 1.4
50.2		4.26	2.6 (3.0)		
60.2		16.0	9.8 (11)		

Initial studies with the chloro derivative *cis*-I gave linear plots, but the values of the constant $(k_1 + k_2)$ varied from run to run. With the suspicion that the rates might be fluctuating because of the catalytic effect of traces of water or other impurities, further runs were carried out with the addition of a small amount of calcium hydride. The rate constants thereafter were reproducible with a value equal to the lowest value previously obtained. It appears highly probable, then, that the reaction being studied under these conditions is the uncatalyzed rearrangement analogous to the uncatalyzed rearrangement of *cis*- to *trans*-azobenzene.[11] The results are presented in Table III.

In order to separate the observed rate constant $(k_1 + k_2)$ into the individual rate constants for the forward and reverse reaction it is necessary to know the equilibrium constant, K, for the *cis–trans* isomerization. The equilibrium constant for the isomerization of the chloroimines I was estimated from the infrared spectra with the aid of the somewhat uncertain assumption that the *p*-substituted phenyl absorption at 827 cm.$^{-1}$ which diminishes during the isomerization is negligible in the spectrum of the *trans* isomer. The only check of this assumption is that it leads to the not unreasonable value of 1.4 for K.[12] Measurements on samples equilibrated at 40.2 and 109.8° showed that the variation of the equilibrium constant with temperature is negligible over the temperature range in which rate measurements were made. For this reason experimental energies and entropies of activation were calculated from a plot of $\ln(k_1 + k_2)$ against $1/T$. The energy and entropy of activation so obtained are the average values of the corresponding quantities for the forward and reverse reaction.[13] Since the E_a's for the forward and reverse reaction differ from their average by only one-half of the difference in enthalpy between starting material and product (*cis*- and *trans*-I), the average E_a calculated in this way must be quite close to the E_a's for the forward and reverse isomerization. Since $k_1 = (k_1 + k_2)K/(K + 1)$ it is relatively insensitive to the equilibrium constant K. Values of k_1 in Table I are based on a K of 1.4. The nitroimines II present more of a problem. An infrared argument similar to that employed with the chloroimines leads to a (maximum) value of the equilibrium constant K of 2.3. A more reliable estimate based on the relative areas of the n.m.r. peaks at 6.72 and 6.79τ in the equilibrium mixture leads to a value of K of 1.6, however. Values of k_1 calculated assuming an equilibrium constant of 1.6 are followed in parentheses in Table I by values based on an equilibrium constant of 2.3. It will be seen that none of the conclusions to be drawn here is affected by this uncertainty.

It is apparent that the effect of substituents is quite small, the rate at 40.2° for the *p*-nitroimine *cis*-II being not more than 1.2 times the rate of the chloroimine *cis*-I. By way of comparison a reaction with a Hammett ρ-value of +0.14 would show a rate difference of this magnitude.[14] At 0°, however, the (extrapolated) rate constants are reversed, the chloroimine *cis*-I being faster than the nitro compound *cis*-II. It may be suggested that there is an isokinetic temperature[15] slightly below 40° at which methylimines such as I or II isomerize at a rate which is independent of the substituent.

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(11) (a) R. J. W. LeFevre and J. Northcott, *J. Chem. Soc.*, 867 (1953); (b) J. Halpern, G. W. Brady and C. A. Winkler, *Can. J. Research*, **28B**, 140 (1950); (c) D. Schulte-Frohlinde, *Ann.*, **612**, 138 (1958); (d) E. W. Malmberg and M. Kaplan, Ph.D. Dissertation of M. Kaplan, Ohio State University, 1954, quoted by E. R. Talaty, ref. (e); (e) E. W. Malmberg and E. R. Talaty, Ph.D. Dissertation of E. R. Talaty, Ohio State University, 1957, Univ. Microfilms, No. 58573, Ann Arbor, Michigan.

(12) Since no change in the stereochemical environment of the methyl group accompanies the isomerization it is expected that the equilibrium constant should be not too far from 1. Equilibration of substituted benzophenone oximes [W. E. Bachmann and M. T. Barton, *J. Org. Chem.*, **3**, 300 (1938)] gave for the *p*-chloro, *p*-methoxy and *p*-methyl compounds values of 0.79, 1.04 and 0.92. It will be noted that if the assumption that the *trans* isomer shows no absorption at 827 cm.$^{-1}$ should be incorrect, the proper value of the equilibrium constant is larger than 1.4 which is therefore a minimum value for K.

