# SOLVENT EFFECTS ON THE *SYN–ANTI* ISOMERIZATION RATES OF HYDRAZONES OF ACETONE

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**Abstract**—The coalescence temperatures for the *C*-methyl peaks in the NMR spectra of hydrazones of acetone are above 200°, indicating an energy barrier for *syn–anti* isomerization greater than 28 kcal mole$^{-1}$. The presence of halogenated compounds decreases the energy barrier, due to the formation of a charge transfer complex between the hydrazone acting as a donor and the halogenated compound acting as the electron acceptor.

The *syn–anti* isomerization of imines may proceed either by rotation about the C=N bond or by inversion of the $sp^2$ hybridized nitrogen.[1,2] In the first case a polar non-linear transition state is involved and in the second a linear, non-polar. According to calculations for methyleneimine the barrier for rotation should be of the order of 60 kcal mole$^{-1}$ and for inversion of only 30 kcal mole$^{-1}$.[3–5] Experimental values for the energy of activation obtained from DNMR fall within the range 10–25 kcal mole$^{-1}$.[6] Furthermore, substituents on the nitrogen affect the isomerization rate in the same direction as they do that of the pyramidal inversion of $sp^3$ hybridized nitrogen,[7] supporting the inversion mechanism.

The above arguments would have some meaning only if the isomerization proceeded without any catalysis. However, most of the data have been obtained in solution and in many cases the coalescence temperature for the same compound is strongly solvent-dependent.[1] In hydrazones inversion was proposed as the mechanism of the *syn–anti* isomerization because relatively low $\Delta G_c^{\neq}$ values were observed in solutions of hexachlorobutadiene.[8] However, in a number of other solvents such as 1-bromonaphthalene, diphenyl ether or nitrobenzene the coalescence temperatures are higher than 200°, implying $\Delta G_c^{\neq}$ values greater than 28 kcal mole$^{-1}$.[9] The present work was designed to elucidate the mechanism of the *syn–anti* isomerization of hydrazones of acetone in various solvents.

## RESULTS

*NMR study of the isomerization process.* The rate of *syn–anti* isomerization of *N*-substituted hydrazones of acetone **1** was followed by analysing the changes in the line shape of the *C*-methyl region in the proton magnetic resonance spectra[10] in the temperature range 60–200°.

$$R^1R^2N \underset{}{\overset{}{\diagdown}} \quad Me_B$$
$$N{=}C$$
$$\mathbf{1} \qquad Me_A$$
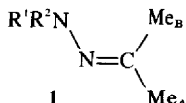
$R^1$ = H, Me
$R^2$ = Me, $C_6H_5$, p-X$C_6H_4$; X = OMe, Me, Br, Cl, F, NO$_2$

All hydrazones examined in the absence of solvent, in the liquid or molten state, showed no changes in line shapes up to 200°. A slight temperature dependence of the chemical shift ($\Delta\nu_{Me_A-Me_B}$) was observed (0–2 cps) according to substitution.

Similarly no coalescence or broadening of the methyl peaks occurred in solutions (0·1–1 M) of hydrazones in the following solvents: n-heptane, 1-bromonaphthalene, 1-chloronaphthalene, diphenyl ether, nitrobenzene and dimethylformamide. It is to be noted that the polarity of the solvents has no effect on the rate of *syn–anti* isomerization.

