Uncatalyzed *syn–anti* Isomerization of Imines, Oxime Ethers, and Haloimines[1]

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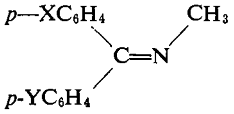
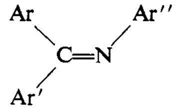
Abstract: The imines $(p\text{-}CH_3OC_6H_4)_2C{=}NC_6H_4X\text{-}p$ with X = $N(CH_3)_2$, CH_3, H, and $COOC_2H_5$ have been found to have nmr spectra near room temperature characteristic of structures with the C_6H_4X *cis* to one of the *p*-methoxyphenyl rings and with interconversion of stereoisomers slow on the nmr time scale. When the samples are heated the spectra change in the way to be expected if isomerization becomes rapid. The coalescence temperatures of the methoxyl absorptions and first-order rate constants (sec^{-1}) at those temperatures are found to be 78.8°, 5.8; 69.5°, 8.7; 62.2°, 10.9; and 29.8°, 12.4. Evidence that the nmr is indeed measuring the rate of the change assumed is provided by studies of the unsymmetrically substituted imines $p\text{-}CH_3OC_6H_4(C_6H_5)C{=}NC_6H_4X\text{-}p$ (with X = $N(CH_3)_2$, CH_3, and Cl) whose infrared spectra suggest that they crystallize preferentially in a single stereoisomeric form but isomerize very rapidly in solution even in nonpolar solvents to a mixture with an equilibrium constant near 1. The rate of isomerization in carbon tetrachloride of *trans*-N-[*p*-dimethylaminophenyl]-*p*-methoxybenzophenone imine in the range −7.2 to 12.5° measured by the change in ultraviolet spectrum leads to a value extrapolated to 62° of 1.0 sec^{-1} in reasonable agreeement with the value estimated from the nmr results jut discussed. The *o*-methyl ethers of *cis*- and *trans*-*p*-chlorobenzophenone oxime have been found to have quite unexpected configurational stability; the *cis* isomer in decane is not appreciably isomerized after 170 hr at 230°. *cis*- and *trans*-*p*-chlorobenzophenone N-chlorimine have been prepared and consideration of their infrared spectra suggests that the configurational assignments previously made on the basis of dipole moments should perhaps be reversed. These compounds and *cis*-*p*-chlorobenzophenone N-bromimine show configurational stability intermediate between the N-alkyl- or arylimines and the oximes but their isomerization is complicated by the incursion of a free-radical reaction involving breaking of the N–halogen bond. Examination of the aromatic proton region of the nmr spectra of the triarylimines prepared in the course of this work leads to the conclusion that the aromatic protons of one aromatic ring are shifted to higher field by a ring *cis* to the first; the shift of the inner protons (*ortho* to the point of attachment of the ring to the imine functional group) amounts to 0.4–0.6 ppm (relative to the *trans* arrangement) whereas the shift of the more remote protons (*meta* to the point of attachment) is only 0.04–0.16 ppm. These shifts are comparable in direction and magnitude to shifts found in other systems. It is proposed from a consideration of the aromatic region near 830 cm^{-1} in the infrared spectra that the absorption associated with the out-of-plane bending motion of the ring protons of a *para*-disubstituted phenyl ring attached to a doubly bound atom occurs at a frequency of from 4 to 10 cm^{-1} higher in that isomer with an adjacent *cis* methyl, methoxyl, or halogen (relative to the *trans* arrangement). Possible limitations to this generalization are cited. A comparison of the ultraviolet spectra of the *para*-substituted benzaldehyde methylimines ($XC_6H_4CH{=}NCH_3$ with X = H, Cl, NO_2) with those of the unsymmetrically substituted benzophenone methylimines ($XC_6H_5(C_6H_4)C{=}NCH_3$) leads, if it is assumed that the benzaldehyde imines are predominately *trans*, to the observation that replacement of the aldehydic hydrogen by an aryl group results in a rather small shift (≤ 8 m*u*) in the absorption maximum and provides further support for the stereochemical assignments.

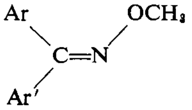
An earlier study[3] of the uncatalyzed *cis–trans* (or *syn–anti*) isomerization of imines of formula A (with X and Y = Cl, NO_2, or H) in inert solvents showed that the *cis–trans* shift of a methyl group occurs at a rate convenient for measurement by conventional methods in the temperature range from 40 to 60°. On the other hand when the migrating group was an aryl ring the evidence suggested that isomerization was too rapid to be followed conveniently by infrared or ultraviolet spectroscopy. This paper reports the measurement of the *cis–trans* isomerization of certain triarylimines (B) and also oxime ethers (C) and haloimines (D).[4]



A



B



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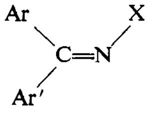

D

Symmetrical Triarylimines. Previous work[3] had suggested that the position in the proton magnetic resonance spectrum of the absorption of a *p*-methoxyl group on a benzene ring might be sufficiently sensitive to the configuration at the carbon–nitrogen double bond to provide a means of following the rate of *cis–trans* isomerization in a molecule such as *p,p'*-dimethoxybenzophenone phenylimine (I).[5] For this reason the synthesis of I[5] and its derivatives II, III, and IV with *para* substituents on the N-phenyl ring was accomplished by treatment of the appropriate substituted aniline with *p,p'*-dimethoxybenzophenone in the presence of phosphorus oxychloride in toluene solution. The imine could in each case be separated from traces of unreacted ketone (revealed by the presence of the car-

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[1] Taken in part from the Ph.D. thesis of C. G. McCarty, University of Illinois, 1963. Grateful acknowledgment is made to the Petroleum Research Fund administered by the American Chemical Society and to the National Science Foundation for grants providing partial support of this work.

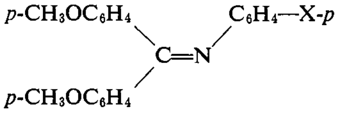
[2] Roger Adams Fellow, 1959–1960. National Science Foundation Fellow, 1960–1961. Standard Oil of California Fellow, 1961–1962. Public Health Service Fellow, 1962–1963.

[3] D. Y. Curtin and J. W. Hausser, *J. Am. Chem. Soc.*, **83**, 3474 (1961).

[4] A part of this work has been reported in preliminary form: D. Y. Curtin and C. G. McCarty, *Tetrahedron Letters*, 1269 (1962).

[5] A. Schönberg and W. Urban, *J. Chem. Soc.*, 530 (1935).

bonyl stretching absorption in the infrared spectrum) by crystallization and chromatography on neutralized alumina. The nmr spectra of the parent imine I and the *p*-dimethylamino and *p*-methyl derivatives II and III, measured at 60 Mc in carbon tetrachloride, showed the *p*-methoxy proton absorption as two peaks of approximately equal intensity with a separation of 0.03–0.08 ppm. The positions of these absorptions at



I, X = H (τ 6.20, 6.28)
II, X = $N(CH_3)_2$ (τ 6.25, 6.28)
III, X = CH_3 (τ 6.26, 6.31)
IV, X = $COOC_2H_5$ (τ 6.26 (broad))

room temperature are indicated next to the formula above. The *p*-dimethylamino proton absorption of II occurred as a singlet at τ 7.19 and the *p*-methyl proton absorption of III as a singlet at 7.80. When the imines I–III were heated to 70°, the methoxyl absorptions coalesced but reverted to their original positions when the sample was cooled. The *p*-carbethoxyimine IV showed its *p*-methoxyl proton absorption as a somewhat broadened peak at τ 6.26, which separated into a doublet when the sample was cooled below 30°.

It was assumed, as a working hypothesis, that the process responsible for the changes in nmr spectra noted above was *cis–trans* isomerization which, when sufficiently rapid, made equivalent the environments of the two methoxyl groups in imines I–IV. Measurement of the coalescence temperatures could be made reproducible to within about ±0.5° and allowed the rate of the process being followed to be calculated at that temperature.[6] The results are presented in Table I. Since the rates of previous imine isomerizations had been found to fluctuate unless calcium hydride was suspended in the medium,[4] a small amount of calcium hydride was added to solutions similar to those discussed above but was found to have no effect on the observed coalescence temperature or on the maximum separation of the methoxyl absorptions. In order to compare the rates of isomerization more directly they were extrapolated to a single temperature, 62.2°, as shown in Table I. Although a knowledge of ΔS^* is required for a rigorous extrapolation it is seen from the data in Table I that there is little difference between rates extrapolated on the basis of $\Delta S^* = 0$ and those based on $\Delta S^* = -10$ eu. Plots of log $k_1^{62.2°}$ *vs.* Hammett σ^{-}[7,8] are reasonably linear and values of ρ and the probable error are $+1.67 \pm 0.15$ from the data based on $\Delta S^* = -10$ eu. The relative insensitivity of ρ to the choice of ΔS^* leads to the conclusion that it is of the order of +1.5.

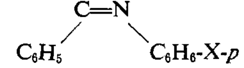
Although it is clear that the nmr has measured the rate of some change in molecular structure, it is not at all evident without further justification that the process followed is the postulated *cis–trans* isomerization. One alternative, for example, is that with the N-aryl group locked in one of its two *cis–trans* positions rotation of the adjacent *p*-methoxyphenyl ring is restricted at low temperatures but accelerated at higher temperatures to a degree which leads to the change observed in the nmr spectra. In order to provide a more direct connection between the nmr measurements and the isomerization process, we undertook the investigation of several unsymmetrical imines.

Table I. Isomerization Rates of *para*-Substituted Dimethoxyimines I, II, III, and IV in Carbon Tetrachloride

Substituent (compd)	Coalescence temp, °C (±0.5°)	Maximum sep, cps at 60 Mc (±0.15)	k_1, sec^{-1} (±0.3)	$k_1^{62.2°}$ (extrapolated)
p-$(CH_3)_2N$ (II)	78.8	2.60	5.8	(1.3)[a]
p-CH_3 (III)	69.5	3.92	8.7	(4.4)[a] (5.0)[b]
p-H (I)	62.2	4.90	10.9	11
p-$COOC_2H_5$ (IV)	29.8	5.59	12.4	(180)[a] (110)[b]

[a] Extrapolation assuming $\Delta S^* = 0$ eu. [b] Extrapolation assuming $\Delta S^* = -10$ eu.

