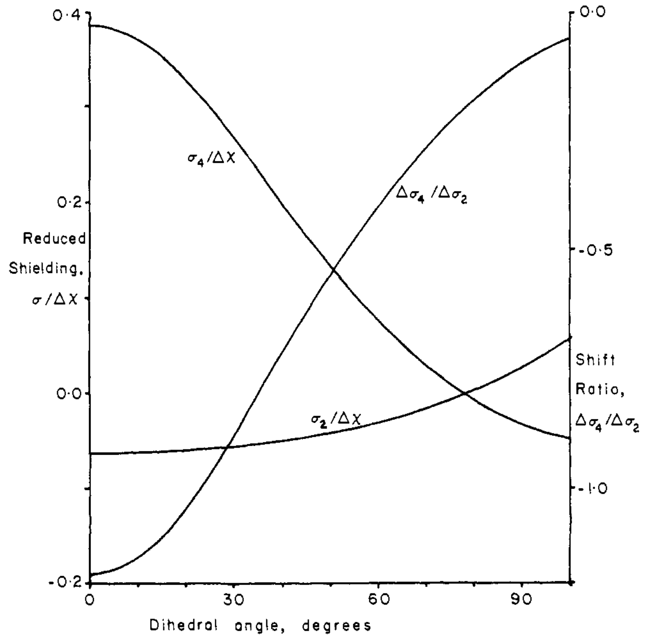

Figure 2. Computed shieldings arising from the ring anisotropy.

of the two upper ones, the observed population-weighted average value, J_{12}, may be used to deduce the fractional population, x, in upper states.

$$x = (J_l - J_{12})/(J_l - J_u)$$

A plot of the logarithm of $x/(1 - x)$ *vs.* $1/T$ yields the energy separation of the conformers, ΔE; the rate of change of τ_2 or τ_4 with x yields the anisotropy, $\Delta\chi$. The values deduced depend on the assumed conformer couplings, J_l and J_u. Table II presents ΔE and $\Delta\chi$ as functions of reasonable choices of the conformer couplings, which are consistent with those in related systems[8] and which also appear to give the most linear $1/T$ plots. The energy separations are consistent with other determinations;[4,9] the values of the anisotropy are somewhat larger than those derived by less direct methods.[3]

Table II. Energy Difference (ΔE) and Anisotropy ($\Delta\chi$) *vs.* Conformer Couplings, J_l and J_u

J_l, cps	J_u, cps	ΔE, kcal	$\Delta\chi \times 10^{30}$, cm^3
11.5	1.5	0.93	51.
12.5	0.5	0.73	62.
12.5	1.5	0.79	57.
12.5	2.5	0.77	52.
13.5	1.5	0.66	62.

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[8] A. A. Bothner-By, S. Castellano, and H. Günther, *J. Am. Chem. Soc.*, **87**, 2439 (1965); A. A. Bothner-By and R. K. Harris, *ibid.*, **87**, 3445 (1965); E. W. Garbisch, Jr., *ibid.*, **86**, 5561 (1964).

[9] H. Günther and D. Wendisch, *Angew. Chem. Intern. Ed. Engl.*, **5**, 251 (1966).

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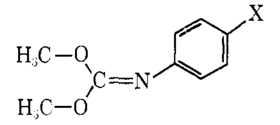
Isomerization Rates of Iminocarbonates

Sir:

Until recently, examples of geometric isomerism due to restricted rotation around a carbon–nitrogen double bond were observed only for those in which an electronegative atom such as oxygen, nitrogen, or halogen was bonded to the imino nitrogen. The isolation of geometric isomers of imines by Curtin[1] was the first unequivocal demonstration of the existence of stereoisomeric compounds in which a carbon atom was bonded to the imino nitrogen. The extraordinary susceptibility of the configurational stability to the group bonded to imino nitrogen in compounds such as $Ar_2C{=}N{-}X$ is exemplified by the fact that the isomerization rate is faster by a factor of 10^{14} for the compound where $X = C_6H_5$ than for that where $X = OCH_3$.[2]

We now wish to report the first stereochemical study of an analogous class of compounds, the iminocarbonates (I). The distinguishing feature of iminocarbonates[3] is that they contain an electronegative hetero atom bonded to the imino carbon. The nmr spectra of compounds I all show a single methoxyl resonance at room temperature. Cooling the sample results first in a broadening of the methyl signal and then in the formation of a distinct doublet. The pertinent nmr and kinetic data are given in Table I.