In contrast solutions of hydrazones in certain chlorinated solvents show coalescence of the *C*-methyl groups at 90–140° and the effect is reversed by lowering the temperature (Fig. 1). The nature of the chlorinated solvent as well as its state of saturation affect slightly the coalescence temperature (Table 1).
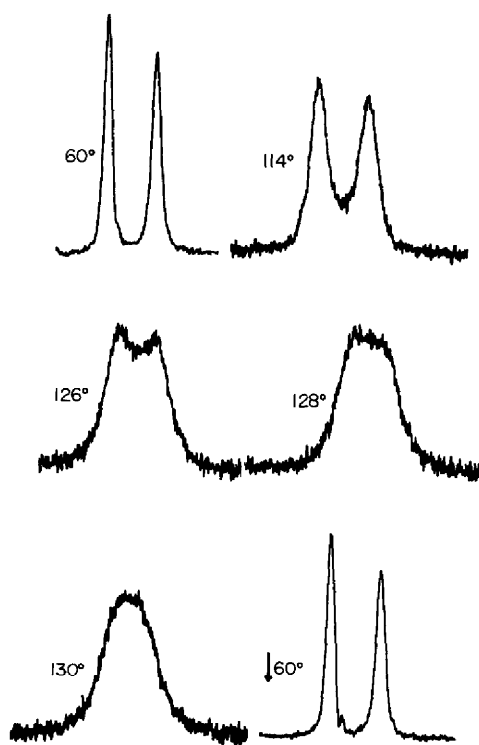


Fig. 1. Line shape changes of the *C*-methyls of *N,N*-dimethylhydrazone of acetone 0.3 M in hexachlorobutadiene as a function of temperature.

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Table 1. Coalescence temperature of hydrazones of acetone in chlorinated solvents[a]

| Substituent | | Solvent | $T_c$ |
|---|---|---|---|
| $R_1$ | $R_2$ | | °C |
| H | $C_6H_5$ | tetrachloroethane | 140 |
| $CH_3$ | $C_6H_5$ | tetrachloroethane | 120 |
| H | $p\text{-}BrC_6H_4$ | hexachlorocyclopentadiene | 90 decomp |
| H | $p\text{-}BrC_6H_4$ | hexachlorobutadiene | 120 |
| H | $p\text{-}CH_3C_6H_4$ | tetrachloroethane | 135 |
| H | $p\text{-}CH_3C_6H_4$ | hexachlorobutadiene | 140 |

[a] No coalescence up to 200°C in 1-bromonaphthalene, 1-chloronaphthalene, diphenylether, nitrobenzene, DMF. No coalescence in the absence of solvent (neat compounds, molten).

A significant decrease of the coalescence temperature ($T_c$) is observed when the concentration of the hydrazone is lowered. For instance, solutions of *N,N*-dimethylhydrazone of acetone in hexachlorobutadiene show a difference of about 30° in coalescence temperature for a range of concentrations 2·2–0·1 M (Table 2). In *N,N*-disubstituted hydrazones of acetone the substitution of methyl by phenyl on the sp³ hybridized nitrogen in solutions of comparable concentration lowers the $T_c$ values by about 30°. The nature of the p-substituent in *N*-phenylhydrazones of acetone has a small effect on the rate of *syn–anti* isomerization (Table 3). It can be seen that this effect cannot be correlated with the Hammett $\sigma_p$ of the substituent.

The addition of hexachlorobutadiene to solutions of hydrazones of acetone in 1-bromonaphthalene increases the rate of isomerization. Thus, a 0·273 M solution of p-chlorophenylhydrazone, in which no change of line shape was observed up to 200°, shows broadening of the *C*-methyl peaks beginning at 120° when a quantity of hexachlorobutadiene equimolar to hydrazone is added to

Table 2. Concentration dependence of $T_c$ and $\Delta G_c^{\neq}$ of solutions of *N,N*-dimethylhydrazone of acetone in hexachlorobutadiene

| Concn M | $T_c$ °C | $\Delta G_c^{\neq}$ kcal/mol | Number of experiments |
|---|---|---|---|
| 0·104 | 116·5 | 21·7 | 2 |
| 0·114 | 122·0 | 22·0 | 1 |
| 0·153 | 129·0 | 22·4 | 3 |
| 0·300 | 128·8 | 22·4 | 7 |
| 0·780 | 143·0 | 23·1 | 2 |
| 2·230 | 147·7 | 23·2 | 3 |