Unsymmetrical Imines. It had been observed previously[3] that unsymmetrical analogs of the *p*-methylimine III, such as *p*-methoxybenzophenone *p*-tolylimine (V), melted over a reasonably narrow range but in carbon tetrachloride solution showed two absorptions attributed to *p*-methoxyl protons. Furthermore when the infrared spectrum of a pressed potassium bromide disk was examined the spectrum had differed significantly from a solution spectrum. When the disk was ground, heated, and repressed, it gave a spectrum similar to that of the solution. This evidence led to the suggestion that N-arylimines of this type were present in solution as a rapidly equilibrating mixture of *cis* and *trans* isomers but crystallized in a single stereoisomeric form. In order to confirm and extend these observations the unsymmetrical *p*-tolylimine[3,9] V and also the corresponding *p*-dimethylaminoimine[10] VI and the *p*-chlorimine[9] VII were prepared. As was implied by the previous investigators[3,9,10] each of these compounds is a crystalline solid with the small melting point range (≤1°) to be expected of a single pure substance (or a eutectic mixture). On the other hand each of the unsymmetrical imines in solution gave rise to two methoxyl proton peaks to be expected of a mixture and with a separation of 0.04–0.06 ppm and to two infrared absorptions in the region near 700 cm^{-1} associated with monosubstituted phenyl rings. The methyl proton absorption of V and the dimethylamino proton absorption of VI also appeared as a doublet but with a smaller separation. As was observed[3] with the unsymmetrical triarylimines previously examined, each of the imines as the solid in a potassium bromide disk



V, X = CH_3 (*trans* isomer shown)
VI, X = $N(CH_3)_2$
VII, X = Cl

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[6] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chapter 13.

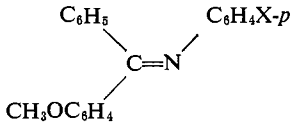
[7] J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chapter 4; H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953); see especially Tables 7 and 10.

[8] The fit was somewhat better when the σ^{-} value rather than σ was employed for the carbothoxyl group.

[9] A. Hantzsch and F. Kraft, *Ber.*, **24**, 3511 (1891).

[10] A. Hantzsch, *ibid.*, **26**, 927 (1893).

Table II. Nmr and Infrared Results for the Unsymmetrical Imines V–VII



$$(C_6H_5)(CH_3OC_6H_4)C{=}N{-}C_6H_4X\text{-}p$$

	Solution spectra (CCl_4)					Potassium bromide spectra, cm^{-1}	
			Estimated ratio of intensities				
X (compd)	Nmr of CH_3O	Nmr of CH_3N or CH_3C	Nmr	Infrared	Infrared, cm^{-1}	Before heat	After heat
$N(CH_3)_2$ (VI)	6.24[a]	7.20[b]	1.4	>1	699	702[c]	702[d]
	6.28	7.18			695		696
CH_3 (V)	6.22[a]	7.80[e]	1.7	>1	700	703	703
	6.28	7.78			695		697
Cl (VII)	6.23[a]	...	1.9	>1	698	701	701
	6.29	...			694		695

[a] This was the larger of the two OCH_3 peaks in the spectrum. [b] This was the larger of the two NCH_3 peaks in the spectrum. [c] Repeated grinding and pressing did not change the spectrum. [d] Heated for 20 min above the melting point of the particular imine. Repeated heating and pressing made no further change in the spectrum. [e] This was the larger of the two CCH_3 peaks in the spectrum.

gave a single absorption in the region of the infrared near 700 cm^{-1}. When the disk was heated and reformed the monosubstituted phenyl absorption shows the development of a well-defined shoulder at lower frequencies. These nmr and infrared results are presented in Table II.

The results of the infrared measurements with pressed potassium bromide disks thus suggest that each of the unsymmetrical imines V–VII crystallizes largely or entirely as a single isomer, in each case with the disubstituted phenyl ring ($CH_3OC_6H_4$) *trans* to the aryl ring attached to the nitrogen atom[11] as shown in Table I. The assignment of configuration to the crystalline solid is based on the previous[3] empirical correlation showing that a monosubstituted phenyl ring attached to a double bond has its absorption in the 700-cm^{-1} region at higher frequency when it is *cis* to another group than when it is *trans*. Spectra, both nmr and infrared, show that in solution a mixture of isomers is present. The relative amounts of the two isomers is not readily determined from the infrared absorptions in the 700-cm^{-1} region since they are only partially resolved and also since extinction coefficients are not necessarily the same for *cis* and *trans* rings. They suggest, however, that in each case the *trans* isomer is in slight excess. The nmr results, although unrefined, suggest that the excess of *trans* imine over *cis* is small but increases with increasing positive σ of the *para* substituent. Similar results, obtained with *p*-chlorobenzophenone *p*-methoxyphenylimine and *p*-chlorobenzophenone *p*-tolylimine, are described in the Experimental Section of this paper.

It was now desired to interrelate the results obtained with the symmetrical and unsymmetrical systems. Previous work with the methylimines[3] showed that the rate of *cis–trans* isomerization was quite insensitive to change of a *para* substituent on a phenyl ring attached to the doubly bound carbon atom. If this is the case with the phenylimines I–IV removal of one methoxyl group to give a corresponding member of the unsymmetrical series V–VII should have little effect on the isomerization rate. Thus, a comparison between a rate measured by the nmr technique used with the symmetrical imines and a rate of isomerization of one of the unsymmetrical imines using a conventional kinetic method is of interest. Such a comparison provides much better evidence than any argument considered thus far that the nmr method is measuring a *cis–trans* interconversion as had been assumed. The correctness of this point of view was supported by the preliminary observation with nmr spectroscopy of the unsymmetrical *p*-tolyl compound V which was found to have a maximum separation of 3.5 cps (60 Mc) for the OCH_3 peaks and 1.5 cps for the CCH_3 peaks. The methoxyl peaks coalesced at about 69° as compared with 69.5° for the analogous dimethoxy compound III and the methyl peaks coalesced at about 50°. Since the two states being equilibrated are not equally populated a rate constant at the coalescence temperature cannot readily be calculated for the unsymmetrical compound V.

Extrapolation to 0° of the data in Table I suggested that the dimethylaminoimine II should have a rate constant for the isomerization reaction of about 10^{-4} and therefore the unsymmetrical dimethylaminoimine VII was expected to isomerize at a rate which could be measured by conventional methods. The ultraviolet spectrum of *trans*-VII freshly dissolved in carbon tetrachloride at 0° had a maximum at 275 mμ (ϵ 29,000) but on standing there developed a broad shoulder at 255 mμ. The spectrum measured at room temperature showed the maximum at 272 mμ (ϵ 21,000) and shoulder at 255 mμ (ϵ 20,000).[12] Following the integrated rate expression for the approach to equilibrium between A and B,[13] plots of $\ln (A_e - A_0)/(A_e - A)$

$$\ln (A_e - A_0)/(A_e - A) = (k_1 + k_{-1})t = k_{obsd}t$$

against t (using the absorbance at 290 mμ) were linear, and the values of k_{obsd} and the standard deviations deter-

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(11) This will be designated as the *trans* isomer, the reference being to the relative positions of the two monosubstituted phenyl rings.

(12) The ultraviolet spectra support the configurational assignment made on the basis of the infrared spectra. Thus, it might be expected[3] that starting with benzophenone *p*-dimethylaminophenylimine and introducing a *p*-methoxyl group on the ring *trans* to the *p*-dimethylaminophenyl ring should produce a larger conjugative shift than introducing the *p*-methoxyl group on the ring *cis* to the adjacent aryl ring. A further argument based on ultraviolet spectroscopy will be discussed in a later section of this paper.

(13) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, pp 96–99 and 172–173.

mined by the method of least squares[14] are presented in Table III. The energy and entropy of activation in Table III were determind from a plot of ln k_{obsd} against $1/T$ and are the average of the quantities for the forward and reverse reactions.[3] The equilibrium constant estimated from the ratio of areas of methoxyl proton absorptions in the nmr in this temperature range was 1.2 and could be used to separate k_{obsd} into k_1 and k_{-1}. Such a refinement would have a negligible effect on the conclusions being drawn, however. The low-temperature rates when extrapolated to 62° give a value of 1 sec^{-1} which is in excellent agreement with the value of $(k_1 + k_{-1})$ $(=2k_1)$ of 2.6 sec^{-1} for the isomerization of the symmetrical dimethylaminoimine II (Table I).

Table III. Rates of Isomerization of the Unsymmetrical Dimethylamino Imine VII (4×10^{-4} *M* in Carbon Tetrachloride Followed by Observation of the Absorption at 290 mμ)

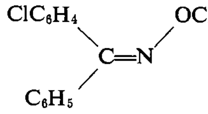
Temp, °C (±0.2)	$10^4 k_{obsd}$, sec^{-1}	E_a, kcal/mole	ΔS*, eu
−7.2	4.08 ± 0.05	19.7 ± 0.4	−2.1 ± 1.5
−7.2	4.37 ± 0.05		
+2.8	15.0 ± 0.2		
+3.3	16.0 ± 0.2		
12.2	53.7 ± 0.5		
12.5	54.2 ± 0.2		
62	$(1.0 \times 10^4)^a$		

[a] Extrapolated value.

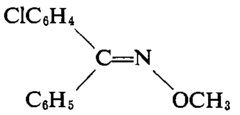
The unsymmetrical tolylimine V when dissolved in carbon tetrachloride also underwent a change in ultraviolet absorption spectrum. This isomerization was so rapid, even at −7.2°, that it was not studied as thoroughly as the dimethylamino analog VI. A single reaction of V with an initial concentration of 5×10^{-4} *M* at −7.2° gave k_{obsd} $23.3 \pm 0.2 \times 10^{-4}$ sec^{-1} when the change of absorption at 280 mμ was observed. This value and that of 4.2×10^{-4} obtained in Table III for the dimethylamino compound VI at −7.2° lead to a value of +1.7 for ρ which is in good agreement with the values estimated earlier in this paper for the effect of substituents on the isomerization of the symmetrical compounds I–IV.

