the complexes are isomerically pure but also show that the *RR* and *SS* nitrogen configurations enhance formation of *cis* structures relative to the *RS* configuration. The chemical behavior of these *trans*-dichloro diastereomers provide a vivid as well as unique illustration of how greatly the configurations about asymmetric coordinated nitrogen can influence the stereochemistry of coordination compounds.[9]

[9] This work was supported in part by National Science Foundation Grant No. GP-6813.

[10] National Science Foundation Summer Teaching Fellow, 1966; NASA Trainee, 1966–1967.

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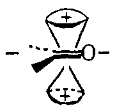
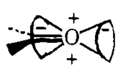
Structure by Nuclear Magnetic Resonance. XIV. On the Anisotropic Effects of the Carbonyl Group

Sir:

It is commonly accepted that a nucleus in conical regions extending above and below the plane of the carbonyl group is shielded; in the plane, it is deshielded (model I).[1] By using the recently published values of



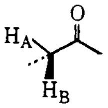
I



II

the three principal magnetic susceptibilities of the carbonyl bond,[2] model II can be constructed. The frequent use of model I in the elucidation of structural and conformational problems prompts us to report on the relative merits of I and II.

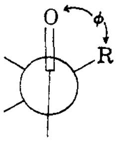
Model I predicts that H_A (III), in the plane of the carbonyl, will resonate at lower magnetic fields than H_B. Model II predicts the reverse, as seen from the



III

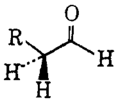
calculated screening constants,[3] σ, that are summarized in Table.

Table I. Calculated Screening Constants, σ (in parts per million), for



R	φ, deg	$\sigma_{H_o} \times 10^6$	$\sigma_{H_m} \times 10^6$	$\sigma_E \times 10^6$
H_A	0	−0.19	+0.18	−0.63
H	60	−0.28		
H	90	−0.43	−0.22	−0.48
H_B	120	−0.50	−0.46	−0.43
H	180	−0.59	−0.70	−0.34
CH_3	0	+0.10		
CH_3	90	−0.11		
CH_3	131	−0.28		
CH_3	180	−0.38		

Table II summarizes chemical shifts, accurate to ±0.017 ppm, of some aldehydes and ketones. It was established[5] that the ratios IV/V and VI/VII decrease as R changes from methyl to ethyl to *t*-butyl. The corresponding upfield shift of the resonance of the α-protons caused by this change can be accommodated if H_A resonates at higher magnetic fields than H_B. Qualitatively, therefore, the experimental results agree with model II, not I. Quantitative agreement, however, between experimental and calculated chemical shifts (Table III) is poor.



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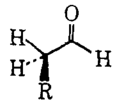

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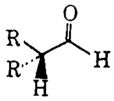
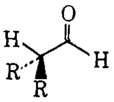


VI



VII

Table II. Chemical Shifts (in parts per million) of Aldehydes and Ketones in Dilute CCl_4

	δ(α-CH_3)	δ(α-CH_2)	δ(α-CH)
$MeCH_2CHO$		2.40	
$EtCH_2CHO$		2.33	
t-$BuCH_2CHO$		2.17	
$(Me)_2CHCHO$			2.40
$(Et)_2CHCHO$			1.93
(*t*-Bu)$_2$CHCHO			1.71
$MeCH_2COCH_3$	2.04	2.35	
t-$BuCH_2COCH_3$	1.98	2.19	
$(Me)_2CHCOCH_3$	2.04		2.50
$(Me)_2CHCOCH(Me)_2$			2.70
$(Me)_2CHCOC(Me)_3$			3.05

Table III. Experimental and Calculated Δδ (in parts per million) for α-Protons of RR′CHCHO

R	R′	Δδ, exptl[a]	Δδ, calcd[b]	Δδ, calcd[c]
Me[d]	H	0.00	0.00	0.00
Et	H	0.067	0.017	0.025
t-Bu	H	0.23	0.070	0.10
Me[d]	Me	0.00	0.00	0.00
Et	Et	0.47	0.047	0.073
t-Bu	*t*-Bu	0.69	0.21	0.31

[a] From relative rotamer populations.[4] [b] From magnetic anisotropy with the magnetic dipole on the oxygen.[2] [c] From the sum of magnetic anistropy[2] and electric field,[4] by placing the dipoles at the center of the carbonyl bond. [d] Standard.