Table 3. Substituent effect on $\Delta G_c^{\neq}$ and $T_c$ of hydrazones in hexachlorobutadiene

| Conc M | Substituent | | $\sigma_p$ Hammett | $\Delta G_c^{\neq}$ kcal/mol | $T_c$ °C |
|---|---|---|---|---|---|
| | $R_1$ | $R_2$ | | | |
| 0·104 | $CH_3$ | $CH_3$ | | 21·7 | 116·5 |
| 0·073 | $CH_3$ | $C_6H_5$ | | 18·5 | 80 |
| 0·085 | H | $C_6H_5$ | | 19·2 | 94 |
| 0·091 | H | $p\text{-}ClC_6H_4$ | 0·227 | 18·9 | 89 |
| 0·073 | H | $p\text{-}BrC_6H_4$ | 0·232 | 18·8 | 88 |
| 0·102 | H | $p\text{-}CH_3C_6H_4$ | −0·170 | 19·5 | 100 |
| 0·086 | H | $p\text{-}NO_2C_6H_4$ | 0·778 | 19·4 | 96 |
| 0·093 | H | $p\text{-}OCH_3C_6H_4$ | −0·278 | 20·7 | 123 |

Table 4. Effect on the isomerization rate from the addition of halogenated solvents in 1-bromonaphthalene solutions of phenylhydrazones of acetone

| Molarity of phenylhydrazone | Hydrazone: Solvent Ratio | $T_c$ °C | $k_{200°}$ sec$^{-1}$ |
|---|---|---|---|
| p-Chlorophenyl-hydrazone | Hexachlorobutadiene | | |
| 0·273[a] | 1:0 | >200 | — |
| 0·262 | 1:1 | >200 | 16 |
| 0·242 | 1:3 | 190 | 60 |
| 0·224 | 1:5 | 192 | 73 |
| 0·190 | 1:10 | 146 | 162 |
| 0·273[b] | 1:22·8 | 144 | 164 |
| Phenylhydrazone | Methylene chloride | | |
| 0·250 | 1:5 | >200 | |
| 0·170 | 1:10 | 186 | |
| Phenylhydrazone | Methylene bromide | | |
| 0·278 | 1:5 | 192 dec | |
| 0·200 | 1:10 | 166 dec | |

[a] No hexachlorobutadiene present. [b] No 1-bromonaphthalene present.

it. The broadening increases as the temperature is raised and is very pronounced at 200° but complete coalescence has yet to occur. For a ratio hydrazone:hexachlorobutadiene equal to 1:3, the coalescence temperature is 190°. The decrease in $T_c$ continues gradually as the concentration of hexachlorobutadiene is increased. Table 4 shows the increase in the rate of the process caused by stepwise addition of hexachlorobutadiene. The rates at 200° were calculated by extrapolation or interpolation of the Arrhenius plot for each of the concentrations.

An increase in the rate of isomerization is also observed when methylene chloride, methylene bromide or even carbon disulfide are added to 1-bromonaphthalene solutions of hydrazones of acetone. The effect is always proportional to the amount of the halogenated compound added. A much more pronounced effect on the barrier of isomerization is observed upon addition of tetrabromomethane in solutions of phenylhydrazone of acetone in nitrobenzene. A 0·3 M solution of phenylhydrazone in nitrobenzene containing equimolar amounts of tetrabromomethane has a $T_c$ of 112°, while a solution of the same molarity of phenylhydrazone in nitrobenzene shows well separated sharp peaks for $Me_A$ and $Me_B$ up to 180°.

Addition of acids to solutions of hydrazones in 1-bromonaphthalene does not promote isomerization. However, decomposition to different degrees depending on the acid concentration was observed when the samples were heated.[9]

*Temperature and solvent effects on the chemical shifts.* Increase of temperature has a very small effect on the *C*-methyl chemical shifts of hydrazones in hexachlorobutadiene solutions whereas when 1-bromonaphthalene is used as the solvent the chemical shifts of the two methyls change appreciably. For instance, the change in $\Delta\nu$ value of the *N*-phenyl and *N*-(p-substituted phenyl)hydrazones is of the order of 10 cps for an increase of temperature of 130°. The corresponding change for the *N,N*-disubstituted hydrazones is of the order of 3–4 cps.[9] The chemical shifts of the two *C*-methyls are not influenced to the same degree by the temperature variation. The change is larger for methyl-B than for methyl-A (Table 5). In the case of *N,N*-phenylmethylhydrazone the change in chemical shift for