I

The first three entries in Table I demonstrate that the process obeys a first-order rate law and is attributed to inversion of the aryl group. The data also show that substituents on the phenyl group have very little effect on the isomerization rate. In acetone solution, there is less than a threefold difference in the first-order rate constants between the chloro- and methyl-substituted compounds. The rate ratio in chloroform is only 1.3. This is unlike the results obtained on isomerization rates of imines for which a ρ value of between +1 and +2 was found.[4] The most important feature of the data is the remarkably low E_a values. Only for the isomerization of a perfluoroalkylimine has an E_a value as low as 13 kcal/mole been obtained.[5] The anils of substituted benzophenones have isomerization E_a values ranging from 17 to 20 kcal/mole, while that of acetone anil measured in quinoline is 21 kcal/mole.[6] A comparison of rates extrapolated to 60°

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

[2] D. Y. Curtin, E. J. Grubbs, and C. G. McCarty, *ibid.*, **88**, 2775 (1966).

[3] The previously unreported *p*-chloro compound (*Anal.* Found: C, 54.23; H, 5.16; N, 6.97) and the *p*-methoxy compound (*Anal.* Found: C, 67.20; H, 7.34; N, 7.68) were prepared by the method described by H. Tieckelmann, and H. W. Post, *J. Org. Chem.*, **13**, 268 (1948), and purified by chromatography through neutral alumina and then distilled at 53° (0.02 mm) and 55° (0.07 mm), respectively. The infrared and integrated nmr spectra were consistent with the assigned structures.

[4] D. Y. Curtin and C. G. McCarty, *Tetrahedron Letters*, 1269 (1962).

[5] S. Andreades, *J. Org. Chem.*, **27**, 4163 (1962).

[6] H. A. Staab, F. Vogtle, and A. Mannschreck, *Tetrahedron Letters*, 697 (1965).

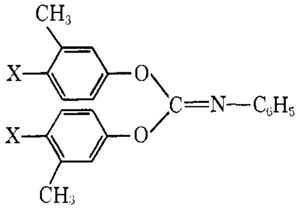
Table I. Data on Isomerization of Iminocarbonates of Structure I[a]

X	Solvent	Concn[b]	Tc, °C	$\Delta\nu$, cps	k^{60}, 10^3 sec^{-1}	E_a, kcal	log A
H	Acetone	25	+0.8	9.13	1.6	13.4 ± 0.3	12.0
H	Acetone	35	+1.2	8.33	1.7	13.2 ± 0.4	11.9
H	Acetone	15	−0.4	9.89	1.7	13.8 ± 0.4	12.4
Cl	Acetone	25	−1.6	7.14	5.1	16.6 ± 0.3	14.6
CH_3	Acetone	25	+2.8	8.03	2.1	15.5 ± 0.3	13.5
H	Chloroform	25	+0.1	11.46	2.8	14.4 ± 0.3	12.9
Cl	Chloroform	25	+3.6	9.22	1.4	13.8 ± 0.3	12.2
CH_3	Chloroform	25	+5.5	10.37	1.1	13.2 ± 0.5	11.7

[a] A Varian A-60 equipped with a Varian variable-temperature probe was used to observe the chemical shift as a function of temperature. Temperatures were measured with an accuracy of ±0.8°. A given temperature could be held constant to ±0.1°. Spectra were calibrated by the side-band method, using a frequency counter to measure the side-band frequency. The method described by J. A. Pople, W. S. Schneider, and H. J. Beinstein ("High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 224) was used to calculate τ values. At each temperature no less than six determinations were made, with 15 determinations being made at the point of maximum separation. All errors are root-mean-square errors. The E_a values represent slopes plotted using no less than seven temperatures. All slopes gave a correlation coefficient of better than 0.99 when treated by the method of least squares. [b] By volume.