(13) Since from the equilibrium expression $k_1/k_2 = K$, where k_1 and k_2 are the rate constants of the forward and reverse reaction, K is the equilibrium constant, k_{obs} is the observed rate constant $(k_1 + k_2)$

$$k_1 = k_{obs}f_1 \text{ and } k_2 = k_{obs}f_2 \text{ where } f_1 = K/K + 1, f_2 = 1/K + 1$$

From these equations and the Arrhenius expressions

$$\ln k_1 = \ln A_1 - E_{a_1}/RT \text{ and } \ln k_2 = \ln A_2 - E_{a_2}/RT$$

$$\ln k_{obs} = {}^1/_2 \ln A_1/A_2 - {}^1/_2\, RT(E_{a_1} + E_{a_2}) - {}^1/_2 \ln f_1f_2$$

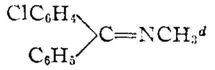
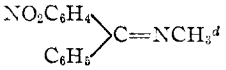
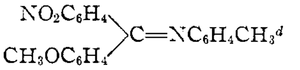
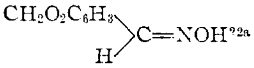
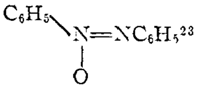
It is seen that the activation energy determined from the slope of a plot of $\ln k_{obs}$ against $1/T$ is the average of the energies of the forward and reverse reactions and also that if the small term $^1/_2 \ln f_1f_2$ can be neglected in the previous equation the entropy determined from the intercept is the average of the entropies of activation of the forward and reverse reactions.

(14) R. W. Taft, Jr., N. Deno and P. Skell, *Ann. Rev. Phys. Chem.*, **9**, 292 (1958).

(15) J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955).

TABLE IV

COMPARISON OF *cis–trans* ISOMERIZATIONS PROCEEDING BY A MOLECULAR MECHANISM

	State	k, 40.2° sec.$^{-1}$	k (rel.)	ΔE^*, kcal./mole	ΔS^*, cal./mole°
$CHD{=}CHD$[19]	Vapor	10^{-30}[a]	10^{-25}	61	-5.2
$CH_3CH{=}CHCH_3$[20]	Vapor	10^{-30}[b]	10^{-25}	63	$+2.8$
$C_6H_5CH{=}CHC_6H_5$[21]	Liquid	10^{-15}[c]	10^{-20}	37	-11.9
 $(ClC_6H_4)(C_6H_5)C{=}NCH_3$[d]	Cyclohexane soln.	6.6×10^{-6}	1.0	25.0	-4.7
 $(NO_2C_6H_4)(C_6H_5)C{=}NCH_3$[d]	Cyclohexane soln.	7.0×10^{-6}	1.1	27.1	$+2.7$
 $(NO_2C_6H_4)(CH_3OC_6H_4)C{=}NC_6H_4CH_3$[d]	Cyclohexane or ether soln.	$(10^{-3}–1)$[e]	$(10^2–10^5)$[e]	(18–20)[e]	(0)[e]
 $(CH_2O_2C_6H_3)(H)C{=}NOH$[22a]	Benzene soln.	3.5×10^{-4}	50	22.6	$+2.6$
$C_6H_5N{=}NC_6H_5$[9b]	Heptane	1.6×10^{-5}	2.5	22.8	$+0.1$
$p\text{-}CH_3OC_6H_4N{=}NC_6H_5$[11c]	Heptane	2.5×10^{-5}	3.8	20.9	-6.2
$p\text{-}ClC_6H_4N{=}NC_6H_5$[11e]	Heptane	2.4×10^{-5}	3.7	22.4	-0.1
$p\text{-}NO_2C_6H_4N{=}NC_6H_5$[11d]	Heptane	2.1×10^{-4}	32	22.4	$+3.2$
$ClC_6H_4N{=}NCN$[22b]	Heptane	4.7×10^{-5}	7.2	22.4	$+1.6$
 $C_6H_5N(O){=}NC_6H_5$[23]	Heptane	1.3×10^{-3}	200	22.8	$+5.1$

[a] Extrapolated from 450°. [b] Extrapolated from 469°. [c] Extrapolated from 200°. [d] Present work. [e] The lower limit was estimated on the basis that a sample dissolved in hexane at room temperature showed no change in the spectrum run immediately, the reaction assumed to be at least 90% complete in 1 min. at 300° K. with the further assumption that ΔS^* is 0 extrapolation to 40° gives $k_1 + k_2 + 2 \times 10^{-3}$ or $k_1 \approx 10^{-3}$ as a conservative lower limit. The upper limit is based on the assumption of a 15-second half-time in the ultraviolet study in diethyl ether assuming a temperature of 10° and extrapolating as before.

