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# STRUCTURAL ORGANIC CHEMISTRY BY NMR. III[1]. ISOMERIZATION OF COMPOUNDS CONTAINING THE CARBON-NITROGEN DOUBLE BOND

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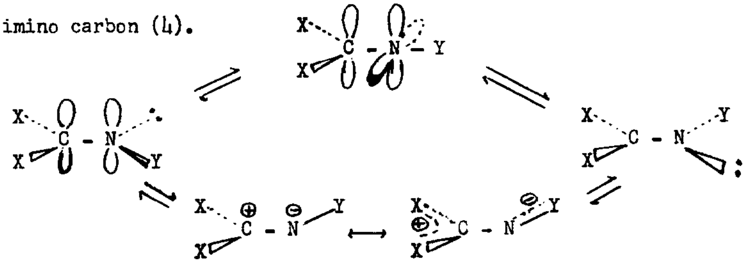
There are two possible limiting mechanisms by which compounds containing the carbon-nitrogen double bond can thermally isomerize. One of these, proposed for the isomerization of imines[2], involves a lateral in-plane shift of the group bonded to the imino nitrogen. The transition state for this process was described as one in which the $\pi$ bond remains intact and the non-bonded electron pair on nitrogen rehybridizes to a p orbital. One of the reasons for this electronic description of the transition state was the relative insensitivity of the isomerization rate to changes in the substituent attached to the phenyl ring bonded to the imino carbon (2). The other limiting mechanism, which has been proposed for the isomerization of iminocarbonates[3], is one which proceeds by rotation about the carbon-nitrogen double bond and involves a polar transition state in which unsharing of the $\pi$ electrons has occurred. There is, of course, the possibility of a continuum of mechanisms between these two limiting extremes and it is therefore possible that the pathway for the isomerization of a given compound is dependent upon the atoms or groups bonded to the carbon-nitrogen double bond. Although the lateral shift mechanism was proposed for imines, this same pathway has been proposed for the isomerization of compounds having heteroatoms bonded to the imino carbon (4).



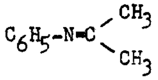
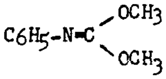
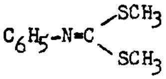
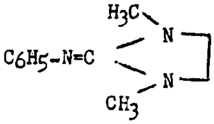
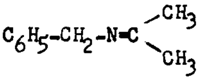
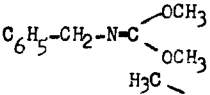
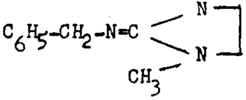
The rotation mechanism for iminocarbonates has recently been challenged[5]. The larger isomerization rate of iminocarbonates relative to imines was attributed[5] to the inductively greater electron withdrawing ability of oxygen relative to carbon and interpreted to be consistent with the lateral shift mechanism. The rationale for this suggestion was the observed increase in isomerization rates of imines with increasing electron withdrawal by substituents on the imino nitrogen [2, 6].

We now wish to report additional data which demonstrate that the isomerization rates of compounds containing the carbon-nitrogen double bond parallel the relative conjugative ability of groups bonded to the imino nitrogen, i.e., X = N > S > O > C[7] rather than their relative electronegativities (O > N > S > C).

The pertinent nmr and kinetic data are given in Table I.

TABLE I.

Isomerization of Compounds with a C - N Double Bond

| Compound | Solvent | $\Delta\nu_{o}$ cps | Tc °C | $\Delta G^{\ddagger}_{Tc}$ Kcal | k-22$^{(a)}$ sec$^{-1}$ | Ref. |
|---|---|---|---|---|---|---|
| 1.  $C_6H_5-N=C(CH_3)_2$ | quinoline | 23 | 140 | 21 | $2.8\times10^{-6}$ | 7 |
| 2.  $C_6H_5-N=C(OCH_3)_2$ | acetone | 9.1 | 0.8 | 14.4 | 1.6 | 3 |
| 3.  $C_6H_5-N=C(SCH_3)_2$ | acetone | 2.5 | -22 | 13.8 | 5.2 | this work |
| | $d_6$-acetone | | -22 | 13.7 | | 5 |
| 4.  | acetone | | -60 | 12$^{(b)}$ | $2\times10^2$ | this work |
| | chloroform | | -60 | 12 | $2\times10^2$ | |
| | pyridine-carbon disulfide | | -60 | 12 | $2\times10^2$ | |
| 5.  $C_6H_5-CH_2-N=C(CH_3)_2$ | neat | 9 | > 170° | > 23 | < $5\times10^{-8}$ | this work |
| | quinoline | | 180° | 23 | | 5 |
| 6.  $C_6H_5-CH_2-N=C(OCH_3)_2$ | acetone | 2.5 | 74° | 19.3 | $8.5\times10^{-5}$ | this work |
| 7.  | acetone | | -60 | 12$^{(b)}$ | $2\times10^2$ | this work |
| | chloroform | | -60 | 12 | $2\times10^2$ | |
| | pyridine-carbon' disulfide | | -60 | 12 | $2\times10^2$ | |

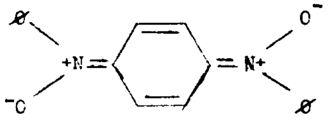
(a) Calculated from $\Delta G^{\neq}_{Tc}$ using the Eyring equation.
(b) Calculated assuming a $\Delta\nu_{o}$ of 1 cps and a coalescence temperature of -60°.