Table 5. Effect of temperature on the chemical shifts of hyd-
razones of acetone in 1-bromonaphthalene solutions

| Temperature °C | Phenylhydrazone | | Phenylmethylhydrazone | | |
|---|---|---|---|---|---|
| | $\tau_{ppm}$ | | | $\tau_{ppm}$ | |
| | $Me_A$ | $Me_B$ | NMe | $Me_A$ | $Me_B$ |
| 60 | 8·247 | 8·850 | 7·210 | 8·205 | 8·478 |
| 80 | 8·230 | 8·800 | 7·170 | 8·187 | 8·455 |
| 100 | 8·230 | 8·766 | 7·155 | 8·170 | 8·433 |
| 120 | 8·210 | 8·725 | 7·128 | 8·150 | 8·400 |
| 130 | 8·208 | 8·708 | — | — | — |
| 140 | 8·191 | 8·675 | 7·110 | 8·142 | 8·383 |
| 160 | 8·183 | 8·641 | 7·092 | 8·128 | 8·360 |
| 180 | — | — | 7·080 | 8·125 | 8·345 |

methyl-B is the same as for the *N*-methyl, but is larger
than that for methyl-A. The difference in the temperature
dependence of the chemical shifts of methyl-A and
methyl-B is more marked in phenylhydrazones of acetone
where the sp³ hybridized nitrogen carries only one sub-
stituent. This behaviour is in agreement with earlier data
according to which the higher field peak (methyl-B) was
assigned to the *syn* position. Karabatsos *et al.*[11a-c] have
found that in hydrazones generally, *α*-hydrogens (CH₃)
resonate at higher field when *cis* (*syn*) to the sp³ hybrid-
ized nitrogen than when *trans* (*anti*).

The nature of the solvent, as expected, influences the
chemical shifts. In Table 6 the individual chemical shifts
of neat phenylmethylhydrazone of acetone are compared
to those of the same compound in various solvents.
Diphenylether has no effect on the chemical shift of the
*C*-methyls. The *N*-methyl peak is shifted by 0·06 ppm
only, to lower field. From all solvents examined,
diphenylether comes closest to an "inert" solvent. 1-
Bromonaphthalene shifts all peaks to higher field with the
*C*-methyls shifted more than the *N*-methyl. Furthermore,
methyl-B is shifted twice as much as methyl-A. 1-
Bromonaphthalene probably complexes with the hyd-
razone in a way analogous to benzene.[11a] Karabatsos *et
al.*[11b,c] have proposed that aromatic solvents can form
complexes with hydrazones in two ways (a) by interaction
of the aromatic π-cloud to the C=N and (b) by hydrogen
bonding of the NH to a nucleophilic site in substituted
benzenes, for instance the nitrogen atom of nitrobenzene.
Aside from the solute-solvent interaction, self-association
occurs in monosubstituted hydrazones by hydrogen bond-
ing via the NH group.

Dilution studies carried out in solutions of hydrazones
in 1-bromonaphthalene, carbon disulphide, n-heptane and
hexachlorobutadiene agree with the above proposed in-
teractions. Both *C*-methyls of phenylhydrazone of
acetone are shifted to higher field upon dilution in 1-
bromonaphthalene. For methyl-B (Fig. 2) the change in
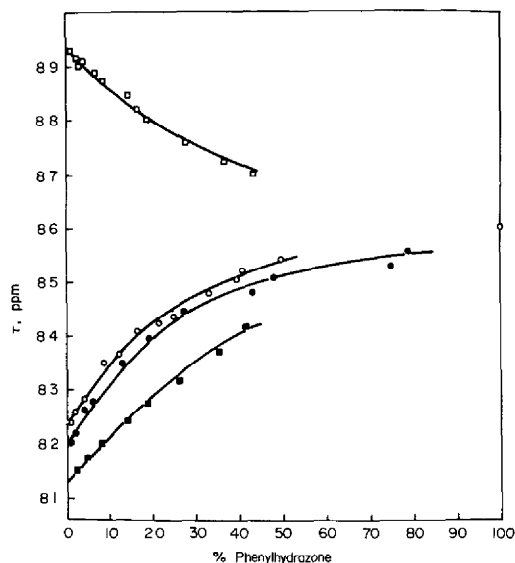chemical shift is more pronounced because the complex