Our results indicate that the *cis–trans* isomerization of imines is much more sensitive to the replacement of the N-methyl group by an aryl group. Although this conclusion must be regarded as tentative, the N-aryl compounds would seem to isomerize more rapidly by several powers of ten as indicated in Table IV. A major part of this difference could be explained readily in terms of the difference in the amounts of steric strain being relieved in going to the transition state. ("Steric strain" is used here to include not only compression destabilization but also other factors such as steric inhibition of resonance which destabilize the *cis* isomer with respect to the *trans*.) Thus, the destabilization introduced by moving two phenyl groups from *trans* to *cis* positions in stilbene has been shown to be some 5.7 kcal.[16] and in azobenzene probably is somewhat higher.[17] The instability introduced by the interaction of a phenyl and a methyl group in *cis*-propenylbenzene (relative to the *trans* isomer) has been estimated[18] to be of the order of only 1 kcal./mole. The difference between the relief of instability due to phenyl and methyl on the one hand and two phenyls on the other could reasonably lead to a rate difference, then, of three powers of ten or more.

The uncatalyzed *cis–trans* isomerization of imines is probably closely related to the isomerizations of azo compounds and certain similar structures which have been studied extensively. Representative data for the uncatalyzed isomerizations of olefins, imines (which may be regarded as having one doubly bound carbon atom replaced by a nitrogen atom) and finally azo compounds (with both doubly bound carbon atoms replaced by nitrogen atoms) are presented in Table IV.

It is seen by comparing the olefins with the imines and azo compounds that replacement of the first doubly-bound carbon atom by a nitrogen atom accelerates the rate of isomerization by some twenty powers of ten but that replacement of the second doubly-bound carbon atom has a relatively very small effect on the rate of isomerization. This suggests (but of course does not prove) that the mechanisms of isomerization of the imines and azo compounds are fundamentally different from that of the olefins[20,24] and may be closely related to each other. Comparison of substituent effects is complicated by a number of factors. Early data on the isomerization of *p*-substituted azobenzenes were considered to give a linear σ–ρ plot[25] with a ρ of -0.64 at 35°. The data also have been fitted to Leffler's isokinetic relationship,[11] the isokinetic temperature (at which $\rho = 0$) being 67°. More

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(16) R. B. Williams, *J. Am. Chem. Soc.*, **64**, 1402 (1942).

(17) R. J. Corruccini and E. C. Gilbert, *ibid.*, **61**, 2925 (1939); see also A. L. Markman and E. R. Zinkova, *Zhur. Obshchei Khim.* (*S.S.S.R.*), **29**, 3093 (1959).

(18) D. Y. Curtin and M. C. Crew, *J. Am. Chem. Soc.*, **77**, 354 (1955).

(19) B. S. Rabinovitch, J. E. Douglas and F. S. Looney, *J. Chem. Phys.*, **20**, 1807 (1952); **23**, 315 (1955).

(20) B. S. Rabinovitch and K. W. Michel, *J. Am. Chem. Soc.*, **81**, 5065 (1959); W. F. Anderson, J. A. Bell, J. M. Diamond and K. R. Wilson, *ibid.*, **80**, 2384 (1958).

(21) T. W. J. Taylor and A. R. Murray, *J. Chem. Soc.*, 2078 (1938).

(22) (a) R. J. W. LeFevre and J. Northcott, *ibid.*, 2235 (1949); (b) 944 (1949).

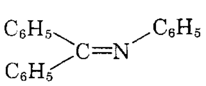
(23) P. Luner and C. A. Winkler, *Can. J. Research*, **30**, 679 (1952).

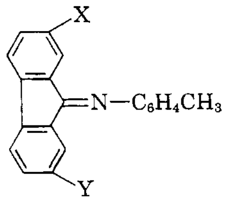
(24) (a) This proposal was made in 1930 by E. Huckel [*Z. Physik.*, **60**, 455 (1930)]; (b) see also ref. 8, p. 991.

