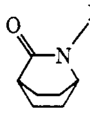
amide linkage there is less conformational ambiguity than for those with the trans amide linkage because the symmetry of the molecule limits the number of allowable conformations. Experimental values of the vicinal H-N-C-H coupling constants for the compounds isoquinuclidone (**4**),[3,9] 5-bromodihydrouracil (**5**),[22] dihydrothymine (**6**),[3] diketopiperazine (**7**),[3] and pyrrolidone (**8**)[9] are plotted in Figure 1 for estimated values of the dihedral angles. Nominal errors of ±5° were assumed for these angles which were based on symmetry or X-ray studies.[3,9] Except in the region of large values of the dihedral angles, which are conformationally inaccessible for the cis amide linkage, there is generally good agreement of calculated and experimental results. The dashed curve in Figure 1 is the one of Thong, *et al.*,[9] which was inferred from the experimental data points.



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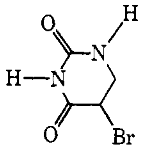

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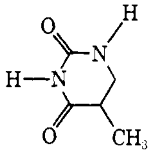

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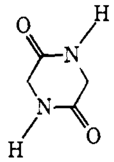

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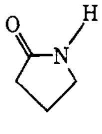

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Experimental data for comparison with the theoretical results for molecules having the trans-amide linkage are based on nmr and X-ray data for cyclic hexapeptides and a tetrapeptide. However, in some cases the interpretations of the nmr data may be confused by the possibility that the conformational details in solution are different from those in the solid.[4f] As a consequence, it is reasonable to expect that the experimental vicinal coupling constant data can reflect more motional averaging than would be expected for the simple compounds **4–8**, which have the cis-amide linkage. Coupling constant data in Figure 2 are from the cyclic hexapeptide alumichrome.[23] This is an aluminum analog of ferrichrome A for which X-ray structural data are available.[24] From a space-filling model of the cyclic tetrapeptide cyclotrisarcosyl-L-alanyl[25] (point 11 in Figure 2), the dihedral angle must be near 180°. Therefore, the disparities between the experimental and theoretical results in Figure 2 for angles greater than about 130° must partially reflect an overestimation of the theoretical formulation. The situation is probably analogous to that for vicinal H-C-C-H coupling for which experimental values are most invariably less than 12 Hz,[14] whereas the theoretical values[26,27] for the trans orientation are closer to the experimental value of about 18 Hz, which is estimated for ethane.[28]

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Michael Barfield,* Harry L. Gearhart
Department of Chemistry, University of Arizona
Tucson, Arizona 85721

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Formation of Methyl Fluoride by Fluorine Atom Cleavage of Tin–Carbon Bonds in Trimethyltin Hydride and Tetramethyltin

Sir:

Fluorine atoms react directly with $(CH_3)_3SnH$ and $(CH_3)_4Sn$ in our experiments to cleave the Sn–C bond with the formation of methyl fluoride, as illustrated in (1). The ^{18}F atoms were formed in an energetic state

$$^{18}F + (CH_3)_3SnH \longrightarrow CH_3{}^{18}F + (CH_3)_2\dot{S}nH \qquad (1)$$

by the $^{19}F(n,2n)^{18}F$ fast neutron nuclear reaction in gaseous SF_6 and are thermalized by multiple collisions with the SF_6 which is present in excess.[1–7] When $(CH_3)_3SnH$ or $(CH_3)_4Sn$ is added in low mole fraction, the product $CH_3{}^{18}F$ can be isolated and measured by radio gas chromatography with yields of about 5.6 and 8.3%, respectively, of the total ^{18}F. By analogy with other systems, most of the remaining ^{18}F atoms can be assumed to react by H atom abstraction to form $H^{18}F$.[3,4] Molecules of $H^{18}F$ so formed would have reacted with the glass sample container walls prior to chromatography and were not measured in these experiments. No attempt has yet been made to search for nonvolatile products from displacement on tin [*e.g.*, $(CH_3)_2SnH^{18}F$ or $(CH_3)_3Sn^{18}F$]. Many macroscopic problems for such systems—such as the corrosive nature of HF and disposal of the heat generated by the exothermicity of its formation—are avoided by the use of tracer levels of atomic fluorine (approximately 10^7 atoms of ^{18}F per experiment). All of the samples have been irradiated at the approximate temperature (10°) of the target area in the fast neutron generator used for formation of ^{18}F atoms.

When ^{18}F atoms are initially formed in an energetic state, a finite possibility exists that any particular reaction might have been initiated by the attack of a still-energetic ^{18}F atom. The probability of such *hot* reactions should be approximately proportional to the mole fraction of substrate $(CH_3)_3SnH$ or $(CH_3)_4Sn$, mixed with the SF_6. In these experiments, however, the

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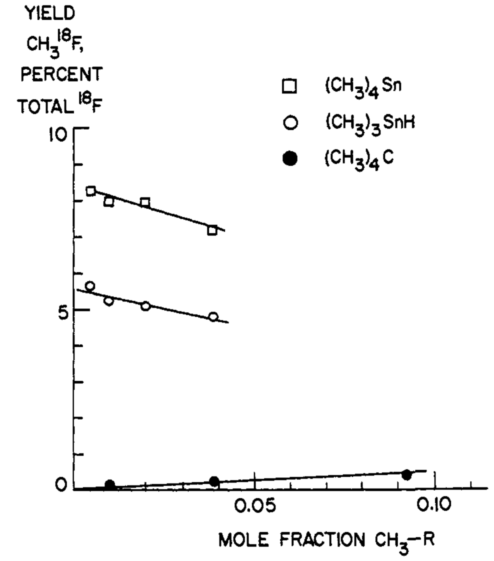

Figure 1. Yields of $CH_3{}^{18}F$ *vs.* mole fraction of substrate in SF_6: □, $(CH_3)_4Sn$; ○, $(CH_3)_3SnH$; ●, $(CH_3)_4C$.