Although none of the lines of evidence cited thus far when taken singly leads convincingly to the conclusions drawn, the combined weight of the nmr, infrared, and ultraviolet spectroscopic studies of the symmetrical and unsymmetrical series taken together provides strong evidence that the processes being studied here are the uncatalyzed *cis–trans* isomerizations of the triarylimines and further that the solid forms of the unsymmetrical imines V–VII are largely or completely the *trans* isomers which undergo rapid equilibration when dissolved in nonpolar solvents, the equilibrium constants in solution lying near 1.

Oxime Ethers. In an effort to extend our knowledge of the effect of structure on the *cis–trans* isomerization of molecules ArAr′C=NX it was desired to obtain quantitative information on isomerization rates of oxime ethers *cis*- and *trans*-VIII.[15] These compounds, chosen because of their structural simplicity and similarity to the series of imines previously described, were prepared by alkylation of the known *syn*- and *anti-p*-chlorobenzophenone oximes.[19] The configurational assignments are consistent with the generalization[3] that



cis-VIII, mp 65°
693 cm^{-1}
829 cm^{-1}
τ 6.19



trans-VIII, mp 45°
705 cm^{-1}
694
833
τ 6.20

the monosubstituted band in the 700-cm^{-1} region of the infrared spectrum is at higher frequency when the phenyl ring is *cis* to another group; in this case the situation is complicated by the fact that *trans*-VIII, with the monosubstituted phenyl ring *cis* to the adjacent methoxy, has two maxima in the 700-cm^{-1} region of the spectrum but each of them is at higher frequency than the corresponding absorption of the *trans* isomer as is indicated under the formulas above.[20,21] The methoxyl proton resonance in carbon tetrachloride in the nmr spectrum was a singlet at τ 6.09 and there was no indication of a doublet in an equimolar mixture of *cis*- and *trans*-VIII. In acetone solution, however, there was a small separation (0.3 cps) and in benzene solution *cis*-VIII had τ 6.19 and *trans*-VIII 6.20. (A 1:1 mixture showed a separation of 0.8 ± 0.1 cps between the methoxyl proton signals.) The oxime ethers *cis*- and *trans*-VIII each showed extreme configurational stability. Initial reactions in which the *cis* isomer was heated at 60° for 96 hr and at 112° for 45 hr in methylcyclohexane solution showed no detectable change. A solution of the *cis* isomer was heated in dried and degassed decane containing a small amount of calcium hydride in a bomb tube for 170 hr at 230°; at the end of this time the infrared spectrum was nearly identical with that of the starting material. Finally *trans*-VIII was heated for 528 hr at 200° in degassed decane solution and the reaction was followed by the change in absorption spectrum. The reaction was too slow to permit the calculation of a reliable rate constant but it seems justified to set 10^{-7} sec^{-1} as a maximum possible value for the rate constant for isomerization at that temperature.

The great configurational stability of the oxime ethers VIII is in striking contrast to the behavior of the imines previously discussed but is at least hinted at by scattered observations in the literature. For example, the α isomer of benzil O-methyl monoxime was unchanged by refluxing in benzene and alcohol for 90 min in the presence of a grade of blood charcoal which had proved

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[14] W. J. Youden, "Statistical Methods for Chemists," John Wiley and Sons, Inc., New York, N. Y., 1951, p 42.

[15] Although the literature contains reports of several studies[16-18] of the isomerization of oximes, these substances offer complications because of the possibility of hydrogen bonding and ionization of the proton introduced by the presence of the hydroxyl group and will not be discussed here.

[16] T. S. Patterson and H. H. Montgomerie, *J. Chem. Soc.*, **101**, 2100 (1912).

[17] R. J. W. LeFevre and J. Northcott, *ibid.*, 2235 (1949).

[18] E. G. Vassian and R. K. Murmann, *J. Org. Chem.*, **27**, 4309 (1962).

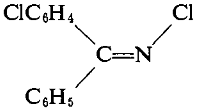
[19] G. H. Coleman and R. E. Pyle, *J. Am. Chem. Soc.*, **68**, 2007 (1946); J. Meisenheimer and W. Theilacker, "Stereochemie," Vol. 3, K. Frerdenberg, Ed., Franz Deuticke, Leipzig, 1932, p 1033.

[20] It is not unlikely that the two maxima are the result of Fermi resonance interaction of a monosubstituted phenyl absorption at 700 cm^{-1} with a nearby vibration frequency.[21]

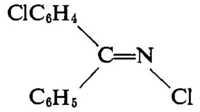
[21] G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. 2, D. van Nostrand Co., Inc., 1945.

active in isomerizing the analogous oximes.[22] The β isomer of O-methyl *m*-nitrobenzaldoxime was not isomerized on melting (75°) and was kept unchanged for 16 yr at ambient temperatures.[23] However, the β forms of the ethers of ten aldoximes were reported[23] to be isomerized readily to the α forms by hydrogen chloride in chloroform.

N-Haloimines. The *p*-chlorobenzophenone N-chlorimines (*cis*- and *trans*-IX) had been prepared previously and configurations assigned[24] by means of dipole moment measurements. Employing an estimate of the theoretical moments which neglected the contribution of the unshared electron pair on nitrogen, it was concluded that the compound with the larger moment was *cis*-IX. Examination of the infrared spectra of *cis*- and *trans*-IX showed the higher melting isomer to have monosubstituted phenyl absorption at 692 and the lower melting isomer to have its corresponding absorption at 698 cm^{-1} which would lead[3] to a reversal of the assignments made previously. Additional support for the correctness of the assignment from the position of the monosubstituted phenyl band in the infrared spectrum can be obtained by development of a further empirical correlation first noted by Hausser;[25] the infrared absorption frequency near 830 cm^{-1} in a molecule with a *para*-substituted phenyl ring[26] attached to a doubly bound carbon atom is shifted to lower frequency when the substituted phenyl ring is *cis* to another atom or group. In Table IV are presented data which form the basis for this generalization. As will be noted it holds without exception for the five pairs of compounds with carbon–nitrogen double bonds and for the first pair of olefins listed. The generalization is seemingly contradicted by the remaining three pairs of olefins. Each of these cases has possible complications referred to in the table so that the true extent of the generalization must await further work. Although application of these principles involves risk inherent in the use of any empirical generalization, they seem more reliable than the argument from dipole moment data and we have accordingly reversed provisionally the previous[24] assignments of configuration to the chlorimines *cis*- and *trans*-IX.



cis-IX, mp 105°
2.47 D.
692 cm^{-1}
826 cm^{-1}



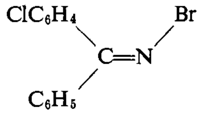
trans-IX, mp 55°
2.67 D.
698 cm^{-1}
836 cm^{-1}

Table IV. Effect of Configuration on the Position of the *para*-Disubstituted Phenyl Absorption (near 830 cm^{-1})

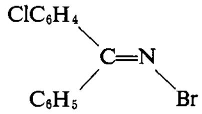
Compound	Absorption of isomer, cm^{-1} With p-XC$_6$H$_4$ *cis* to adjacent group[a]	With p-XC$_6$H$_4$ *trans* to adjacent group[a]
Imines, Haloimines, Oxime Ethers		
p-Chlorobenzophenone N-methylimine[b,c]	824	(835)
p-Nitrobenzophenone N-methylimine[c,d]	(847)	850
p-Chlorobenzophenone O-methyloxime[e,f]	829	833
p-Chlorobenzophenone N-chloroimine[d,e,g]	826	836
p-Chlorobenzophenone N-bromine[d,e,g]	829	(839)
Olefins		
1-*p*-Chlorophenyl-1-phenyl-2-bromoethylene[b,h]	836	844
4-Phenylethynylstilbene[i,j]	834, 848	823
p-Methoxystilbene[k,l]	832	822
1-*p*-Chlorophenyl-1,2-diphenylethylene[b,m]	819	815 (sh 820)

[a] Values in parentheses inferred from spectrum of mixture of two isomers. [b] In cyclohexane solution. [c] J. W. Hausser, Ph.D. Thesis, University of Illinois, Urbana, Ill.,1960, pp 104, 106, 108; ref 3. [d] In carbon tetrachloride solution; it has been pointed out (K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p 6) that the per cent transmission of carbon tetrachloride in a 0.2-cm cell drops below 35% in a region from 730 to 834 cm.$^{-1}$. [e] Present work. [f] In carbon disulfide solution. [g] The spectrum of the *cis* isomer shows that the absorption at 826 cm^{-1} is on the edge of the carbon tetrachloride absorption which may make the reported absorption a bit higher than the true value. [h] E. W. Flynn, Ph.D. Thesis, University of Illinois, Urbana, Ill., 1956, p 105. [i] Potassium bromide disk. [j] Sadtler Standard Spectra, Sadtler Research Laboratories, Philadelphia, Pa., No. 24049, 24050. [k] In chloroform solvent; chloroform has strong, sharp absorption at 924 cm.$^{-1}$ (see ref *d*) which makes these numbers difficult to interpret. [l] Y. G. Hendrickson, Ph.D. Thesis, University of Illinois, Urbana, Ill., 1955, p 84. [m] W. J. Koehl Jr., Ph.D. Thesis, University of Illinois, Urbana, Ill., 1960, p 97.

cis- and *trans*-*p*-chlorobenzophenone N-bromimine (*cis*- and *trans*-X) were first reported[27] to melt at 85 and 109° but a more recent paper[24] described the isolation of substances melting at 73 and 102°. No configurational assignments were made. When we attempted to separate the isomeric bromimines by fractional crystallization from petroleum ether there was obtained the *cis* isomer in what was apparently a pure state with mp 104° and with single absorptions at 690 and at 829 cm^{-1}. Although other lower melting fractions were obtained, they were apparently not the *trans* isomer but mixtures of the two since they showed strong absorption at 697 and 839 cm^{-1} (reasonable for the *trans* isomer *trans*-X) but in addition the spectrum showed weaker absorptions at 690 and 829 cm^{-1} characteristic of the *cis* isomer.



cis-X, mp 104°
690 cm^{-1}
829 cm^{-1}



trans-X, mp ?
(697 cm^{-1})
(839 cm^{-1})

The literature suggests that halomines like IX and X should have considerable thermal stability to *cis–trans*

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(22) T. W. J. Taylor and E. M. W. Lavington, *J. Chem. Soc.*, 980 (1934).