A most dramatic demonstration that H_A resonates at higher magnetic fields[6] than H_B is shown in Figure 1.

Further evidence that II, or a similar model, might be more realistic to use than I is the observation that in

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(1) See L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, Chapter 7, p 124.

(2) J. W. ApSimon, W. G. Craig, P. V. Demarco, D. W. Mathieson, A. K. G. Nasser, L. Saunders, and W. B. Whalley, *Chem. Commun.*, 754 (1966).

(3) Negative σ denotes deshielding and positive σ shielding. σ_{H_o} is the magnetic anisotropy screening calculated from the anisotropies of ref 2, and by placing the magnetic dipole on the oxygen atom; σ_{H_m} is that by placing the dipole at the midpoint of the carbonyl. σ_E is the electric field shielding calculated by using published data,[2,4] with the dipole at the mipoint of the carbonyl bond.

(4) A. D. Buckingham, *Can. J. Chem.*, **38**, 300 (1960).

(5) G. J. Karabatsos and N. Hsi, *J. Am. Chem. Soc.*, **87**, 2864 (1965).

(6) Rotamer populations were calculated from the dependence of J_{HH} on temperature and solvent, as in ref 5. Details of the work on dichloroacetaldehyde and bromoacetaldehyde will appear in a full paper.

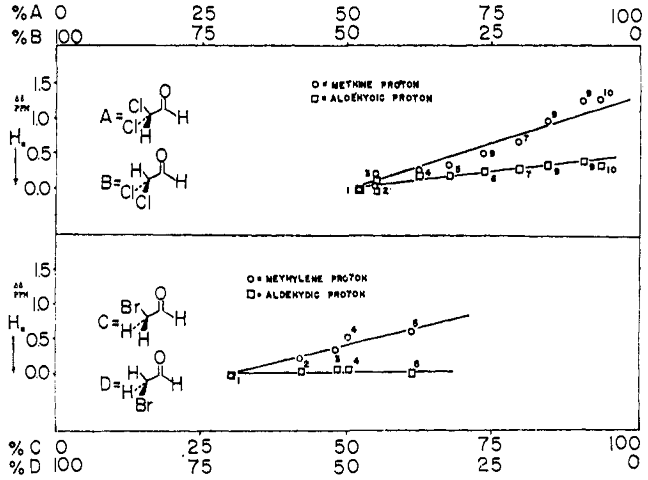
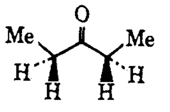
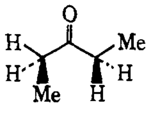


Figure 1. Dependence of the chemicals shifts of α protons and aldehydic protons of dichloroacetaldehyde and bromoacetaldehyde on rotamer populations. The chemical shifts of dichloroacetaldehyde were determined in the following solvents: (1) pentane; (2) *trans*-decalin; (3) carbon tetrachloride; (4) chloroform; (5) methylene chloride; (6) neat; (7) nitrobenzene; (8) acetone; (9) dimethylformamide; (10) dimethyl sulfoxide. The chemical shifts of bromoacetaldehyde were determined in the following solvents: (1) pentane; (2) methylene chloride; (3) nitrobenzene; (4) acetone; (5) formamide.

steroidal α-acetoxy[7] and α-halo ketones[8] and α-bromocyclohexanones[9,10] α-protons resonate at lower magnetic fields when axial than when equatorial. Additionally, δ(CH_2) of diethyl ketone shifts upfield[11] by 0.08 ppm and δ(CH_3) downfield by 0.05 ppm when the temperature changes from −61 to 104°. As rotamer VIII is more stable[12] than IX, the ratio IX/VIII increases


VIII


IX

with increase of temperature. Model II, therefore, correctly predicts the respective upfield and downfield shift of δ(CH_2) and δ(CH_3); model I predicts the reverse.