(25) H. H. Jaffé, *Chem. Revs.*, **53**, 208 (1953).

recent kinetic studies,[9c,9d] however, show that the data do not fit a Hammett plot but that substituents both with positive and negative σ-constants accelerate the reaction.[26] It seems unprofitable to consider these rather small substituent effects further at the present time.

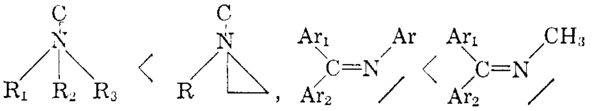
Previous Work on Isomerism of Imines.—Although in a number of instances imines have been obtained in more than one crystalline form[27] there seem to be no cases where true stereoisomerism has been demonstrated unequivocally and the danger of confusing polymorphism with stereoisomerism is indicated by the observation that benzophenone phenylimine (VIII) itself exists in two crystalline forms even though no stereoisomerism is possible.[28] More recently[29] the acid catalyzed condensation of 2-nitrofluorenone with *p*-toluidine resulted in a product, m.p. 193°, to which was assigned the structure *trans*-IX. A second substance, m.p. 218°, resulting from the base-catalyzed condensation 2-nitrofluorene with *p*-nitrosotoluene was assigned the structure *cis*-IX. The unusual stereospecificity of these two reactions and the fact that the isomers showed configurational stability which is most surprising in view of our results led to their reinvestigation. Repetition of the condensation of 2-nitrofluorenone with *p*-toluidine gave an imine of which the properties agreed with the previous report. The condensation of 2-nitrofluorene and *p*-nitrosotoluene gave a crude product which had the melting point obtained before but after several recrystallizations the melting point rose and a substance was obtained which did not have the correct composition for the imine IX. Paper chromatography indicated that a mixture was still present. It is not clear why our results disagree with the earlier report but it seems unwise to accept the assigned structures without further experimental work.


VIII

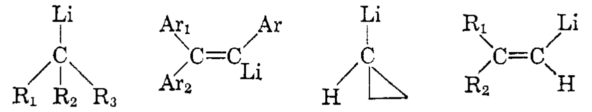


cis-IX, X = NO_2, Y = H
trans-IX, X = H, Y = NO_2

Comparison of Stereochemical Stability of Amines and Imines with Lithium Reagents.—The series of nitrogen compounds shown below can now be written in order of increasing steric stability.[30]



The corresponding series of lithium reagents is[4c,31]



Although more data are needed throughout both series before final conclusions can be drawn, it can be seen that there is a pattern of similar trends in the two series. Factors responsible for the difference between aliphatic, olefinic and cyclopropyl anions have been discussed previously.[31]

Experimental[32]

***cis*-*p*-Chlorobenzophenone Methylimine** (*cis*-I).—When 40% aqueous methylamine (60 g., 0.75 mole) and 27.4 g. (0.1 mole) of *p*-chlorobenzophenone dichloride,[33] b.p. 138–139° at 1.0 mm., were stirred for 4 hr. the reaction temperature rose to 50°. After 20 g. (0.25 mole) of additional methylamine solution was added and stirring continued for 1 hr. the organic material was extracted with ether and dried over magnesium sulfate. Removal of the ether and distillation at 0.12 mm. pressure gave 16.9 g. (72%) of cloudy colorless oil, b.p. 100–102°. The cloudiness, due to methylamine hydrochloride, was removed by filtration and the oil allowed to stand. After 3 days crystals appeared and in 2 weeks the product was mostly crystalline. Collection by filtration and recrystallization from hexane and ethanol gave *cis*-I, m.p. 90–91°.

Anal. Calcd. for $C_{14}H_{12}ClN$: C, 73.2; H, 5.3; N, 6.1. Found: C, 73.4; H, 5.3; N, 5.8.

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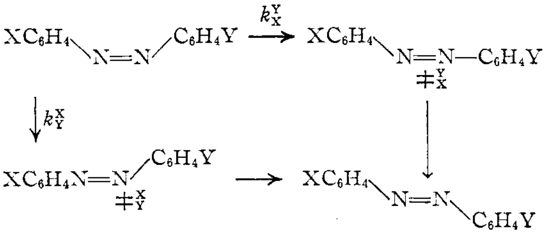
[26] It will be seen that if the mechanism involves a linear transition state of the kind previously proposed, the two ends of the transition state are non-equivalent and a simple plot of the logarithm of the experimental rate constant against σ should not lead to a straight line. Thus, if the reaction proceeds as