(23) O. L. Brady and L. Klein, *ibid.*, 874 (1927).

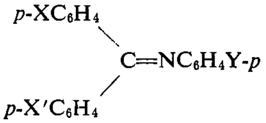
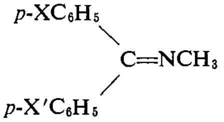
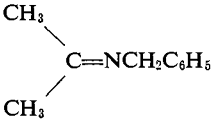
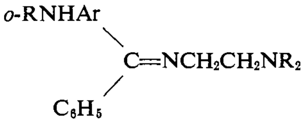
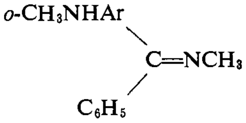
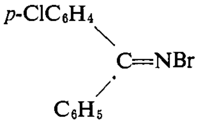
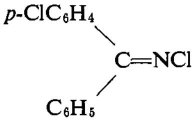
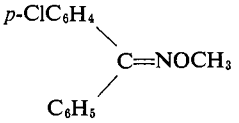
(24) W. Theilacker and K. Fauser, *Ann.*, **539**, 103 (1939); see G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p 204 ff, for difficulties in the interpretation of dipole moments of complex molecules.

(25) J. W. Hausser, Ph.D. Thesis, University of Illinois, 1960, pp 21, 24.

(26) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p 67.

(27) H. D. Young, Abstracts of Theses, University of Chicago Science Series, Vol. 4, 1925–1926, p 203.

Table V. Data on the Unimolecular *cis–trans* (*syn–anti*) Isomerization of Imines

	Structure	$k^{60°}$	E_a, kcal/mole	Solvent	Method employed
A	$(CF_3)_2C{=}NCF(CF_3)_2$	10^8	13	None	Nmr[a]
B	$C_6H_5CH{=}NC_6H_5$	...	16–17	Methylcyclohexane	Flash phot–ultraviolet[b]
		20	16.5	Ethanol	Flash phot–ultraviolet[c]
	$o\text{-}HOC_6H_4CH{=}NC_6H_5$	10	14.2	Ethanol	Flash phot–ultraviolet[c]
C	 $(p\text{-}XC_6H_4)(p\text{-}X'C_6H_4)C{=}NC_6H_4Y\text{-}p$	10	17–20	Carbon tetrachloride, cyclohexane	Nmr, ultraviolet[d]
D	$(CH_3)_2C{=}NC_6H_5$	10^{-1}	21	Quinoline	Nmr[e]
E	 $(p\text{-}XC_6H_5)(p\text{-}X'C_6H_5)C{=}NCH_3$	10^{-4}	25–27	Cyclohexane	Ultraviolet[f]
F	 $(CH_3)_2C{=}NCH_2C_6H_5$		>23	Quinoline	Nmr[e]
G	 $(o\text{-}RNHAr)(C_6H_5)C{=}NCH_2CH_2NR_2$	$\ll 10^{-4}$	...	...	Isomers isolated[g,h]
	 $(o\text{-}CH_3NHAr)(C_6H_5)C{=}NCH_3$	...	...	...	Isomers isolated[i]
H	 $(p\text{-}ClC_6H_4)(C_6H_5)C{=}NBr$	$<10^{-6}$	...	Cyclohexane	Ultraviolet[d]
I	 $(p\text{-}ClC_6H_4)(C_6H_5)C{=}NCl$	$<10^{-8}$	...	Cyclohexane	Ultraviolet[d]
J	 $(p\text{-}ClC_6H_4)(C_6H_5)C{=}NOCH_3$	$<10^{-13}$[j]	...	Decane	Ultraviolet[d]

[a] See ref 30. [b] See ref 31. [c] See ref 32. [d] Present work. [e] See ref 33. [f] See ref 3. [g] See ref 34. [h] Interconversion by heating at 140–150° without solvent reported. [i] See ref 35. [j] Extrapolated from value of 10^{-7} sec^{-1} at 200° assuming E_a 30 kcal/mole.

isomerization; for example Peterson[28] had found that similar compounds could be recovered from solution, melt, or vapor phase in the presence of crystals of the stereoisomeric form and were stable when heated with chlorine for as long as 3 hr at 100°. We could detect no isomerization of the chlorimine *cis*-IX in cyclohexane at 60° after 500 hr with ultraviolet spectroscopy as the analytical method. The maximum possible value for the rate constant for isomerization ($k_1 + k_{-1}$) at this temperature is estimated to be 10^{-8} sec^{-1} assuming that the analytical method might have been unable to detect as much as 3% of the rearrangement product. Similar experiments with the bromimine *cis*-X lead to an upper limit of ($k_1 + k_{-1}$) of 5×10^{-7} at the same temperature. Although the haloimines could be made to undergo *cis–trans* interconversion in cyclohexane or carbon tetrachloride solution at higher temperatures it was found that a free-radical process involving the breaking of the nitrogen–halogen bond occurred and so made impossible any further conclusions concerning the uncatalyzed *cis–trans* isomerization of interest here.[29]

Discussion of Results. Since the previous reports of our work[3,4] several other investigators have published studies relevant to this work. These studies have used a variety of methods and covered a range of experimental conditions but it is of interest to attempt to compare the results thus far accumulated by extrapolation to a single reference point insofar as this can be done. The results are shown in Table V.

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(28) P. P. Peterson, *Am. Chem. J.*, **46**, 325 (1911).

(29) The study of the free-radical reactions will be reported elsewhere: D. Y. Curtin and C. Gordon McCarty, in preparation.

(30) S. Andreades, *J. Org. Chem.*, **27**, 4163 (1962).

(31) E. Fischer and Y. Frei, *J. Chem. Phys.*, **27**, 808 (1957).

(32) G. Wettermark and L. Dogliotti, *ibid.*, **40**, 1486 (1964); D. G. Anderson and G. Wettermark, *J. Am. Chem. Soc.*, **87**, 1433 (1965).

(33) H. A. Staab, F. Vögtle, and A. Mannschreck, *Tetrahedron Letters*, No. **12**, 697 (1965).

(34) S. C. Bell, G. L. Conklin, and S. J. Childress, *J. Am. Chem. Soc.*, **85**, 2868 (1963); *J. Org. Chem.*, **29**, 2368 (1964).

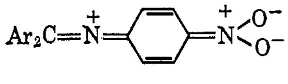
(35) G. Saucy and L. H. Sternbach, *Helv. Chim. Acta*, **45**, 2226 (1962).

The rate of isomerization of the parent imine with the formula $S_1S_2C{=}NH$ (S_1 and S_2 = alkyl or aryl groups) would be of particular interest. Lambert and Roberts[36] have found evidence using nmr spectroscopy that *sec*-butylphenylketimine-^{15}N in pentane at -60° exists as a mixture of *cis* and *trans* isomers. The equilibration process, studied by nmr between -60 and -20°, is not unimolecular, however, and probably involves a second-order double-proton exchange between two molecules. Since the velocity of this second-order process may be presumed to be greater than that of a simple first-order isomerization, it may be calculated from the data of Roberts and Lambert that k_1 must be less than 43 $\sec^{-1}$ at -20°. Unfortunately this is not a sufficient restriction to allow comparison to be made with any of the compounds referred to in Table V.[37]

The most remarkable feature of the data in Table V is the range of rates of isomerization of at least 16 powers of 10. While there is no direct kinetic evidence on the reaction order in the fastest and in the very slow examples, examples B, C, and E have been shown to isomerize by a process which is first order and hence unimolecular in the inert solvents employed. Two possible mechanisms have been most commonly considered. One involves a rotation of one-half of the molecule with respect to the other half around an axis through the doubly bound carbon and nitrogen atom and will be referred to as the "internal rotation mechanism." It is generally agreed that the stereoisomeric dideuterioethylenes,[38] 2-butenes,[39] stilbenes,[40] and dicarbomethoxyethylenes[41] isomerize by this kind of process with essentially complete unsharing but not unpairing of the electrons in the p orbitals of the π bond. These olefin isomerizations require temperatures of over 200° and as high as 470° with the simpler molecules and have activation energies ranging from 36 to 60 kcal/mole and entropies of activation of from -12 to $+2$ eu. The second isomerization mechanism which is available to imines and azo compounds but not olefins is what might be termed the "lateral shift mechanism" and consists of the shift of the substituent attached to nitrogen from one side of the molecule through a linear transition state, the nitrogen atom adopting linear sp bonds, the π bond remaining intact, and the unshared electron pair occupying the perpendicular p orbital of nitrogen in the transition state.[42]

The enormously faster isomerization rates of the imines A–E in Table V as compared to the olefins suggest that a particularly ready mechanism is available to the imines but not the olefins and therefore supports the lateral shift mechanism for these imines.

The data thus far accumulated, though limited, provide certain tentative generalizations which will be summarized here. The most striking result is the very great steric stability of the halomines and the oxime ether (H, I, and J). It is not possible to decide whether the origin of this stability is unusual stability of the bent initial state or unusual instability of the linear transition state. Comparison of examples B–F supports the generalization[3] that N-aryl groups undergo isomerization considerably faster than N-alkyl groups. The perfluorinated compound (example A) is clearly very much faster than would have been expected from the data on other alkyl groups. This may be associated with unusual behavior originating with the fluorine atoms, a possibility suggested by the authors. However, more direct evidence appears desirable that the nmr measured the rate of a *cis–trans* isomerization and not some other structural change. It will be noted that the extrapolated rate constants of examples A–E in Table V parallel the E_a values which suggests that the changes in rate are due in large measure to changes in potential energy of activation.[43] Comparison of the value of ρ[3] of about $+0.1$ for the effect of substituents on an aryl group attached to the doubly bound carbon (example E) with that of about $+1.5$ for substituents attached to the phenyl ring bound to nitrogen (example C) leads to the tentative conclusion that in more comparable cases also the isomerization reaction can be expected to have a greater sensitivity to substituents on a ring attached to the nitrogen atom. The sign and size of the larger ρ is consistent with the lateral shift mechanism with the added postulation of some contribution of dipolar resonance structures such as E to the linear transition state.



