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SYN-ANTI ISOMERIZATION INVOLVING THE N-CYANOIMINO GROUP

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Because of our recent interest in the configurational stability of imines and related compounds (1,2) and the lack of available data on the syn-anti isomerization of N-cyanoimines (3) we looked for evidence of such isomerization in a series of compounds of the type $X_2C{=}N{-}CN$. We report here the preliminary results of this investigation.

I X = CH_3 III X = OCH_3 V X = $N(CH_3)_2$

II X = SCH_3 IV X = $NDCH_3$

The nmr spectrum of compound I in d_6-acetone shows, at room temperature, two sharp signals for the methyl groups in a 1:1 area ratio. As the sample is warmed to 85° the lines coalesce into a single peak. The process is reversible and has been observed in several different solvents. The spectra of II-V, on the other hand, at room temperature consist of only a single sharp resonance peak for the methyl groups. However, cooling causes a separation into two peaks of 1:1 ratio in II-IV.

The most logical explanation for the observed changes in the nmr spectra of these compounds is syn-anti isomerization at the carbon-nitrogen double bond.

The free energies of activation ($\Delta G_c^{\ddagger}$) for the observed process at the temperature of coalescence (T_c) in each compound can be calculated in the usual way (5) from the maximum chemical shift separation ($\Delta\nu$) of the two methyl resonances and from T_c using the Eyring equation with the transmission coefficient taken as unity. The pertinent data and results are summarized in Table 1.

TABLE I. NMR Data For Compounds I-V[a]

Compd.	X	$\Delta\nu$ (H_z)[b]	T_c(°C)	$\Delta G_c^{\ddagger}$ (Kcal/mole)
I	CH_3	8.5	85	18.9
II	SCH_3	14.5	1	14.1
III	OCH_3	2.5	-16	14.1
IV	$NDCH_3$	5.0	-43	12.3
V	$N(CH_3)_2$	---	<-90	<10[c]

[a]Spectra were recorded on a Varian HA-60 spectrometer equipped with a variable temperature probe. The temperature T_c is accurate to $\pm$ 0.5°. Temperature could be held constant to $\pm$ 0.2°. Sample concentrations were 10% w/v in d_6-acetone.

[b]Maximum chemical shift separation at low temperature.

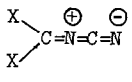
[c]Estimated using T_c = <-90° and $\Delta\nu$ = 5 H_z.

Considerable attention has been focused recently on the sensitivity of configurational stability to the nature of the groups or atoms bonded to the imino nitrogen and to the imino carbon in compounds such as $X_2C{=}N{-}Y$. It has been established, for example, that for a given substituent X the isomerization rate is lowest for compounds with a hetero atom directly bonded to the imino nitrogen (1,2,6). Thus, isomers of oximes, N-haloimines, hydrazones, etc. have been separated and are configurationally stable in many cases. When Y is alkyl or aryl the isomerization rate is much greater and aryl is the faster of these two by several powers of ten (1,2,6). For a given Y the rate of isomerization has been found to be greatest for compounds such as iminocarbonates which bear an electronegative hetero atom on the imino carbon (4,7). Some compounds selected from these studies on substituent effects have been included in Table II for sake of comparison with the N-cyanoimino compounds in Table I (realizing that any comparisons must be qualitative because $\Delta G_c^{\ddagger}$ values are being compared at several different temperatures and from several solvents but also realizing the negligible sensitivity of these isomerizations to various aprotic solvents (8) and the small temperature dependence of $\Delta G^{\ddagger}$ relative to the large differences being compared).

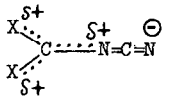
TABLE II. NMR Data For the Isomerization of Some Imines, $X_2C{=}NY$

Compd.	X	Y	Solvent	T_c(°C)	$\Delta G_c^{\ddagger}$ (kcal/mole	Ref.
VI	CH_3	$CH_2C_6H_5$	quinoline	>180	>23	6
VII	CH_3	C_6H_5	diphenyl ether	126	20.3	9
VIII	OCH_3	C_6H_5	acetone	0	14.3	4
IX	SCH_3	C_6H_5	d_6-acetone	-22	13.7	4
X	$N(CH_3)_2$	C_6H_5	CS_2	-35	12.1	8

Comparison of the data in Tables I and II reveals that the cyano group is about the same as phenyl in its effect on configurational stability. Furthermore, the marked decrease in $\Delta G^{\ddagger}$ in going from I to II, III, or IV is about the same as that observed in going from VII to VIII, IX, or X. The similarity between cyano and phenyl on the imino nitrogen and the effect of CH_3O, CH_3S, and CH_3ND when on the imino carbon are consistent with the ability of these groups to stabilize a linear transition state such as has been proposed (2) for the "lateral shift" mechanism of isomerization of imines (10). Such stabilization would be expected to be much less significant in alkylimines such as VI.



X = CH_3



X = CH_3O, CH_3S, CH_3ND

The lack of observed separation of methyl signals in V may be due to insufficient chemical shift difference but data on similar compounds (8,11) suggest that further studies in other solvents and at lower temperatures may be fruitful. Work is continuing on this. It should also be mentioned that hindered rotation about the C-N single bond has been observed in N-cyanoimines related to V. The kinetics of this process will be reported elsewhere.

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3. During the course of this investigation, data for compound II were reported (4). Our results are in excellent agreement with those reported.

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