the measured over-all rate constant is

$$k_{\text{obs}} = k_Y^X + k_X^Y \text{ with } \log k_Y^X = \sigma_X\rho_m + \sigma_Y\rho_n$$
$$\text{and } \log k_X^Y = \sigma_Y\rho_m + \sigma_X\rho_n$$

if the Hammett expression is assumed to hold. (Here the σ's have their usual meaning and ρ_m is the ρ expressing the effect of substitution on the migrating group and ρ_n the effect of substitution on the non-migrating group. It is clear that even when Y = H and the expression reduces to

$$k_{\text{obs}} = 10^{\sigma_X\rho_m} + 10^{\sigma_X\rho_n}$$

no linear Hammett plot should be expected. This is not the whole source of the trouble, however, since when X = Y the equation reduces to

$$k_{\text{obs}} = 2k_X^X \text{ and } \log k_{\text{obs}} = \log 2 + \sigma_X(\rho_m + \rho_n)$$

That plots of log k_{obs} against σ_X, however, do not give a straight line may be seen from even casual inspection of the rates of isomerization of the symmetrical disubstituted azobenzenes reported by Schulte-Frolinde[9c] which again show that substituents with either positive or negative σ-constants accelerate the reaction. This leads to the conclusion that non-linearity is influenced also by other factors, such as steric inhibition of resonance in the *cis*-azo compound which is partially relieved in the transition state.

[27] See ref. 8, p. 1095 ff., for a review of the older work.

[28] E. Knoevenagel, *J. prakt. Chem.*, [2] **89**, 38 (1914).

[29] M. E. Taylor and T. L. Fletcher, *J. Am. Chem. Soc.*, **80**, 2246 (1958).

[30] See A. T. Bottini and J. D. Roberts [*ibid.*, **80**, 5203 (1958)]; A. Loewenstein, J. F. Neumer and J. D. Roberts, *ibid.*, **82**, 3599 (1960), for the experimental results with the amines and ethyleneimines.

[31] See D. E. Applequist and A. H. Peterson, *ibid.*, **83**, 862 (1961).

[32] All melting points are corrected. Microanalyses were performed by Mr. J. Nemeth, Miss C. Higham, Mrs. R. Ju, Miss J. Liu and Mrs. A. Bay. All spectra are available in the Ph.D. Thesis of J. W. H.[1] Infrared spectra were obtained with a Perkin-Elmer model 21 infrared spectrophotometer by Mr. P. McMahon, Mr. W. Dalton, Mr. D. Johnson and Mrs. J. Verkade. Ultraviolet spectra were obtained with a Cary model 14M recording spectrophotometer and a Beckman model DU spectrophotometer. N.m.r. spectra were obtained with a Varian nuclear magnetic resonance spectrometer at 60 Mc. by Mr. O. Norton.

[33] P. P. Paterson, *Am. Chem. J.*, **46**, 332 (1911).

trans-p-**Nitrobenzophenone Methylimine** (*trans*-II).—Anhydrous methylamine was bubbled through 20 g. (0.071 mole) of *p*-nitrobenzophenone dichloride[34] m.p. 51–53°, in 150 ml. of diethylene glycol dimethyl ether for 4 hr. at 100°. To ensure complete reaction 80 g. (1.0 mole) of 40% aqueous methylamine was added over an additional 4-hr. period. Extraction with ether, drying over magnesium sulfate and removal of the solvent at reduced pressure gave 8 g. (47%) of a colorless oil which had almost completely crystallized after 2 weeks to give crude *trans*-II, m.p. 105–120°. Purification by passing the product through a 1.5 in. column of neutralized alumina using hexane and ether as eluents and recrystallization from hexane and ethanol gave *trans*-II (1.3 g., m.p. 127–128°).

Anal. Calcd. for $C_{14}H_{12}N_2O_2$: C, 70.0; H, 5.0; N, 11.7. Found: C, 70.2; H, 5.0; N, 11.5.

Determination of the Equilibrium Constants for the Equilibrations of the Imines *cis*- **and** *trans*-**I and** *cis*- **and** *trans*-**II.**—A calibration curve showing the variation of the absorbance at 827 cm.$^{-1}$ with concentration over the range 200–800 mg./ml. in cyclohexane was prepared. With the assumption that all of the absorption at 827 cm.$^{-1}$ was due to the *cis* isomer (*p*-substituted phenyl ring) the % *cis* was calculated from the spectrum of the equilibrium mixture at each of two concentrations (400 and 800 mg./ml.). The equilibration at 100° (sealed tube) was repeated (with the preparation of new calibration curves) with new samples of the compounds to give the same results.