It is unlikely that the singlet methyl for 4 and 7 is the result of accidental equivalence rather than exchange averaging. Models show that the two methyl groups in 4 and 7 are even more exposed to anisotropy effects than they are in 2 and 6. A cyclic rather than acyclic guanidine was chosen in order to avoid the ambiguity of interpreting a temperature dependent spectrum as due to isomerization about the C=N or rotation about the C-N.

Inspection of Table I shows that the $\Delta G^{\neq}_{Tc}$ decreases by 9 or more Kcal in going from 1 to 4 and from 5 to 7. Furthermore, a comparison of rate constants calculated at -22°, the coalescence temperature of 3, shows that the cyclic guanidine 4, isomerizes at least 8 powers of 10 faster than the imine 1 and compound 7 isomerizes at least 10 powers of 10 faster than 5. This demonstrates the remarkable susceptibility of the isomerization rate to the group bonded on the imino carbon.

It is particularly important to compare compound 2 with 4 and compound 6 with 7. It would be predicted on the basis of electronegativities, that 2 undergo isomerization faster than 4 and that 6 isomerize faster than 7. Instead the data show that 4 isomerizes at a rate at least 100 times faster than 2 and that 7 isomerizes at least 7 powers of ten faster than 6. This clearly establishes that the rates and barriers parallel the relative conjugative abilities of the groups bonded to the imino carbon.

It should also be mentioned that one reason for the initial suggestion of lateral shift rather than rotation mechanism for imines, was the small isomerization barriers found for imines relative to olefins. It was reasoned from this that imines underwent isomerization by a mechanism different from that of olefins. Recently however, a number of substituted olefins have been found to have isomerization barriers of less than 20 Kcal.[9-11]. In addition the amino methyls of 8 were found[12] to be equivalent at room temperature and the $\Delta G^{\neq}_{Tc}$ for 9 was measured[13] as 12 Kcal. The only possible way by which these compounds can isomerize is by a rotation mechanism.



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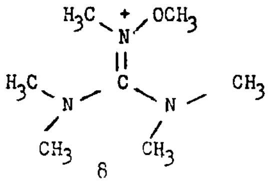

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In conclusion it should be pointed out that if the original electronic description of the transition state for the lateral shift mechanism is modified to include $\pi$ bond participation, then both the rotation and lateral shift mechanisms are consistent with the data and electronic effects cannot be used to make a choice between the two pathways. The transition states for the two pathways however differ in geometry and a choice between them must await experiments[14] which will unambiguously give information on this parameter.

## References

1. For the preceding paper in this series, see N. P. Marullo, C. B. Mayfield, and E. H. Wagener, J. Am. Chem. Soc., **90**, 510 (1968).
2. D. Y. Curtin, E. J. Grubbs and C. G. McCarty, J. Am. Chem. Soc., **88**, 2775 (1966).
3. N. P. Marullo and E. H. Wagener, J. Am. Chem. Soc., **88**, 5034 (1966).
4. H. Kessler, Tetrahedron Letters, 2041 (1968).
5. F. Vogtle, A. Mannachreck and H. A. Staab, Ann. Chem., **708**, 51 (1967).
6. G. Wettermark, J. Weinstein, J. Sousa and L. Dogliotti, J. Phys. Chem., **69**, 1584 (1965).
7. The rotational rates of a variety of thioamides have been found to correlate with the conjugative ability of substituents bonded to the thiocarbonyl carbon. J. Sandstorm, J. Phys. Chem., **71**, 2318 (1967).
8. H. A. Staab, F. Bogtle and A. Mannschreck, Tetrahedron Letters, 697 (1965).
9. S. Kende, P. T. Izzo and W. Fulmer, Tetrahedron Letters, 3697 (1966).
10. Y. Shio, E. C. Taylor and J. Bartulin, Tetrahedron Letters, 3259 (1967).
11. G. Isakason, J. Sandstrom and J. Wennerbeck, Tetrahedron Letters, 2233 (1967).
12. V. J. Bauer, W. Fullmer, G. O. Morton and S. R. Safir, J. Am. Chem. Soc., **90**, 6847 (1968).
13. R. W. Layer and C. J. Carman, Tetrahedron Letters, 1285 (1968).
14. There have been a number of recent theoretical calculations on the isomerization barriers of compounds having $sp^2$ nitrogen. One of these, J. M. Lehn and B. Munsch, Theor. Chim. Acta, **12**, 91 (1968), computes a smaller activation energy for the lateral shift pathway for the isomerization of $H_2C=NH$ than for a bond rotation process. However, the liquid phase isomerization of imines with hydrogen bonded to the imino nitrogen undergo fast bimolecular ixomerization (J. B. Lambert, W. L. Oliver and J. D. Roberts, J. Am. Chem. Soc., **87**, 5085 (1965). Another calculation, M. S. Gordon and H. Fischer, J. Am. Chem. Soc., **90**, 2471 (1968), shows that large changes can occur in going from one compound to another. The computed activation energies for the isomerization of $HN=(C=)_nNH$ are 46.2 and 23.6 Kcal when $n = 0$ and 2 respectively and the lateral shift pathway requires less energy than rotation. However, for $n = 1$ and 3 the activation energies are computed as 8.0 and 6.9 Kcal and the rotation pathway is slightly favored.