Fig. 2. Concentration dependence of $Me_B$ chemical shift of
phenylhydrazone of acetone in 1-bromonaphthalene,□; n-heptane,
O; hexachlorobutadiene, ●; and carbon disulfide, ■; at room
temperature.

formed is more exposed to the paramagnetic region of the
aromatic ring current. In n-heptane, hexachlorobutadiene
and carbon disulphide solutions both methyls shift to
lower field than in neat hydrazone.

*Absorption spectra of hydrazones.* All p-substituted
phenylhydrazones of acetone, even when frozen, are
unstable in the presence of air. Solutions of hydrazones in
different solvents turn yellow to orange by standing. The
stability in different solvents was studied in the region
600–220 mμ. Fresh solutions prepared in an inert atmos-
phere by using degassed solvents showed the usual ab-
sorption at 270 mμ with a molar extinction coefficient of
the order of 20000 depending on the solvent. When the
solutions were prepared in the presence of air, a new
broad band appeared at 400 mμ with a molar extinction
coefficient of 30–90 depending on the solvent. The absorp-
tion of this band which increases with time is probably
due to oxidation of the hydrazones to the corresponding
1-hydroperoxy-1-phenylazoalkanes.[12] For instance, at
zero time the molar extinction coefficient at 400 mμ of the
phenylhydrazone of acetone is 20 in methanol and 90 in
hexachlorobutadiene. After 3 hr the absorption reaches
the value of 100 in methanol and 250 in hexach-
lorobutadiene. It has been reported that phenylazoalkanes
and 1-hydroperoxy-1-phenylazoalkanes have comparable
molar extinction coefficients (100–140) in the region of
400 mμ.[12a] The oxidation of phenylhydrazone to 1-
hydroperoxy-1-phenylazoalkane is promoted by light. The

Table 6. Effect of solvent on the chemical shifts of phenylmethylhydrazone
protons at room temperature and concentration 4% by volume

| Solvent | NMe | | $Me_A$ | | $Me_B$ | |
|---|---|---|---|---|---|---|
| | $\tau$ | $\Delta\tau$ | $\tau$ | $\Delta\tau$ | $\tau$ | $\Delta\tau$ |
| — (neat) | 7·170 | — | 8·100 | — | 8·300 | — |
| Diphenylether | 7·110 | −0·060 | 8·100 | 0·000 | 8·300 | 0·000 |
| 1-bromonaphthalene | 7·235 | +0·065 | 8·233 | +0·133 | 8·516 | +0·216 |
| Hexachlorobutadiene | 7·025 | −0·145 | 7·950 | −0·150 | 8·133 | −0·167 |
| Tetrachloroethane | 6·760 | −0·410 | 7·485 | −0·615 | 7·690 | −0·610 |

increase in absorption at 400 m$\mu$ is followed by a slow decrease in absorption at 270 m$\mu$. For instance the molar extinction coefficient of phenylhydrazone of acetone in degassed heptane at 270 m$\mu$ is log $\epsilon$ = 4·11 at zero time and after 3 hr it drops to log $\epsilon$ = 3.84. This drop in absorption is much slower in degassed methanol. The decrease in absorption at 270 m$\mu$ and the increase at 400 m$\mu$ are probably due to the destruction of the oxidized hydrazone molecule. This behaviour was not observed with solutions of methylphenylhydrazone of acetone in methanol which shows no absorption at 400 m$\mu$ (in the presence or absence of air) and a stable absorption at 280 m$\mu$ with log $\epsilon$ = 3.74 and at 250 m$\mu$ with log $\epsilon$ = 4·20.