The % *cis*-I found in this way were 42.0, 41.8, 41.8, 42.2, with the average 42.0 and K(*trans*/*cis*) at 100° 1.38. Constants at 40.2° and 109.8° determined by the same method were found to be 1.43 and 1.38, respectively.

Equilibrium constants for the equilibration of the nitroimines starting with *trans*-II were determined similarly using the absorbance at 864 cm.$^{-1}$. The equilibrium concentration of *cis*-II in a solution equilibrated by heating a solution of *trans*-II at 100° for 15 min. was 30.5% corresponding to a K (*trans*/*cis*) of 2.28. Additional measurements at 40.2° and 109.8° gave values of 2.51 and 2.28, respectively, again showing that the relative concentrations of the two isomers changed little over the temperature range employed for the kinetic work.

Areas of the n.m.r. absorptions at 6.72 and 6.79τ were obtained by making a visual resolution of the two partially overlapping curves into their components and measuring the areas with a polar planimeter. The areas so obtained were 2.3 ± 0.1 and 1.4 ± 1 cm.^{2} with the ratio equal to 1.6 ± 0.1. Making the resolution of the two curves in different ways did not affect this ratio significantly. Another sample was heated in cyclohexane for 1 hr. at 90° and then allowed to stand at room temperature for 2 days and the areas of seven tracings made at various r.f. fields measured as before. The average value and probable error of the ratio were 1.59 ± 0.05, the ratio being independent of r.f. field over the range employed.

p-**Chlorobenzophenone phenylimine (III)**[35] prepared from *p*-chlorobenzophenone, aniline and phosphorus pentachloride in toluene, and purified by chromatography on alumina with hexane as the eluent had m.p. 65–66° (lit.[35] 64–65.5°).

p-**Chlorobenzophenone** *p*-**Tolylimine** (IV).—A solution of 54.5 g. (0.25 mole) of *p*-chlorobenzophenone, 35.7 g. (0.3 mole) of *p*-toluidine and 0.1 g. (0.005 mole) of phosphorus pentachloride in 200 ml. of toluene was heated under reflux for 72 hr. After filtration of the hot solution the solvent was removed by vacuum distillation to give 80 g. (100%) of a yellow oil which on standing crystallized to a solid, m.p. 88–89°. A portion of the imine IV recrystallized from hexane and from ethanol had m.p. 90–91°.

Anal. Calcd. for $C_{20}H_{16}ClN$: C, 78.6; H, 5.3; N, 4.6. Found: C, 78.8; H, 5.3; N, 4.6.

p-**Methoxybenzophenone** *p*-**tolylimine** (V)[36] purified by chromatography on neutralized alumina with hexane as the eluent and then recrystallization and sublimation (90°, 0.2 mm.) had m.p. 97–97.5° (lit.[36] 96°).

p-**Methoxy**-*p*′-**nitrobenzophenone** *p*-**Tolylimine** (VI).—A solution of 12.9 g. (0.05 mole) of *p*-methoxy-*p*′-nitrobenzophenone,[37] 6.48 g. (0.06 mole) of *p*-toluidine and 25 mg. of phosphorus pentachloride in 250 ml. of toluene was heated at reflux temperature for 72 hr., during which time water was distilled from the reaction mixture. The hot solution was filtered, and on cooling large yellow prisms (8.0 g., 46%, m.p. 172–174°) crystallized from the toluene solution. The product was purified by recrystallization from ethanol and an analytical sample, m.p. 174–175°, was prepared by sublimation at 170° (0.2 mm.).

Anal. Calcd. for $C_{20}H_{18}N_2O_3$: C, 72.8; H, 5.2; N, 8.1. Found: C, 72.6; H, 5.2; N, 8.1.