E

Use of Nmr and Ultraviolet Spectral Methods for Differentiation of and Configurational Assignment to *cis* and *trans* (*syn* and *anti*) Imines and Related Compounds. Although nmr spectroscopy has been used rather extensively in studies of stereoisomeric olefins,[44–46] oximes,[47] hydrazones,[48] and imines,[3,4,32,36] it is often

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(36) J. B. Lambert, W. L. Oliver, and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 5085 (1965).

(37) A study (J. S. Smith, unpublished work) of the proton resonance (N-H) of *p*-trifluoromethylbenzophenone imine in carbon tetrachloride (25% solution) carried out before we were aware of the results of Lambert and Roberts[36] showed a broad doublet at room temperature which coalesced when the solution was heated to 60° or when the imine concentration is increased to 50%. From the limiting separation (9.6 cps) and coalescence temperature, a rough estimate gives 40 $\sec^{-1}$ as the upper limit for k_1 at 60°.

(38) B. S. Rabinovitch, J. E. Douglas, and F. S. Looney, *J. Chem. Phys.*, 20, 1807 (1952); 23, 315 (9155).

(39) 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).

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

(41) W. W. Kwie and W. C. Gardiner, *Tetrahedron Letters*, **No. 6**, 405 (1963).

(42) There are the usual complications (found in almost all considerations of mechanism) of a possible continuum of mechanisms between the two extremes and of the possibility that there is dip in the top of the energy curve for the rearrangement which leads to an intermediate with a lifetime long enough to have chemical interest. Neither of these possible complications will be considered further at this point.

(43) L. P. Hammettt, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p 78.

(44) (a) See L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press Inc., New York, N. Y., 1959, p 119 ff; (b) A. A. Bothner-by and J. A. Pople, *Ann. Rev. Phys. Chem.*, **16**, 43 (1965).

(45) T. Hayashi, I. Hori, H. Baba, and H. Midorikawa, *J. Org. Chem.*, 30, 695 (1965); A. N. Kurtz, W. E. Billups, R. B. Greenlee, H. F. Hamil, and W. T. Pace, *ibid.*, **30**, 3141 (1965), and references therein cited.

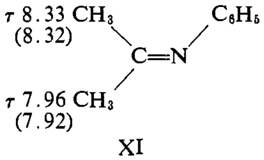
(46) D. Y. Curtin and S. Dayagi, *Can. J. Chem.*, **42**, 867 (1964).

(47) (a) W. D. Phillips, *Ann., N. Y. Acad. Sci.*, **70**, 817 (1958); (b) E. Lustig, *J. Phys. Chem.*, **65**, 491 (1961); (c) E. J. Poziomek, D. N. Kramer, W. A. Mosher, and H. O. Mickel, *J. Am. Chem. Soc.*, **83**, 3916 (1961); (d) G. Slomp and W. J. Wecheter, *Chem. Ind.* (London), 41 (1962); (e) I. Pejković-Tadić M. Hranisavljević-Jakovljević, S. Nešić, C. Pascula, and W. Simon, *Helv. Chim. Acta*, **48**, 1157 (1965).

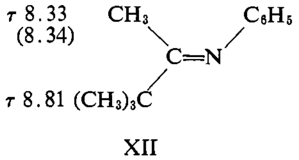
(48) G. J. Karabatsos, F. M. Vane, R. A. Taller, and N. H. Hsi, *J. Am. Chem. Soc.*, **86**, 3351 (1964), and references cited therein; G. Karabatsos, R. A. Taller, and F. M. Vane, *Tetrahedron Letters*, **No. 18**, 1081 (1964).

difficult to decide in advance whether differences in chemical shifts between *cis* and *trans* isomers will be sufficiently large to differentiate the two. It has been pointed out[47b] that with a given pair of isomers, sufficiently large differences may be found only in certain solvents as was found with oxime ethers *cis*- and *trans*-VIII discussed earlier in this paper.

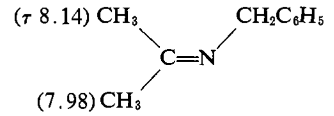
The two imines XI[49] and XII, prepared during the course of the present work, are of interest in relation to the general problem of stereoisomer differentiation by nmr. The dimethyl compound XI in carbon tetrachloride showed two methyl peaks of equal intensity at τ 7.96 and 8.33 (separation of 23 cps at 60 Mc). The mono-*t*-butyl compound XII, which is assumed to be the isomer with the bulky phenyl and *t*-butyl groups *trans* to one another, showed a single methyl absorption at τ 8.33 and the *t*-butyl absorption at τ 8.81 (ratio of areas 1:3). Since the completion of this work[1] Staab, Vögtle, and Mannschreck[33] have reported chemical shifts for the methyl groups in XI and XII and also in the related benzyl compound XIII. Our values are in agreement with theirs which are presented in parentheses next to the appropriate formulas. The deduction that the methyl group *cis* to the aromatic ring in XI is the one with the resonance at higher field may be attributed to a phenyl ring-current effect.[44] In contrast to these results a series of compounds including XIV, with R = ethyl and *n*-propyl, was reported by Lambert, Oliver, and Roberts[36] to show a single methyl absorption, possibly, as the authors have suggested, because there is a preponderance of one stereoisomer present.



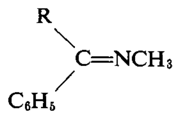
XI



XII

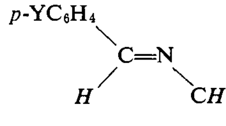


XIII

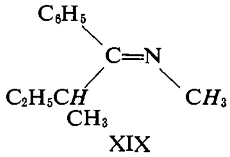


XIV

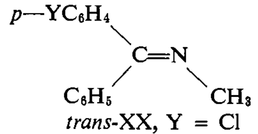
The methylimines XV–XVIII were also prepared during the course of this work and appeared to exist in each case as a single stereoisomer (presumably *trans*) in solution. The methyl absorption appeared as a doublet but this was due to spin–spin coupling with the proton on the doubly bound carbon atom which in turn appeared as a poorly resolved quartet. That the methyl doublet was due to coupling was verified by comparing spectra obtained at 40 and 60 Mc which showed the same separation. The value of J (1.45 ± 0.05 cps) was the same for compounds XV–XVIII to within the limits of our error and similar to the analogous coupling in propenylbenzenes.[50] It is of interest in this connection that coupling through four atoms was observed in compound XIX by Lambert, Oliver, and Roberts[36] with $J = 1$ cps.



XV, Y = H
XVI, Y = Cl
XVII, Y = CH_3O
XVIII, Y = NO_2



XIX



trans-XX, Y = Cl
trans-XXI, Y = NO_2

Consideration of the aromatic proton spectrum of the imines XV–XVIII and of the N-aryldimethoxyimines II–IV has led to an interpretation which, although it may be lacking in quantitative accuracy, provides considerable further support for the assumption that it is *cis–trans* isomerization which is responsible for the change of the nmr spectrum with changing temperature. Studies of the spectra of 1,2-diaryl compound[46] suggest that the ring protons associated with the *cis* and *trans* rings of the triarylimines I–IV should show up at different positions. When the rings are monosubstituted the spectra are expected to be complicated by spin–spin coupling of the five ring protons but in a substance with *para* substitutents on each of the three rings it might be hoped that each of the sets of ring protons might show up at least in the first approximation as an AB quartet. Examination of the spectra of the *p*-dimethylamino compound II and the *p*-methyl compound III does indeed lead to dissection of the spectra into separate absorptions attributed to the three aryl groups (the absorption attributed to the protons of the *p*-dimethylamino phenyl ring is a single peak; the remaining rings in these compounds give rise to partially overlapping quartets. While analysis of spectra taken individually is difficult, consideration of the available data of these and related compounds has led to the tentative assignments of absorption frequencies shown in Table VI. Although the point half-way between a pair of peaks of an AB system[51a] is not precisely the chemical shift value it is a sufficient approximation for the treatment of the present data and is the basis of the numbers in Table VI. The assignment of peaks has been in accord with principles found to hold in the study of other *cis* and *trans* isomers; for example, replacement of a hydrogen atom by a methoxyl group shifts the resonances of the other protons on the ring to higher field, the shift being greater for the protons *ortho* to the substituent (H_X), and replacement of a hydrogen atom by a nitro group shifts the resonances of the other protons on the ring to lower field, the shift being greater for the protons *ortho* to the substituent (H_X). It will be noted that the effect of substitution of a methoxyl group on either a *trans* or *cis* ring (H_X in examples XVII, III, II) is to shift the protons *ortho* to it +0.42–0.59 ppm from the corresponding position in the unsubstituted compound. The shift on the *meta* protons (H_R) is smaller, amounting to +0.04–0.16 ppm. Similarly the shift caused by replacement of a hydrogen atom by a nitro group is −0.82–(−)1.10 for H_X and −0.07–(−)0.24 for H_R. Also $[H_X{}^{cis}] - [H_X{}^{trans}]$ is +0.06–0.17 and $[H_R{}^{cis} - [H_R{}^{trans}]$ is 0.54 − 0.67 ppm. These values are both qualitatively and quantitatively similar to those obtained previously[45,47e] in different systems. The effects on positions of chemical shifts of changes in substitution on the aromatic

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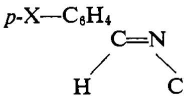
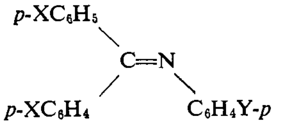
(49) R. Kuhn and H. Schretzmann, *Chem. Ber.*, **90**, 557 (1957).

(50) See ref 6, p 241.

(51) (a) J. D. Roberts, "An Introduction to Spin-spin Splitting in High Resolution Nuclear Magnetic Resonance Spectra," W. A. Benjamin, Inc., New York, N. Y., 1961, pp 49–60.

