lar structural parameters to gaseous molecular ions is right on.

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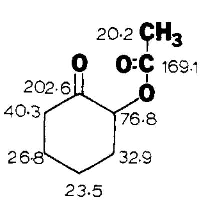

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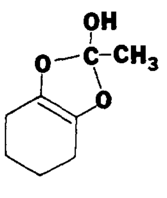

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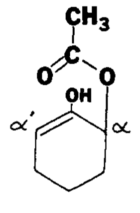


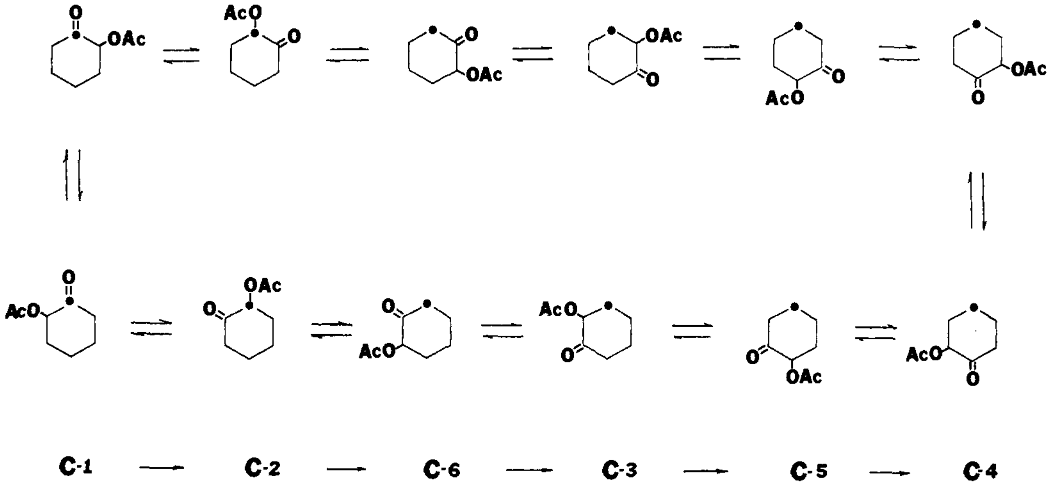
3

A ^{13}C Nuclear Magnetic Resonance Study of the Interchange–Transfer Rearrangement of α-Acyloxy Ketones[1,2]

Sir:

Recently, presumptive evidence for a degenerate rearrangement of α-acyloxycycloalkanones was found in the fact that all hydrogen atoms in a series of such compounds were labile in acetic acid-d_4.[3] The mechanism suggested (Scheme I) for the complete deuterium exchange involved both an enediol derivative **2** for *interchange* of the two oxygen functions and an allylic rearrangement of the enol **3** to *transfer* the acyloxy group from the α to the α' position. By means of ^{13}C nmr spectroscopy we have now been able to provide strong support for this mechanism and to acquire additional information not readily discernible by other means.

Scheme I



The proposed migration of oxygen functions around the intact carbon skeleton requires that a labeled carbon atom be equally distributed among all positions of the ring at equilibrium. The ^{13}C nmr signals from each carbon atom of 2-acetoxycyclohexanone (**1**) are well separated and assignable (see **1**).[4] 2-Acetoxycyclohexanone-*1*-^{13}C (60% enriched) was prepared in 66% yield by successive enol acetylation and epoxidation of cyclohexanone-*1*-^{13}C, which was made in 55% yield by the reaction of 1,5-dilithiopentane with $^{13}CO_2$.

After treatment of **1**-*1*-^{13}C in HOAc–KOAc at 142° for 12 hr, the recovered **1** had the excess ^{13}C label equally distributed between C-1 and C-2. With the same temperature and time, unlabeled **1** in DOAc-d_3–KOAc-d_3 incorporated up to five D atoms at C-2, C-3, and C-6.[5] Unlabeled **1** in propionic acid–KOAc (135°, 24 hr) gave recovered **1** but no 2-propionoxycyclohexanone. However, when the temperature of the reaction of **1**-*1*-^{13}C in HOAc–KOAc was raised to 218° for 22 hr, the recovered **1** now had the label equally distributed among all six carbon atoms of the ring. Furthermore, the ratio of the ring carbon signals to the acetate methyl signal was 10:1 as demanded by the suggested mechanism. Thus, in the HOAc–KOAc medium at the lower temperature, enolization and intramolecular functional group interchange occur readily, whereas the $\alpha \rightarrow \alpha'$ transfer occurs at a detectable rate only at temperatures above ~200°.