Infrared spectra of the imines in potassium bromide disks were obtained in 0.5% potassium bromide, the sample being ground and pressed[38] until the spectrum was constant. The spectra of "heated" samples were obtained by heating the mixture to the m.p. of the compound being examined (a color change was apparent at the m.p.). The disk was pressed immediately and the spectrum measured.[32]

The most significant spectral features in the spectra of the nitromethoxyimine VI are: A doublet partially resolved consisting of peaks of nearly equal intensity at 955 and 967 cm.$^{-1}$ in the solution spectrum (5% chloroform solution) becomes an unsymmetrical doublet (the 955-cm.$^{-1}$ peak being relatively intense) in the spectrum of the potassium bromide disk, and reverts to the nearly symmetrical pair of absorptions when the disk is heated. An intense band at 1255 cm.$^{-1}$ in the solution spectrum is only a shoulder on a new intense absorption at 1264 cm.$^{-1}$ in the spectrum of the disk and reverts to 1255 cm.$^{-1}$ when the disk is heated. A broad absorption maximum at 1302–1315 cm.$^{-1}$ separates into a doublet with a weaker band at 1304 and a stronger one at 1315 cm.$^{-1}$ in the spectrum of the disk. The doublet returns to its original shape in the spectrum of the heated disk. Finally an intense band at 1595 cm.$^{-1}$ in the solution spectrum develops a partially resolved sister peak at 1620 cm.$^{-1}$ in the potassium bromide disk which reverts to the single band in the spectrum of the heated disk.

Isomerization of the Imine VI.—Approximately 0.5 mg. of *p*-methoxy-*p*′-nitrobenzophenone *p*-tolylimine (VI) was added to 25 ml. of diethyl ether containing about 0.1 g. of calcium hydride and cooled in an ice–salt-bath to 0°. The solution was transferred immediately to a cell which had been placed in the Cary spectrophotometer of which the cell compartment had been flushed with dry nitrogen. The absorbance at a fixed wave length of 277 mμ was measured within 10 sec. after the solution was added to the cell, and found to increase from an initial value of 1.22 to a final value reached after 1 min. of 1.45. An ether blank showed no absorption in a similar experiment.

In another experiment, from a potassium bromide disk of the imine VI (approximately 0.001%), the ultraviolet spectrum was obtained using a blank potassium bromide disk in the reference beam. The absorption maximum appeared at 278 mμ (compared to a maximum at 274 mμ in cyclohexane solution). When the disk was ground, heated to the m.p. of the compound and pressed again a spectrum was obtained with a maximum at 277 mμ, essentially unchanged in position, but with an increase in absorbance from 0.57 in the original sample to a value of 0.71.

Kinetics of Isomerization of the *cis*-**Chloroimine** *cis*-**I.**—All equipment was soaked in cleaning solution, rinsed with dilute ammonium hydroxide, demineralized water, and absolute methanol, dried for 1 hr. at 125° and cooled in a desiccator with potassium hydroxide as desiccant.

The reaction flask used for the kinetics was fitted with an inlet for nitrogen and an outlet closed off with a Teflon stopcock and a rubber cap to allow the removal of samples with a hypodermic syringe while a positive pressure of nitrogen was maintained. Into the reaction flask were placed 1 to 2 mg. of the *cis*-isomer and *ca.* 30 mg. of calcium hydride. The flask was placed in a constant temperature bath, 10 cc. of cyclohexane was added with a hypodermic syringe and 10 min. was allowed for temperature equilibration. Samples were removed with a hypodermic syringe and diluted to a concentration convenient for measuring the ultraviolet absorbances at 245 and 255 mμ. The absorbances were measured with a Beckman DU spectrophotometer. Rate constants were calculated from the plot[39]

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(34) A. Bayer and V. Villiger, *Ber.*, **37**, 606 (1904).

(35) E. C. Britton and F. Bryner, U. S. Patent 1,938,890 [*C. A.*, **28**, 17156 (1928)].

(36) A. Hantzsch and F. Kraft, *Ber.*, **24**, 3511 (1891).

(37) K. Auwers, *ibid.*, **36**, 3898 (1903).

(38) E. H. White, *J. Chem. Educ.*, **34**, 41 (1957).

of $\ln[(A_e - A_o)/(A_e - A)]$ against t, the constant $k_1 + k_2$ being obtained by the method of least squares.[40] Here A_e and A_o are absorbances at equilibrium and initially, A is the instantaneous absorbance during the reaction and t is the time. Rate constants and their probable errors are presented in Table VI.