Solutions of N,N-dimethylhydrazone of acetone in methanol or heptane absorb at 268 m$\mu$ (log $\epsilon$ = 2·87 and log $\epsilon$ = 2·70 respectively). When a strong acceptor such as tetracyanoethylene (TCE) is added to a solution of N,N-dimethylhydrazone of acetone in methanol a strong absorption at 412 and 432 m$\mu$ is observed which intensity depends on the ratio of hydrazone to TCE. For a ratio 1 : 1 hydrazone to TCE log $\epsilon$ = 2·11. This band is probably due to the formation of a charge transfer complex. The band intensity decreases slowly with time and after 20 hr the maximum is shifted to 398 m$\mu$. Attempts to isolate and identify the material absorbing at 398 m$\mu$ failed due to the extensive decomposition of the starting material or the complex.

Similarly, solutions of phenylhydrazone and methylphenylhydrazone in methanol absorb strongly at 425 and 435 m$\mu$ respectively when TCE is added. The band intensity for a ratio 1 : 1 of hydrazone to TCE has a log $\epsilon$ = 2·43 and log $\epsilon$ = 2·7 respectively for phenylhydrazone and methylphenylhydrazone. Both absorption bands decrease rapidly with time. In the case of phenylhydrazone while the band at 425 m$\mu$ decreases a new broad band with low intensity appears at 510 m$\mu$ and the yellow solution turns pink. In addition broad absorption bands at around 400 m$\mu$ are observed with solutions of phenylhydrazone of acetone in degassed methanol when equimolar amounts of tetrabromomethane (CBr$_4$) are added. For a 1 : 1 ratio of phenylhydrazone to CBr$_4$ log $\epsilon$ = 1·9. It has been reported that triethylenediamine forms a complex with CBr$_4$ which absorbs at 400 m$\mu$.[13] Solutions of phenylmethylhydrazone and N,N-

dimethylhydrazone of acetone in methanol in the presence of equimolar amounts of CBr$_4$ show only a broad trail of absorption of very low intensity at 400 m$\mu$.

The complexes of the hydrazones with TCE are intensely coloured but very unstable. The colours of the solutions change upon standing or when heated. A 1 : 1 complex of phenylhydrazone of acetone in nitrobenzene or methanol is cobalt blue at liquid nitrogen temperature. By increasing the temperature the colour goes through olive green to blood red at room temperature.

The NMR spectra of the above solutions in methanol show decomposition starting from −50°. The decomposition is more extensive in methanol than in nitrobenzene. Due to this decomposition we were not able to make any structural assignments for the complexes from their NMR spectra. Similar results were observed with solutions of N,N-dimethylhydrazone of acetone in nitrobenzene in the presence of equimolar amounts of TCE.

### DISCUSSION

It is clear from the above results that the energy barrier for the *syn–anti* isomerization of hydrazones is significantly decreased in the presence of halogenated compounds and that this effect is directly proportional to their concentration.

The findings from UV spectroscopy implicate the formation of a charge transfer complex between the hydrazones acting as electron donors and the halogenated solvents, with their empty d-orbitals acting as electron acceptors. The unusual behavior of the rate of *syn–anti* isomerization of hydrazones in these solvents can be explained if we assume that the mechanistic path involves a charge transfer complex. Thus, halogenated solvents (S), act as acceptors of an electron from the hydrazone. The resulting cation radical is expected to isomerize faster than the hydrazone itself. Unfortunately, the removal of an electron from the hydrazone would lower the energy of activation for either the linear or the nonlinear mechanistic path. Thus, no distinction can be made between the two paths.
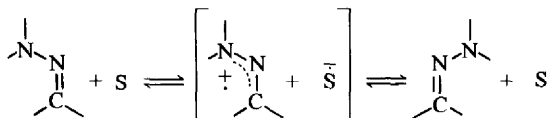