Whether the $\alpha \rightarrow \alpha'$ transfer in HOAc was intra- or intermolecular could not be established by substitution of propionic acid because acyl exchange occurred at temperatures much above 140°, but it was possible to show that the HOAc is not essential and also to provide strong evidence that the allylic rearrangement can be intramolecular. A dilute toluene solution (100 mg/5 ml) of **1**-*1*-^{13}C in a sealed glass tube at 240–250° for 75 hr[6]

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(1) Part XVIII in the series ^{13}C Nuclear Magnetic Resonance Studies.

(2) Part XVII: P. de Mayo, J. B. Stothers, and M. C. Usselman, *Can. J. Chem.*, in press.

(3) I. S. Y. Wang and E. W. Warnhoff, *Chem. Commun.*, 1158 (1969).

(4) The ^{13}C spectra were determined for benzene-d_6 solutions of **1** using a Varian XL-100-15 system. With proton noise decoupling and time averaging, satisfactory spectra could be obtained with samples of *ca.* 50 mg in 1.5 ml, although more concentrated solutions were employed for precise integrations. The shieldings were measured relative to internal TMS. The well-established additivity of substituent effects for ^{13}C chemical shifts allowed estimates of the shieldings for C-3, -4, -5, and -6 in **1** from the data for the monosubstituted cyclohexanes. The assignments for the carbonyl, carbinyl, and methyl carbons are unambiguous.

(5) Location of deuterium at C-3 and C-6 was established by comparison of the proton-decoupled ^{13}C nmr spectra of **1** and the ring-pentadeuterated **1**.

(6) Compound **1** in a sealed tube without solvent under these conditions undergoes considerable decomposition. Similarly, if **1** is heated in toluene solution in a sealed tube from which oxygen has not been removed, extensive decomposition occurs. However, removal of oxygen

exhibited extensive scrambling of the label around the ring. From the ^{13}C spectrum, the enrichment at the ring carbons was estimated (±5%) as 15% (C-1, C-2), 12% (C-6), 8% (C-3), 5% (C-4, C-5). With shorter times or at slightly lower temperatures, the ^{13}C scrambling observed was also in agreement with the suggested mechanism. The excess ^{13}C initially entered C-2, but then began to appear at C-6 and to a lesser extent at C-3 while the ^{13}C content of C-2 and C-1 (ratio 1:5) was far from equivalent. This sequence of incorporation is that expected from the suggested mechanism if the rate of enolization has been drastically slowed in toluene,[7] thus making the rate of the combined enolization (→ C-2)-interchange comparable with the rate of enolization (→ C-6)-$\alpha \rightarrow \alpha'$ transfer. It is apparent that the $\alpha \rightarrow \alpha'$ transfer in toluene solutions of **1** is closely related to the thermal rearrangement of allylic esters,[8] and this transfer might be a source of side products in the preparation of unsaturated ketones by the pyrolysis (350–500°) of α-acetoxy ketones.

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by bubbling in nitrogen gas before sealing the tube is sufficient to prevent decomposition.

[7] Enolization is apparently occurring on the glass surface or as a result of collision. The possibility that enolization in the toluene reactions is mainly catalyzed by traces of HOAc formed by slight hydrolysis of **1** by traces of water is discounted because the ^{13}C scrambling results are reproducible, and the addition of 0.1 mol equiv of HOAc to one reaction gave no noticeable increase in the ^{13}C scrambling rate.

[8] E. S. Lewis, J. T. Hill, and E. R. Newman, *J. Amer. Chem. Soc.*, **90**, 662 (1968).

[9] Holder of a National Research Council of Canada Scholarship, 1967–1970.

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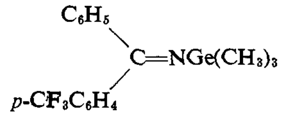
Barrier to Planar Inversion in an *N*-Germyl Imine[1]

Sir:

It has been shown that barriers to pyramidal inversion are significantly lowered when higher row atoms belonging to group IVa (silicon, germanium, tin) are attached to the inversion center.[2] This effect is correlated with the electronegativity of the group IVa element.[2] We now wish to report the first experimental demonstration of a similar effect on the barrier to planar nitrogen inversion.[3] This is also the first reported experimental barrier to inversion (planar *or* pyramidal) at nitrogen bonded to a group IVa element other than carbon.