TABLE V

RATE OF ISOMERIZATION OF *cis-p*-CHLOROBENZOPHENONE METHYLIMINE (*cis*-I) IN CYCLOHEXANE AT 40.20 ± 0.05°, C_0 6.5 × 10^{-4} *M*

Time, hr.	Ratio A_{245}/A_{255}	% *trans*	$\ln (A_e - A_o/A_e - A)$	$k_1 + k_{-1} \times 10^5$ sec.$^{-1}$
0.0	1.365	2.6	0.045	
1.0	1.337	5.3	.096	1.11
2.0	1.311	8.2	.153	1.35
3.0	1.319	7.4	.138	0.76
15.0	1.149	28.2	.665	1.13
16.0	1.129	31.1	.767	1.23
20.0	1.116	32.8	.834	1.08
24.0	1.086	37.4	1.035	1.13
26.0	1.084	37.7	1.050	1.06
			Av.	1.11
			Least squares	1..11 ± 0.03

TABLE VI

RATES OF ISOMERIZATION OF *cis*-I IN CYCLOHEXANE

T (°C. ± 0.05°)	$10^4\ C_0$, moles/l.	$10^5\ (k_1 + k_2)$, sec.$^{-1}$
40.2	6.5	1.11 ± 0.03
40.2	43.5	1.07 ± .02
40.2	6.5	1.22 ± .03
50.2	7.4	4.04 ± .03
60.2	8.7	12.2 ± .4
60.2	8.7	13.0 ± .3
40.2	0.43[a]	1.06[b]
40.2	0.4–0.5[a]	1.09[b]

[a] These reactions were carried out in decalin. [b] The best slopes were determined graphically in these cases.

E_a was obtained by a least squares treatment of a plot of $\log (k_1 + k_2)$ *versus* $1/T$ (data in Table VI). ΔH^* was obtained[41] from the expression $\Delta H^* = E_a - RT$ and ΔS^* from $\Delta S^* = 2.303R \log (A/T) + 2.303R \log (h/k) - R$. These quantities and their probable errors are presented in Table III.

Kinetics of the Isomerization of *p*-Nitrobenzophenone Methylimine (*trans*-II) in Cyclohexane.—The cyclohexane used was purified and the equipment was cleaned in the same manner as that used in the rate determinations of *cis*-I. The standard ultraviolet spectra of the equilibrium mixture were prepared by heating a sample of the *trans* isomer in a sealed tube in the presence of a small amount of calcium hydride. The method of Dewar and Urch[42] was used for the ultraviolet spectral analysis of each kinetic point. The method involves the graphical solution of the equation

$$R = x\frac{R_a}{C_a} + y\frac{R_b}{C_b}$$

for x and y, the respective concentrations of A and B in the unknown, at a number of different wave lengths, where R is the absorbance of the unknown, and R_a and R_b are the respective absorbances of components A and B, in concentration C_a and C_b. The absorbances for the standards and a set of sample data are given in Table VII.

TABLE VII

CALCULATION OF COMPOSITION OF MIXTURE IN REARRANGEMENT OF *trans*-II

mμ	R_{trans}[a]	$R_{eq.}$[a]	$\frac{R_{trans}}{R_{eq.}}$	$\frac{R_{eq.}}{R_{trans}}$	R	$\frac{R}{R_{trans}}$	$\frac{R}{R_{eq.}}$
290	0.837	0.617	1.357	0.737	0.618	0.738	1.001
280	.969	.756	1.281	.781	.745	.769	0.984
270	.839	.739	1.136	.881	.708	.843	.957
260	.617	.672	0.904	1.107	.563	1.010	.912
250	.426	.631	.674	1.483	.503	1.301	.877
240	.333	.544	.614	1.629	.422	1.412	.866

[a] Concentration 5.83 × 10^{-5}*M*.

The general procedure for the measurement of the rate of isomerization of *p*-nitrobenzophenone methylimine was the same as that for the *p*-chlorobenzophenone methylimine, except that the ultraviolet spectra were measured with a Cary model 14 recording spectrophotometer at a chart speed of 6 mμ/in. The data are presented in Table VIII.

TABLE VIII

RATES OF ISOMERIZATION OF *trans*-II IN CYCLOHEXANE

T (°C. ± 0.05°)	$10_4\ C_0$, moles/l.	$10_5\ (k_1 + k_2)$, sec.$^{-1}$
40.2	29	1.24 ± 0.02
40.2	4.2	1.08 ± .03
50.2	8.3	4.26 ± .17
60.2	8.3	16.0 ± .1
60.2	8.3	15.9 ± .2

Energies and entropies of activation calculated as described for *cis*-I are presented with their probable errors in Table III.

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(39) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 173.

(40) L. P. Hammett, "Introduction to the Study of Physical Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1952, p. 410.

(41) See ref. 39, pp. 97, 98.

(42) M. J. S. Dewar and E. S. Urch, *J. Chem. Soc.*, 345 (1957).