Table VI. Positions in the Nmr of the Aromatic Proton Resonances of the Imines

X (Compd)	*trans* ring H_X[a]	 H_R[b]	*cis* Ring H_X[a]	 H_R[b]	=N ring H_Y[a]	 $H_{N=}$[b]
						
H (XV)	2.57^c (0.00)	2.22^c (0.00)	...	...	...	...
CH_3O (XVII)	3.16 (+0.59)	2.38 (+0.16)	... ...	... ...	... ...	... ...
Cl (XVI)	2.73 (+0.16)	2.45 (+0.23)	... ...	... ...	... ...	... ...
NO_2 (XVIII)	1.75 (−0.82)	2.15 (−0.07)	...	...	...	...
						
X = H, Y = CH_3	2.75^c (0.00)	2.32^c (0.00)	2.92^d (0.00)	2.92^d (0.00)	3.20 (0.00)	3.56 (0.00)
X = CH_3O, Y = CH_3	3.24 (+0.49)	2.36 (+0.04)	3.36 (+0.44)	3.03 (+0.11)	3.21 (+0.01)	3.55 (−0.01)
X = NO_2, Y = CH_3 (III)	1.76 (−0.99)	2.14 (−0.18)	1.82 (−1.10)	2.68 (−0.24)	3.00 (−0.20)	3.42 (0.14)
X = CH_3O, Y = $N(CH_3)_2$ (II)	3.28 (+0.53)	2.39 (+0.07)	3.34 (+0.42)	3.03 (+0.11)	3.57 (+0.37)	3.57 (+0.01)
X = CH_3O, Y = COOEt	*e*	*e*	*e*	*e*	2.26 (−0.94)	3.42 (−0.14)
X = Cl,[f] Y = OCH_3 (IV)	2.85^f	2.33^f	...	...	3.45 (+0.25)	3.45 (−0.11)

[a] H_X protons are those *ortho* to substituent X. When X = H the complex pattern resulting is attributed to the three protons *meta* and *para* to the point of attachment of the doubly bound carbon atom. [b] H_R protons are those *meta* to the substituent X (or when X = H the two protons *ortho* to the point of attachment of the doubly bound carbon atom). H_N protons are the ring protons *ortho* to the nitrogen atom. [c] Approximate center of a complex multiplet. The assignment was based on the assumption that the multiplet with a relative area of 3 corresponds to the three *meta* and *para* protons, that with the area of 2 to the two *ortho* protons. [d] The distinction between *cis* and *trans* rings is based on the presumed analogy with olefins and other 1,2-diaryl compounds in which the *cis*-phenyl protons are shifted to higher field.[43,45] [e] Methoxylphenyl proton spectrum was smeared—probably due to the effect of *cis–trans* isomerization. [f] There is a chlorine atom on only one of the two rings—this assignment is uncertain.

ring attached to the imine nitrogen show good internal consistency. Thus, with a *p*-methyl group on this ring change of the *para* substituents on the other two rings from H to CH_3O has a negligible effect on either H_Y or $H_{N=}$ (±0.01 ppm) and a change to NO_2 a small effect (−0.20, +0.14). The origin of these shifts is probably similar to those which have been discussed.[44b,46] The internal consistency and reasonable magnitudes of the shifts support the assignments made here and also the conclusion that the change of spectrum with temperature is indeed due to an increase in the rate of *cis–trans* isomerism. The change with temperature of the aromatic proton spectra of the imines I, II, III, and IV appears to be consistent with the postulated isomerization but has thus far been too complex for detailed interpretation.[52]

The ultraviolet spectra of XV, XVI, and XVIII are of interest in connection with the assignment of configurations to the *p*-chloro and *p*-nitrobenzophenone methylimines XX and XXI.[3] The spectral data for these compounds are summarized in Table VII. It will be seen that the aldehyde methylimines XV, XVI, and XVIII may be regarded as derived from the benzophenone imines XX and XXI by removal of one of the aryl groups of the latter and replacement by a hydrogen atom; for example, such a replacement of the phenyl group (*cis* to the methyl group) of the *trans*-chloroimine *trans*-XX gives rise to the chlorimine XVI whereas the analogous replacement when carried out with *cis*-XX gives the unsubstituted compound XV. The interesting generalization is suggested by inspection of the data in Table VII that such a replacement, at least to a first approximation, leaves unchanged (Δ ≤ 8 mμ) the position of the absorption maximum in the ultraviolet spectrum. Alernatively, the existence of such a correlation, which would fail completely if the configurational assignments to the imines XX and XXI

Table VII. Ultraviolet and Nmr Spectra of *para*-Substituted Benzaldehyde Methylimines (XV–VIII) and Benzophenone Methylimines (*cis*- and *trans*-XX and -XXI)

Compd (substituent)	λ_{max}, mμ, of cyclohexane	ε	Nmr (CCl^4), τ^a CH_3	 $CH{=}N$
XV (H)	244	14,400	6.55	1.76
XVI (Cl)	251	21,700	6.60	1.95
XVII (CH_3O)	260	20,600	6.61	1.91
XVIII (NO_2)	275	16,000	6.42	1.67
cis-XX (Cl)[b]	236	15,100	6.76^c	...
trans-XX (Cl)[b]	255	18,500	6.76^c	...
cis-XXI (NO_2)[b]	245	16,200	6.79	...
trans-XXI (NO_2)[b]	280	16,700	6.72	...

[a] Center of multiplet. [b] Ref 3. [c] Solvent was deuteriochloroform.

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(52) J. S. Smith, unpublished results.

were reversed, is support for the previous configurational assignments[3] to these compounds.

Experimental Section[53]

p,p'-**Dimethoxybenzophenone arylimines** I, II, III, and IV were prepared by heating under reflux 6.1 g (0.025 mole) of *p,p'*-dimethoxybenzophenone with 0.030–0.035 mole of the appropriate amine in 25–50 ml of toluene for 60–72 hr. The hot solution was filtered to remove amine hydrochloride and the solvent removed by vacuum distillation leaving an oil which in each case solidified.

Phenylimine (I).[5] The infrared spectrum of the 8.1 g of sodilified oil showed the presence of dimethoxybenzophenone which could not be removed by crystallization from ethanol. Chromatography on neutralized alumina (elution with 1:1 Skelly B–carbon tetrachloride) gave, on collection of the first two 50-ml fractions after removal of the solvent, a solid whose spectrum no longer showed the presence of ketone. Recrystallization twice from ethanol gave light crystals, mp 102–103° (lit.[5] mp 95°). The infrared spectrum showed an intense maximum at 1600 cm^{-1} with a shoulder at 1575 cm^{-1}. The ultaviolet spectrum had λ_{max} at 222 mμ (ϵ 27,700), 276 (25,500), and 332 (4400).

Anal. Calcd for $C_{21}H_{19}NO_2$: C, 79.5; H, 6.0; N, 4.5. Found: C, 79.4; H, 6.0; N, 4.6.

p-**Dimethylaminophenylimine** (II). The orange oil (10.5 g) from the procedure above only partially solidified when held at 6° for several hours and the infrared spectrum showed the presence of ketone which was removed by chromatography on neutralized alumina (elution with Skelly B and Skelly B–carbon tetrachloride) to leave 6.0 g of II as orange crystals which after crystallization from ethanol gave bright yellow II, mp 129–130°. The infrared spectrum showed broad absorption at 1610 cm^{-1} (sh 1595 cm^{-1}) and a smaller absorption at 1573 cm^{-1}. The ultraviolet maxima were at 275 mμ (ϵ 29,200) and 379 mμ (ϵ 10,700). The nmr spectrum was of particular interest because in addition to the two methoxyl peaks discussed in the text there were in the aromatic region two partially overlapping quartets (τ 2.31, 2.47, 3.20, 3.37; 2.95, 3.10, 3.28, 3.40) attributed to the protons of the two *p*-methoxy phenyl rings approximated as an AX system and with the protons of the third ring (presumed to be the *p*-dimethylamino-substituted ring) as a singlet at higher filed (τ 3.57).

Anal. Calcd for $C_{23}H_{24}N_2O_2$: C, 76.7; H, 6.7; N, 7.8. Found: C, 76.6; H, 6.6; N, 8.0.

The *p*-**tolylimine** III gave, when purified by chromatography like I, 4.7 g of yellow crystals, mp 97–98°. The melting point was unchanged when the compound was recrystallized from ethanol (lit.[3] mp 97–97.5°). The nmr showed, in addition to the methyl and methoxyl proton absorption discussed in the text, a complex aromatic spectrum which could be interpreted as three overlapping quartets (τ 2.29, 2.43, 3.17, 3.31; 2.95, 3.10, 3.29, 3.42; 3.12 unresolved, 3.28, 3.48, 3.61). The infrared spectrum showed a large complex absorption at 1600 and a smaller absorption at 1573 cm^{-1}. Ultraviolet maxima occurred at 274 mμ (ϵ 24,600) and 338 mμ (ϵ 4600).

The *p*-**carbethoxyphenylimine** IV, purified by chromatography on alumina (elution with carbon tetrachloride), gave 5.8 g of light yellow needles which when recrystallized from ethanol had mp 85–86°. The infrared spectrum showed, in addition to the ester carbonyl absorption at 1714 cm^{-1}, broad, strong absorption at 1590 (shoulder 1605 cm^{-1}) and a smaller absorption at 1570 cm^{-1}. The ultraviolet spectrum showed a maximum at 281 mμ (ϵ 29,400) and a shoulder falling off to past 370 mμ. The aromatic region in the nmr was too complex to permit interpretation except for a quartet at τ 2.19, 2.32, 3.34, 3.50.

Anal. Calcd for $C_{24}H_{23}NO_4$: C, 74.0; H, 5.9; N, 3.6. Found: C, 73.8; H, 6.0; N, 3.6.