N-(Trimethylgermyl)-*p*-trifluoromethylbenzophenone imine (**1**) was synthesized by the method of Chan and Rochow,[4] involving the addition of *p*-lithiobenzotrifluoride[5] to benzonitrile with subsequent addition of trimethylgermanium bromide. Distillation (bp 118–119° (0.1 mm)) yielded an analytically pure,[6] clear, yellow oil whose pmr spectrum (*ca.* 15 v/v % solution in CDCl$_3$ with *ca.* 1 v/v % tetramethylsilane) is consistent with the assigned structure: δ 7.60 (s, aromatic H), 7.41 (s, aromatic H), 0.17 (s, GeCH_3).



$$(C_6H_5)(p\text{-}CF_3C_6H_4)C{=}NGe(CH_3)_3$$

1

At temperatures below −110° the trimethylgermyl pmr absorption[7] of **1** consists of two overlapping singlets (limiting $\Delta\nu_{AB} = 1.1$ Hz at 60 MHz) attributed to the syn and anti forms of the imine. These signals coalesce at −108°, and become a sharp singlet at higher temperatures (above −70°). Coalescence is between two uncoupled sites of apparently equal populations, and a first-order rate constant is readily calculated ($k_{-108} = 2.4$ sec^{-1}) using the Gutowsky–Holm equation.[8] Substitution of this rate constant into the Eyring equation (assuming a transmission coefficient of unity) leads to $\Delta G^{\ddagger}_{-108} = 9.2$ kcal/mol. This value is remarkably low when compared to typical inversion barriers of *N*-alkyl and *N*-aryl imines (similarly substituted at the imino carbon) which range from 17 to 27 kcal/mol.[3a]

Because a modified Pople–Santry–Segal CNDO/2 SCF-MO scheme has been successfully used[9] to calculate barriers to pyramidal inversion for first- and second-row elements, preliminary calculations were performed in the same manner to obtain planar nitrogen inversion barriers of simple imine systems. However, values obtained by this method proved to be appreciably lower than representative experimentally determined barriers.

Use of the standard CNDO/2 parameters,[10,11] with d orbitals deleted from the basis set,[12] afforded barriers to inversion for model imine systems which are in good agreement with the trend exhibited by experimentally measured values.[13] As shown in Figure 1 (solid line), the computed energy barriers correlate reasonably well with the Allred electronegativity[15] values of the N substituents, with the unexplained exceptions of hydrogen and chlorine. This correlation indicates that an *N*-

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[1] This work was supported by the National Science Foundation (GP-22542).

[2] R. D. Baechler and K. Mislow, *J. Amer. Chem. Soc.*, **93**, 773 (1971), and references cited therein.

[3] For a discussion of possible mechanisms of stereomutation at the carbon–nitrogen double bond, see, for example: (a) J. M. Lehn, *Fortschr. Chem. Forsch.*, **15**, 311 (1970); (b) H. Kessler, *Angew. Chem., Int. Ed. Engl.*, **9**, 219 (1970); (c) M. Raban and E. Carlson, *J. Amer. Chem. Soc.*, **93**, 685 (1971). The lateral shift mechanism is assumed to account for the present results, even though the less likely alternatives (torsion or torsion–inversion) cannot be rigorously excluded.

[4] L.-H. Chan and E. G. Rochow, *J. Organometal. Chem.*, **9**, 231 (1967).

[5] Prepared from the metal–halogen exchange reaction of *n*-butyllithium and *p*-bromobenzotrifluoride.

[6] *Anal.* Calcd for C$_{17}$H$_{18}$NF$_3$Ge: C, 55.80; H, 4.96; N, 3.83. Found: C, 55.97; H, 4.88; N, 3.80.

[7] A *ca.* 20 v/v% sample of **1** in dimethyl ether with *ca.* 5 v/v% dichloromethane as internal reference was used for the variable temperature study.

[8] H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

[9] A. Rauk, J. D. Andose, W. G. Frick, R. Tang, and K. Mislow, *J. Amer. Chem. Soc.*, **93**, 6507 (1971).

[10] As contained in the program CNINDO (P. A. Dobosh) received from the Quantum Chemistry Program Exchange (QCPE), Bloomington, Ind.

[11] The CNDO/2 scheme has previously been used to study the effects of heteroatoms attached to the imino carbon upon both the inversional and the torsional mechanisms of isomerization: see M. Raban, *Chem. Commun.*, 1415 (1970).

[12] With d orbitals included, minima were not obtained in the potential curve for inversion for reasonable values of the out-of-line angle when the substituent on nitrogen was SiH$_3$ and Cl.

[13] The barriers for a majority of these systems appear to be too high to be experimentally accessible. However, the calculated values are consistent with the available data for imines of the type ArAr′C=NX[3a] (all numerical values in kilocalories per mole): X = CH$_3$, 25–27; OCH$_3$, >39; Cl, >31. When X is C$_6$H$_5$, the measured barrier range is 17–20, compared to a calculated value of 23.2. Inversion barriers for imines with X = OH, NR$_2$, and F are not available, and for X = H, bimolecular proton exchange interferes with a barrier determination.[14]

[14] J. B. Lambert, W. L. Oliver, and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 5085 (1965).

[15] A. L. Allred, *J. Inorg. Nucl. Chem.*, **17**, 215 (1961).