Acknowledgment. We thank the Petroleum Research Fund (2722-A1,4), administered by the American Chemical Society, and the National Science Foundation (GP-3343) for financial support.

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(7) K. L. Williamson and W. S. Johnson, *J. Am. Chem. Soc.*, **83**, 4623 (1961).

(8) A. Nickon, M. A. Castle, R. Harada, C. E. Berkoff, and R. O. Williams, *ibid.*, **85**, 2185 (1963).

(9) E. W. Garbish, Jr., *ibid.*, **86**, 1780 (1964).

(10) K. M. Wellman and F. G. Bordwell, *Tetrahedron Letters*, 1703 (1963).

(11) R. N. Jones and K. Noack, *Can. J. Chem.*, **39**, 2214 (1961).

(12) C. Romers and J. E. G. Creutzberg, *Rec. Trav. Chim.*, **75**, 331 (1956).

(13) National Science Foundation Predoctoral Fellow, 1966–1967.

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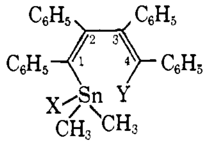
Hindered Diene Rotation by Virtue of Intramolecular Sn–Br Coordination

Sir:

Our original observation that the nmr spectra of the stannole dihalides[1] (I–III) display nonequivalent methyl



I, X = Y = Br
II, X = Y = Cl
III, X = Y = I
IV, X = Br; Y = H

resonances in carbon tetrachloride solution has prompted a detailed investigation of the conformation of I in both the solid state and in solution. The results reveal that molecular dissymmetry is introduced into diene I by an internal Sn–Br interaction which stabilizes a nonplanar cisoid conformation. This molecule is believed to be the first example of a diene whose rotational barrier about the central single bond is directly observable, as well as to represent the first X-ray crystallographic report of an organotin compound involving intramolecular Sn–Br interaction.[2]

The two equal-intensity methyl resonances exhibited at 36° by I at δ 0.48 and 0.98 in CCl_4 merge into a single broad peak when warmed to the coalescence temperature of ~87°. There is also a pronounced solvent effect on the methyl bands: use of solvents of marked Lewis basicity (ethers, alcohols, etc.) or addition of 6 *M* excess of pyridine to the CCl_4 solution leads to a sharp singlet at 0.73. However, in thionyl chloride, a nonbasic but strongly ionizing solvent, the coalescence temperature was closely similar to that in CCl_4, thus ruling out any methyl equilibration mechanism involving ionization of Br (on Sn).

The origin of the methyl nonequivalence may be attributed to one of the following possibilities:[3] (a) the presence of two rotamers (*cf. s-cis* and *s-trans*) in which each methyl singlet represents both methyls of a particular rotamer and these are interconverted by rotation about C(2)–C(3) at elevated temperatures, (b) hindered rotation about the C(1)–Sn bond, but free rotation about C(2)–C(3), and (c) a nonplanar diene conformation in which methyl nonequivalence is inherent in the molecular dissymmetry thus produced and disappears when rotation about C(2)–C(3) becomes fast.

Since mechanism a requires exactly equal populations of the two different rotamers, we regard it as extremely unlikely. Further, the solvent effects are not easily explainable with this mechanism. Likewise, mechanism b can be rejected on the basis of the solvent studies: bulky solvents which can coordinate with the tin would be expected to hinder rather than accelerate rotation, in contrast to the observed results. Mechanism c re-

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(1) H. H. Freedman, *J. Org. Chem.*, **27**, 2208 (1962).

(2) The subject of pentacoordinate Sn has recently been reviewed: M. Gielen and N. Sprecher, *Organometal. Chem. Rev.*, **1**, 455 (1966). Structures of intermolecular pentacoordinate tin compounds have been published; *cf.* H. C. Clark, R. J. O'Brien, and J. Trotter, *Proc. Chem. Soc.*, **85** (1963); I. R. Beattie, G. P. McQuillan, and R. Hulme, *Chem. Ind.* (London), 1429 (1962).

(3) A monomer–dimer equilibration mechanism has been ruled out by isopiestic molecular weight determinations which indicate that I is monomeric in CCl_4.