$CH_3{}^{18}F$ yield actually increases with decreasing substrate concentration, as shown in Figure 1. The $CH_3{}^{18}F$ yield from ^{18}F reaction with neopentane, on the other hand, displays the typical behavior of a "hot" product extrapolating to zero yield at high dilution in SF_6. The failure of the $CH_3{}^{18}F$ yield to diminish with decreasing alkyl tin concentration indicates that an overwhelmingly large fraction of the substitutions in (1) is initiated by *essentially thermal* ^{18}F atoms.[8] Since abstraction of H by a fluorine atom occurs on nearly every collision with alkyl groups,[3,4,9] the efficiency of displacement of $SnH(CH_3)_2$ or $Sn(CH_3)_3$ on carbon must be quite high and roughly proportional to the number of Sn–C bonds. The activation energy for this substitution process must, therefore, be ≤ 1 kcal/mol. Indeed, the noticeable upward trend in $CH_3{}^{18}F$ yield with diminishing substrate concentration suggests that the activation energy for this substitution is slightly less than that for H abstraction from the molecules (but for both reactions ≤ 1 kcal/mol).

The cleavage of Sn–Sn bonds by F atoms has been suggested previously in explanation of the formation of $(CH_3)_3SnF$ in uv-irradiated $(CH_3)_3Sn$–$Sn(CH_3)_3$ mixtures with C_2F_4.[10–12] Such a mechanism is qualitatively consistent with our present results but does not seem quantitatively capable of explaining the high yields of $(CH_3)_3SnF$ actually found, for the great majority of F atoms formed in such a mixture would be expected to react by other pathways: abstraction of H atoms with the formation of HF,[3,4] or addition to C_2F_4. No comparable experiments involving cleavage of Sn–C bonds by F appear to have been performed.[12]

The free-radical chain attack of bromine atoms on R_4Sn has been presumed to go first with the displacement of R to form R_3SnBr, followed by the attack of the displaced R on Br_2 to form RBr.[13] However, the identifiable products would be the same if the first step were displacement of Sn on C with the formation of RBr, followed by the attack of R_3Sn on Br_2 to form R_3SnBr. The two sequences can only be distinguished by experiments in which the initial radical source and the radical terminator (both Br_2) are not identical. The generality of these displacement reactions at Sn–C bonds is now being tested with other substrates.

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(8) The term "thermal" implies a Maxwell–Boltzmann distribution of fluorine atoms at the 10° temperature of the system. For species such as atomic fluorine which react on nearly every collision with some substrates, the maintenance of a true *thermal* distribution is often quite difficult. For us "essentially thermal" means roughly that >95% of the ^{18}F atoms have <1 kcal/mol of kinetic energy at reaction.

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John A. Cramer, R. Subramonia Iyer, F. S. Rowland*
Department of Chemistry,[14] University of California
Irvine, California 92664
Received October 27, 1972

*Book Reviews**

Chemical Substructure Index (CSI) 1970 (2 volumes). Institute for Scientific Information, Philadelphia, Pa. 1971. xix + 2722 pp. $1000.00 (includes 11 monthly indexes as well).

This brave venture represents a major commitment to provide a literature-searching tool for chemists that is properly described as unique. It is an index to new compounds reported in *Current Abstracts of Chemistry* and *Index Chemicus* (CAC and IC) during the year. The special feature that justifies the existence of such a work is that it is not an index of names, but of line-notation structures, a characteristic that greatly increases the power of the permuting method for bringing common structural features together.

Line notations can be quite easy to read, and no one should allow himself to be put off by an imagined great barrier. The Wiswesser notation (WLN) used in this index can be more quickly learned than can systematic nomenclature, and, indeed, the simple elements needed to make use of the CSI can be picked up in less than an hour (a table of the WLN code symbols for the principal functional groups is included). Thereafter, one can confidently locate all new compounds having a given functional group, regardless of what else may be present, by looking under only a single heading. Under "KO," for example, all compounds containing the amine oxide function can be found, even though the KO portion of the line notation may ordinarily be buried in the middle. If one further restricts his interest to amine oxides containing a carbonyl group in addition, it is simple to use the "Quikscan" column, in which, for each compound, the other functional groups are listed (in WLN) separate from the detail of the code for the carbon skeleton. Having located these by checking off each entry in which the Quikscan includes a V (carbonyl), one can also restrict the search even further, such as, for example, to carbocyclic compounds. If one has become "fluent" in WLN, it may be worth-

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