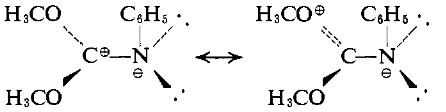
for acetone anil to that for I, X = H, shows that substitution of methoxyl for methyl increases the isomerization rate by a factor of 10,000. This demonstrates the susceptibility of the isomerization rate to the nature of the group bonded to the imino carbon.

Further evidence for this is found in the fact that iminocarbonates II[7] in acetone, chloroform, or diphenyl ether give one temperature-invariant signal for the *m*-methyl protons.



II, X = H, Cl, CH_3, NO_2

The low activation energy for the isomerization of imines relative to olefins and the effect of substituents on the rate, particularly the insensitivity of the isomerization rate to substituents on the aryl group bonded to the imino carbon in compounds such as $Ar_1Ar_2C{=}N{-}CH_3$, have been interpreted in terms of a mechanism which proceeds *via* a linear transition state in which the π bond remains intact and the nonbonded electron pair on nitrogen rehybridizes to a p orbital.[2] The very low activation energy and large isomerization rate found for the iminocarbonates is more easily explained in terms of a mechanism proceeding through a polar transition state in which unsharing of the electrons of the π bond has occurred.



Since oxygen is more electronegative than carbon, substitution of methoxyl for alkyl or aryl groups attached to the imino carbon might be expected to decrease the extent of polarization of the carbon–nitrogen double bond. Resonance effects would operate in an opposite fashion, but can be neglected as making an important contribution to the ground state. The over-all effect should be a stabilization of the ground state. However, resonance effects become important in excited states and, in this case, would be expected to stabilize the transition state by delocalization of the positive charge being generated on the imino carbon. The expected net effect should be a decrease in the required activation energy.

The large isomerization rates found for N-aryliminocarbonates suggest that stereoisomeric compounds of this type cannot be isolated with the possible exception of those bearing an electronegative atom on the imino nitrogen. In order to test this, the N-chloro compound, $(H_3CO)_2C{=}N{-}Cl$,[8] was examined in the solvents chloroform, carbon tetrachloride, methylcyclohexane, acetonitrile, and diphenyl ether. In all cases, a methyl doublet was observed at room temperature and there was no change in the nmr spectrum when heated in methylcyclohexane to 105° or diphenyl ether to 170°.[9] This result demonstrates the extraordinary susceptibility of the isomerization rates of iminocarbonates as well as imines to the group on the imino nitrogen.

Acknowledgment. We wish to thank the Army Research Office, Durham, and donors to the Petroleum Research Fund administered by the American Chemical Society for financial assistance.

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[7] Prepared by heating phenylimido phosgene with the appropriate phenol in collidine. All compounds were solids and purified by recrystallization to constant melting point. Physical properties found were as follows: for X = H, mp 68–69° (*Anal.* Found: C, 79.36; H, 6.24; N, 4.48); for X = Cl, mp 115–116° (*Anal.* Found: C, 65.53; H, 4.60; N, 3.54); for X = CH_3, mp 72–73° (*Anal.* Found: C, 80.19; H, 6.84; N, 4.12); and for X = NO_2, mp 125° (*Anal.* Found: C, 61.77; H, 4.31; N, 10.35). The infrared and integrated nmr spectra were consistent with the assigned structure.

(8) E. Ofstead, Ph.D. Thesis, University of Maryland, College Park, Md., 1963, p 39.

(9) We are grateful to F. Vogtle for communicating to us the result in diphenyl ether.

(10) National Aeronautics and Space Administration Predoctoral Fellow.

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Synthesis of Metal–Metal Bonds *via* Iridium and Rhodium Anions[1]

Sir:

The preparation of compounds containing covalent metal–metal bonds is a subject of extensive current in-

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