Table 7. $T_c$ and $\Delta G_c^{\neq}$ values of

| Ref. | Z | X | $T_c$ °C | $\Delta G_c^{\neq}$ kcal/mol | Solvent |
|------|---|---|------|------|---------|
| 8 | N(CH$_3$)$_2$ | CO$_2$CH$_3$ | 156 | 23·2 | Hexachlorobutadiene |
| 8 | N(C$_6$H$_5$CH$_2$)$_2$ | CO$_2$CH$_3$ | 145·5 | 21·2 | Hexachlorobutadiene |
| 8 | N(C$_6$H$_5$CH$_2$)$_2$ | CH$_3$ | 143 | 21·6 | Hexachlorobutadiene |
| 14 | C$_6$H$_5$ | CH$_3$OC$_6$H$_4$ | 62 | 18·1 | Carbon tetrachloride |
| 2 | N=C(CH$_3$)$_2$ | CH$_3$ | 170 | 23·9 | Trichlorobenzene |
| 15 | N=C(CH$_3$)$_2$ | CH$_3$ | >180 | — | Diphenyl ether |
| 16 | N(CH$_3$)$_2$ | N(CH$_3$)$_2$ | >200 | >25 | Diphenyl ether |
| 16 | N(CH$_3$)$_2$ | OCH$_3$ | >200 | >25 | Diphenyl ether |
| 17 | CH$_2$C$_6$H$_5$ | CH$_3$ | — | >23 | Neat |
| 17 | CH$_2$C$_6$H$_5$ | CH$_3$ | — | >23 | Quinoline |
| 17 | N(C$_6$H$_5$)$_2$ | A | >175 | >23·2 | Nitrobenzene |
| 18 | N(CH$_3$)$_2$ | A | >135 | >21·1 | Nitrobenzene |
| 18 | N(CH$_3$)(C$_6$H$_5$) | A | >170 | >24·2 | Nitrobenzene |

A = 2,6-di-t-butyl-p-benzoquinone.

The possibility of a nucleophilic attack by the halogen of the solvent on the charge transfer complex which would promote a separation of charges on the C–N bond cannot be excluded by the present data. In such a case, the mechanism would obviously involve rotation not inversion. It is clear, in any case that the criterion of low energies of activation as one favouring inversion over rotation is at best very weak.

In the light of the above suggestions it is pertinent to reexamine some data from the literature (Table 7) on the *syn–anti* isomerization processes. Low free energies of activation are indeed obtained in solvents that can act as electron acceptors and this further supports the mechanism that we have proposed. Kessler[19] has noticed the effect of chlorinated solvents on the rate of isomerization and suggested the existence of a solute-solvent complex without giving more details on the nature of the association.

## EXPERIMENTAL

The various hydrazones of acetone were prepared according to known methods[11b] from the corresponding free hydrazines and acetone in the presence of acetic acid. The hydrazones were purified by recrystallization or distillation and their purity was checked from their melting points and their proton NMR spectra. As they decompose very easily the solutions were made immediately before the NMR temperature study from freshly synthesized and thoroughly dried compounds. The solutions of hydrazones were degassed by the standard freezing thawing technique and sealed under vacuum. Conditions such as duration of degassing, of temperature equilibration in the probe and recording of spectra were kept practically identical for all samples. The homogeneity of the system was optimized and two to three recordings of the spectrum were taken at each temperature. A Varian A-60 A NMR spectrometer equipped with a variable temperature control unit V-4341/V-6057 was used. The temperature of the probe was calibrated with ethylene glycol and checked with a thermocouple introduced in a measuring tube containing ethylene glycol or hexachlorobutadiene. It was found to be accurate within one degree centigrade. The computer program CLATUX by Binsch[20] was used for the line shape analysis.

The absorption spectra were recorded with a Cary-15 double beam spectrophotometer. All spectra were recorded using the appropriate blank solution, i.e. solvent containing the same concentration of halogenated compounds or TCE except the hydrazone. The solvents used were purified according to known methods and by fractional distillation. To remove oxygen from the solvents dried, oxygen free argon was bubbled through for 2 hr. Tetracyanoethylene was recrystallized from chloroform and tetrabromomethane was distilled under reduced pressure.

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