The Unsymmetrical Triarylimines V–VII. These imines were prepared by heating 5 g (0.025 mole) of *p*-methoxybenzophenone with 0.03–0.034 mole of the appropriate amine and 0.1–0.25 g of phosphorus pentachloride in 50 ml of toluene for 60–72 hr. Purification was carried out as with the symmetrical imines I–IV by chromatography and crystallization from ethanol. Significant spectral features of these compounds are presented in Tables II and VII.

p-**Methoxybenzophenone** *p*-**tolylimine** (V) (solid, *trans*), mp 97–98° (lit.[3] mp 97–97.5°), was obtained as light yellow needles in 68% yield.

p-**Methoxybenzophenone** *p*-**(N,N-dimethylamino)phenylimine** (VI) (solid, *trans*), orange crystals, mp 116–117° (lit.[10] mp 116°), was obtained in 85% yield. The infrared spectrum showed a strong broad band at 1612 (sh 1595) and a smaller band at 1573 cm^{-1}.

p-**Methoxybenzophenone** *p*-**Chlorophenylimine** (VII). Chromatography gave, after removal of solvent, 1.8 g of yellow oil and 1.6 g of light yellow crystals (solid, *cis*). The crystals, recrystallized from ethanol gave light yellow platelets, mp 105–106° (lit.[9] mp 104°). When the oil was dissolved in a small amount of ethanol and the solution was cooled, fine, white needles settled out of solution. On melting, the white solid contracted and turned yellow in the region 95–105° and melted sharply at 106°. It seems possible that isomerization to the *trans* isomer occurred but this point was not investigated further. The infrared spectrum showed absorption at 1600 (sh 1590 and 1615 cm^{-1}).

p-**Chlorobenzophenone** *p*-**methoxyphenylimine** (solid, *cis*), prepared and purified in the same manner as the other unsymmetrical imines above, was obtained in 31% yield as yellow solid, mp 105.5–106.5°. The nmr showed methyl proton absorptions at τ 6.33 and 6.35 and a complex aromatic proton spectrum in which could be discerned a quartet (τ 2.26, 2.39, 2.79, 2.91) and a strong singlet at 3.45. The infrared spectrum showed strong absorption at 1613 with shoulders at 1590 and 1575 cm^{-1}. The solid (KBr disk) showed monosubstituted phenyl absorption at 692 cm^{-1}. When the disk was ground, heated, and repressed, there was a doublet at 692 and 702 cm^{-1}. The solution spectrum showed absorption at 698 and 693 cm^{-1}.

Anal. Calcd for $C_{20}H_{16}ClNO$: C, 74.6; H, 4.9; N, 4.4; Cl, 11.1. Found: C, 74.8; H, 5.1; N, 4.4; Cl, 11.0.

p-**Chlorobenzophenone** *p*-**Tolylimine.** A sample of this compound (solid, *trans*) which had been prepared by Hausser[3] showed a single methyl proton absorption in the nmr. The solid (KBr disk) showed monosubstituted phenyl absorption at 699 cm^{-1} and a heated disk at 700 and 695 cm^{-1}. The solution spectrum had maxima at 699 and 693 cm^{-1}.

cis-*p*-**Chlorobenzophenone oxime,**[19] mp 159.3–159.8° (lit.[19] mp 155–157°), was obtained in 42% yield by fractional crystallization from ethanol-water (80:20) of the mixture of isomers formed in the reaction of the ketone with hydroxylamine hydrochloride in aqueous ethanol.[19] The infrared spectrum in chloroform solution showed a single, monosubstituted phenyl absorption at 690 and a single 1,4-disubstituted phenyl absorption at 830 cm^{-1}. (A potassium bromide disk showed more complicated absorption at 825, 833, 688, and 696 cm^{-1}.) The ultraviolet spectrum in cyclohexane showed a maximum at 235 mμ (ϵ 21,000) with a shoulder at 258 mμ (ϵ 13,000).

Anal. Calcd for $C_{13}H_{10}ClNO$: C, 67.4; H, 4.4; N, 6.0. Found: C, 67.4; H, 4.4; N, 6.3.

trans-*p*-**Chlorobenzophenone oxime,**[19,54] mp 102.5–103.5° (lit.[54] mp 96–97°), was separated from the mother liquors remaining from the preparation of the *cis* isomer and purified by a combination of repeated fractional crystallization and mechanical separation of crystals to give an over-all yield of 0.24% based on ketone. The infrared spectrum in carbon disulfide showed a doublet in the monosubstituted phenyl region at 693 and 701 and a single absorption at 829 cm^{-1} in the 1,4-disubstituted benzene region. The ultraviolet spectrum in cyclohexane showed two maxima of nearly equal intensity at 237 mμ (ϵ 15,000) and 257 mμ (ϵ 14,000).

cis-*p*-**Chlorobenzophenone oxime methyl ether** (*cis*-VIII), mp 63.9–64.8°, was prepared in 70% yield by alkylation of 5.0 g of *cis* oxime with 37 g of methyl iodide and 7.0 g of silver oxide, under

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(53) All melting points are corrected. Microanalyses were performed by Mr. J. Nemeth and his associates. Infrared spectra were obtained in part by Mr. Dick Johnson and his associates with a Perkin-Elmer Model 21 spectrophotometer. Unless specified otherwise 10% w/v solutions in carbon tetrachloride were employed. Nmr spectra were obtained in part by Mr. Dick Johnson and Mr. O. Norton and their associates with Varian Model A-60 and Varian Model V-4300-B instruments. Signal positions are reported in parts per million relative to tetramethylsilane (10.00) used as an internal standard (τ values). When not otherwise indicated nmr spectra were measured in carbon tetrachloride with concentration given as per cent (w/v). Ultraviolet spectra were obtained in cyclohexane unless indicated otherwise with a Bausch and Lomb Spectronic 505, or, in part, by Mr. P. Hon with a Cary Model 14M spectrophotometer. Vapor phase chromatography was carried out with an Aerograph A-300 dual-column instrument equipped with a Brown recorder and disk integrator. Important spectra and other detailed data may be found in the Ph.D. thesis of C. G. McCarty[1] available on microfilm from University Microfilms, Ann Arbor, Mich.

(54) A. Hantzsch, *Ber.*, **24**, 56 (1891).

reflux for 45 min. Filtration gave 5.4 g of oil which crystallized from absolute methanol at −70°. Sublimation at 60° (0.1 mm) did not affect the melting point. The ultraviolet spectrum (*n*-decane) showed λ_{max} 238 mμ (ϵ 18,500) and 264 mμ (ϵ 10,600).

Anal. Calcd for $C_{14}H_{12}ClNO$: C, 68.4; H, 4.9; N, 5.7. Found: C, 68.2; H, 4.9; N, 5.8.

***trans*-*p*-Chlorobenzophenone oxime methyl ether** (*trans*-VIII), mp 43.5–44.5°, was obtained in 25% yield by carrying out the reaction as with the *cis* isomer. The product failed to crystallize from methanol but was crystallized from methanol–ether–hexane (10:1:1) at −70°. The ultraviolet spectrum (*n*-decane) showed λ_{max} 238 mμ (ϵ 15,000) and 267 mμ (ϵ 13,500).

Anal. Calcd for $C_{14}H_{12}ClNO$: C, 68.4; H, 4.9; N, 5.7. Found: C, 68.4; H, 4.6; N, 5.9.

Solutions of the *trans* isomer in decane which had been purified, dried, and degassed were sealed in bomb tubes and heated at 200 ± 5°. No significant change in the ultraviolet absorption was noted during the course of many hours. A similar study of the *cis* isomer indicated that even after 233 hr the solution consisted of 82% of the *cis* isomer and 19% of the *trans* although a plot by the method of Dewar and Urch[55] deviated from linearity in a way that suggested the presence of side products.

***cis*- and *trans*-*p*-Chlorobenzophenone N-Chlorimine** (*cis*- and *trans*-IX).[24,28] The mixture of imines was prepared by chlorination of *p*-chlorobenzophenone imine hydrochloride (5.1 g) with a solution of chlorine (7.0 g) in aqueous potassium bicarbonate at 0° and extraction of the product with chloroform.[24] After drying and removal of the solvent by vacuum distillation there was obtained 3.90 g (77%) of a partially crystallized oil from which the *cis* isomer (1.79 g, mp 100–102°) was induced to crystallize by the addition of 12 ml of 1:1 low- and high-boiling petroleum ether[56] after filtration to remove impurities and cooling to 6°. The *trans* isomer (1.48 g, mp 51–54°) was obtained by concentration of the filtrate to 7 ml and cooling to −20°. Recrystallization of the two isomers from low-boiling petroleum ether raised the melting points to 103–104° (lit.[28] mp 105°) and 53–54° (lit.[28] mp 55°). *cis*-IX had λ_{max} 251 mμ (ϵ 17,000), *trans*-IX had λ_{max} 263 mμ (ϵ 17,800).

The thermal equilibration of *cis*- and *trans*-IX was carried out in degassed tubes sealed under high-vacuum both with and without the addition of calcium hydride as an acid scavenger. The reaction was followed by a two-point ratio method[57] employing the isoabsorptive point, 256 mμ in the ultraviolet spectrum and 270 mμ, a point of maximum difference in absorbances of the two isomers. A semiquantitative check was provided by observation of the 690- and 830-cm^{-1} regions in the infrared spectrum. The products to be expected if a Beckmann rearrangement[58] of the chloroimines IX were to occur, N-phenyl-*p*-chlorobenzimidyl chloride, *p*-chlorobenzanilide, N-*p*-chlorophenylbenzimidyl chloride, and benz-*p*-chloroanilide, were prepared and comparison of their ultraviolet and infrared spectra with isomerization reaction mixtures showed no detectable amounts of these products in agreement with previous observations.[28] There was no detectable isomerization of either *cis*- or *trans*-IX in cyclohexane at 60° for 500 hr. If it is assumed that 3% of rearrangement might have been overlooked and that K_{eq} is 1.45 (as found in isomerizations without solvent at 120°) the maximum value of 3.2×10^{-8} sec^{-1} is calculated for the hypothetical first-order isomeration. Reactions of a 60-hr duration at 120 and 140° in carbon tetrachloride or benzene gave estimated times for half-reaction of 500 hr at the lower temperature and 80 hr at the higher but no more meaningful data were obtained since longer reactions at these temperatures showed that decomposition by other paths was occurring.

***cis*-*p*-Chlorobenzophenone N-Bromoimine** (*cis*-X). Bromination of the imine was carried out in the manner previously reported[24] to give a mixture of *cis*- and *trans*-X from which the *cis* isomer, mp 103–104° (lit.[24] mp 102°), was isolated by repeated crystallization from petroleum ether. Other fractions had melting points near the values of 73°[24] and 85°[43] previously reported but showed in every case two absorptions in the 690- and 830-cm^{-1} regions of the infrared spectrum and are therefore believed to be mixtures of the two isomers. An attempted isomerization in cyclohexane at 60° for 60 hr as in the case of the chloroimines IX gave no spectral change. With a possible 5% of rearrangement unobserved the maximum value of $k_1 + k_{-1}$ is then 5×10^{-7} sec^{-1}. Runs at 60, 100, and 110° were not reproducible; a run which showed no isomerization when repeated gave 100% isomerization. It seems likely that small amounts of impurities initiated an ionic or free-radical path in the more rapid runs.

Acetone phenylimine (XI), bp 65–66° (7 mm) (lit.[49] bp 78° (10 mm)), was prepared by the method of Kuhn and Schretzmann.[49] It had strong C=N absorption at 1660 cm^{-1}. In the atmosphere at room temperature it was rapidly converted to acetone and aniline; spectra were obtained within a few minutes after distillation.

Pinacolone phenylimine (XII), bp 84–86° (4 mm), was obtained in 50% yield by azeotropic distillation over a 12-hr period of the theoretical amount of water from a solution of 8.0 g of pinacolone, 9.3 g of freshly distilled aniline, and 30 mg of phosphorus pentachloride in 50 ml of toluene. After filtration of aniline hydrochloride removal of the solvent gave an oil purified by distillation. Redistillation (bp 85–86° (4 mm)) gave a sample used for spectral and microanalyses. There was a strong C=N absorption at 1652 cm^{-1}. Three maxima occurred in the ultraviolet spectrum at 199 (ϵ 21,400), 223 (1000), and 275 mμ (2300).

Anal. Calcd for $C_{12}H_{17}N$: C, 82.3; H, 9.7; N, 8.0. Found: C, 82.5; H, 9.7; N, 8.1.

Benzaldehyde methylimine (XV), bp 89–90° (30 mm) (lit.[59] bp 92–93° (34 mm)), and ***p*-methoxybenzaldehyde**[60] (XVII), bp 125–126° (15 mm) (lit.[60] bp 129–130° (18 mm)), were prepared from the aldehyde and methylamine by the procedure of Moffett.[59] Unreacted aldehyde which was difficult to remove by distillation was converted to the oxime by treatment with a small amount of hydroxylamine hydrochloride in 10% aqueous sodium hydroxide. Extraction of the imine with ether and distillation gave imine with only a trace of carbonyl absorption at 1710 cm^{-1} in the infrared region.

***p*-Chlorobenzaldehyde methylimine** (XVI), bp 65–66° (1.5 mm) (lit.[61] bp 69–70° (2 mm)), was prepared by the procedure above. After the hydroxylamine treatment there was no carbonyl absorption in the infrared spectrum.

***p*-Nitrobenzaldehyde methylimine** (XVIII), mp 105–106° (lit.[62] mp 106°), was purified by crystallization from ethanol. The purified product showed no carbonyl absorption in the infrared spectrum.

Variable-Temperature Nmr Study. Imines I–VII (75 mg) were dissolved in 0.5 ml of reagent grade carbon tetrachloride containing 1% tetramethylsilane as an internal standard and 100 mg of 4–40 mesh calcium hydride was added as a scavenger of water and acid. Nmr tubes were prepared by cleaning successively with chromic acid, dilute ammonium hydroxide, and deionized water, and stored in an oven at 120° until use. After addition of the solution and displacement of air over the solution with a stream of dry nitrogen the solution was frozen and the tube sealed to give solutions approximately 12% (wt/v) of imine with some suspended calcium hydride present.

Spectra were obtained with a Varian Associates high-resolution spectrometer with a Model V-K3506 superstabilizer and a Model V-4311RF probe for operation at 60 Mc. The Varian Model V-4340 variable-temperature probe and the Model V-4331 dewar probe insert were used in the high- and low-temperature studies. Sample temperatures from −40 to +30° were achieved by means of a Nichrome immersion heater placed in a 25-l. Dewar flask containing liquid nitrogen with an exit to the variable temperature probe accessory. A stream of air heated by the probe accessory gave temperatures from +30 to +110°. Sample temperatures were monitored by a copper–constantan thermocouple in a dummy sample tube containing carbon tetrachloride and employing a Leeds and Northrup Model 8662 potentiometer. The thermocouple had been calibrated against National Bureau of Standards thermometers over the range of −36 to +150°. The dummy tube was then replaced by the sample tube which was allowed to come to thermal equilibrium and the spectra measured. The sample tube was replaced by the dummy tube to check for a drift in temperature; in no case was the final temperature different from the initial temperature by more than 0.1°, the error in making potentiometer readings.

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

(56) Low-boiling petroleum ether refers to the fraction bp 30–60°; high-boiling petroleum ether refers to the fraction bp 90–110°.

(57) R. C. Hirt, F. T. King, and R. G. Schmitt, *Anal. Chem.*, **26**, 1270 (1954).

(58) L. G. Donaruma and W. Z. Heldt, *Org. Reactions*, **11**, 46 (1960).

(59) R. B. Moffett, *Org. Syn.*, **34**, 65 (1954).

(60) P. Kording, *Ann.*, **431** 222 (1923).

(61) R. E. Lutz, P. S. Bailey, R. J. Rowlett, Jr., J. W. Wilson, III, R. K. Allison, M. T. Clark, N. H. Leake, R. H. Jordan, R. J. Keller, III, and K. C. Nicodemus, *J. Org. Chem.*, **12**, 760 (1947).

(62) A. Burawoy and J. P. Critchley, *Tetrahedron*, **5**, 340 (1959).

Table VIII. Temperature Dependence of the Separation of the Methoxyl Proton Resonances, $\delta\nu$ (cps), of Imine I[a]

Temp, °C	$\delta\nu$	Temp, °C	$\delta\nu$
72.3	0	40.7	4.46
62.8	0	30.8	4.59
62.2	0	20.6	4.67
61.5	2.12	11.1	4.72
60.7	2.88	.6	4.83
59.3	3.37	−10.0	4.86
54.3	4.06	−18.7	4.88
50.1	4.25	−29.5	4.90

[a] $T_c = 62.2°$; $k_1 = \pi\delta\nu_0/\sqrt{2} = 10.9 \pm 0.3\ \text{sec}^{-1}$; $\delta\nu_0 = 4.90 \pm 0.15$ cps; $\Delta F^* = 18.1 \pm 0.1$ kcal/mole.

Table IX. Isomerization of the Dimethylaminoimine VII in Carbon Tetrachloride at $-7.2 \pm 0.2°$; $c_0\ 4.2 \times 10^{-4}\ M$

Time, min	$A_e - A$	$k_1 + k_{-1}$ $\times 10^4$ sec^{-1}
0.0	0.215	
10.0	0.168	4.11
20.0	0.130	4.17
30.0	0.102	4.15
40.0	0.990	4.13
50.0	0.067	3.89
60.0	0.050	4.05
70.0	0.043	3.83
80.0	0.030	4.10
90.0	0.023	4.14
	Least-squares value[14]	4.08

All samples had spectra recorded at room temperature before and after the high-or low-temperature spectra in order to obtain assurance of the thermal stability of the imines. Audiofrequency side bands of tetramethylsilane, generated by a Hewlett-Packard Model 200CD audio oscillator and calibrated by a Model 521C electronic counter, were used to determine chemical shift differences, $\delta\nu$, between the lines of the methoxyl doublet of the imines. Of the four to six spectra recorded at each temperature for each imine, usually one but sometimes two gave values well beyond the range of the others. This left three to five values which were used to obtain an average at each temperature. The deviation from the average, in each case, was less than 0.15 cps. Representative data for the phenyl imine I are presented in Table VIII.

Infrared Spectra of Unsymmetrical Imines IV, V, and VII. Solution spectra (10% in carbon tetrachloride) were measured with a Perkin-Elmer Model 21 spectrophotometer with a 4X scale expansion and the slowest sweep rate in the region 750–650 cm^{-1}. Potassium bromide disks of each imine were prepared from 1 mg of imine and 200 mg of oven-dried potassium bromide ground in a mullite mortar. The disks were pressed under vacuum for 3–5 min and of a pressure of 15 tons/2.1 in.^{2}. Regrinding and repressing did not change the spectrum appreciably. The heated sample was prepared by heating the pulverized mixture of imine and then preparing a disk as before. The spectra were calibrated with ammonia vapor and water vapor.

Use of Ultraviolet Spectroscopy to Follow the Isomerization Rates of Imines V and VII. Spectra were measured with a Bausch and Lomb Spectronic 505 spectrophotometer with an external Sargent Model SR recorder and employing matched 5.0-cm quartz opticells. Sample temperatures of −7.2 to +12.5° were maintained by means of a stream of cold nitrogen gas through the cell jacket and exiting into the cell compartment to reduce condensation of moisture; the nitrogen flow was controlled by varying the output of a Nichrome immersion heater in a 15-l. dewar flask containing liquid nitrogen whose exit tube went to the cell jacket. The temperature in the cell was monitored with a copper–constantan thermocouple and maintained during a run to within ±0.2°.

Thermal equilibrium was first reached with carbon tetrachloride in each cell. The carbon tetrachloride in the sample cell was discarded and a solution prepared by the addition of weighed 0.11–0.18-mg samples of imine to 25 ml of reagent carbon tetrachloride which had been precooled to 3° below the cell temperature and cleaned with about 200 mg of calcium hydride in a "tea bag" of filter paper; vigorous shaking for several seconds dissolved the imine. Addition of the imine solution to the sample cell, wiping of the cell windows with lens tissue, and closing the door to the cell compartment (which automatically started the recording of absorbance at a fixed wavelength as a function of time) required less than 30 sec. Typical data for an isomerization of the dimethylaminoimine are presented in Table IX.