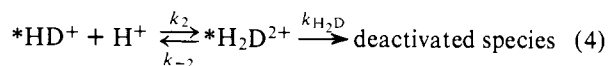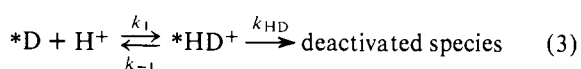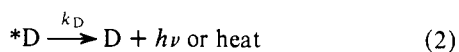**Figure 1.** Ru(bpy)$_2$(CN)$_2$ spectra: Top, relative luminescence quantum yield in deoxygenated aqueous acid at ~21 °C. Each curve is normalized to unity, and yields at different acid concentrations cannot be compared. Bottom, absorption spectra (—) for acid concentrations of 0 M (1), 0.3 M (2), 0.6 M (3), 1.0 M (4), 1.5 M (5), and 2.5 M (6). Corrected excitation spectra at 0 M (O), 1 M (□), and 2.5 M (●). Absorbance measured in a 10-cm cell with 7.7 × 10^{-6} total donor concentration.

we measured the relative quantum yield of the *D emission vs. excitation energy $\bar{\nu}$:

$$\theta(\bar{\nu}) = \frac{O(\bar{\nu})}{GI(\bar{\nu})[1 - \exp(-2.303A(\bar{\nu}))]} \quad (1)$$

where $O(\bar{\nu})$ is the observed luminescence intensity of *D, $I(\bar{\nu})$ is the corrected excitation intensity determined with a rhodamine B quantum counter (5 g/l. in methanol),[14] $A(\bar{\nu})$ is the *total* solution absorbance in the 1-cm spectrofluorimeter cell (<0.1), and thus $\theta(\bar{\nu})$ is the efficiency of *D emission on excitations of the mixture. G is a scale factor chosen to give each curve an average value of unity.[15]

Figure 1 shows that for $0 \leq [\text{H}^+] \leq 2.5$ M, $\theta(\bar{\nu})$ is independent of excitation wavelength within our experimental error. The slight decrease in $\theta(\bar{\nu})$ of acidic samples with decreasing $\bar{\nu}$ is in the same direction as the excitation scan, and we attribute it to photodecomposition. We estimate the following solution compositions: 0 M H$^+$-100% D; 0.6 M H$^+$-50% D, 40% HD$^+$, 10% H$_2$D^{2+}; 2.5 M H$^+$-8% D, 27% HD$^+$, 65% H$_2$D^{2+}. Thus, regardless of whether D, HD$^+$, or H$_2$D^{2+} is excited in a given solution, *D is produced with constant efficiency. The following model explains our results:

$$\text{*D} \xrightarrow{k_\text{D}} \text{D} + h\nu \text{ or heat} \quad (2)$$

$$\text{*D} + \text{H}^+ \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \text{*HD}^+ \xrightarrow{k_\text{HD}} \text{deactivated species} \quad (3)$$

$$\text{*HD}^+ + \text{H}^+ \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \text{*H}_2\text{D}^{2+} \xrightarrow{k_{\text{H}_2\text{D}}} \text{deactivated species} \quad (4)$$

where k_D, k_HD, and $k_{\text{H}_2\text{D}}$ are the sum of the first-order or [H$^+$] independent pseudo-first-order processes deactivating *D, *HD$^+$, and *H$_2$D^{2+}, respectively. The $\theta(\bar{\nu})$ data show that both excited state deprotonation reactions proceed with 100% efficiency; consequently, $k_{-2} \gg k_{\text{H}_2\text{D}}$ and $k_{-1} \gg k_\text{HD}$.

Further, since the absolute luminescence quantum yields and τ's of *D in the mixtures decrease with increasing [H$^+$],[16] the back reaction(s) must be important. Since direct deacti-

vation of a CT excited state by H$^+$ has never been observed, we discount the reaction *D + H$^+$ → deactivated products. The most reasonable interpretation is that very small steady-state concentrations of *HD$^+$ and possibly *H$_2$D^{2+} are generated with k_HD and possibly $k_{\text{H}_2\text{D}} \gg k_\text{D}$. In summary, our data seem consistent with an excited state equilibrium among *D, *HD$^+$, and *H$_2$D^{2+} with the concentrations of the latter two being too low to detect directly by emission, but large enough that k_HD and $k_{\text{H}_2\text{D}}$ can reduce the decay time and emission intensity of *D. The long lifetime of *D (100–260 ns) in these experiments should favor such an equilibrium situation. Further work is in progress.

Estimates of the first and second excited-state equilibrium constants by a Förster cycle also support our inability to see emission from *HD$^+$ or *H$_2$D^{2+}. We estimate $K_1 = 0.75 \pm 0.1$ M and $K_2 = 2 \pm 1$ M from ground state spectra and K_1* $= 5 \times 10^5$ M and K_2* $= 2 \times 10^8$ M using the principal CT absorption maximum of each of the three species to locate the relative zero-point energies of their excited states; the zero point energy of D is 1.85 μm^{-1},[5] and the absorption maxima for D, HD$^+$, and H$_2$D^{2+} are 2.32, 2.60, and 2.70 μm^{-1}, respectively.

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(15) Because HClO$_4$ solutions of D are somewhat thermally and photochemically unstable, especially at the higher [H$^+$], absorption and excitation spectra were run concurrently on the same freshly prepared acidic samples. We do not yet know the nature of these reactions.
(16) A true excited state equilibrium with k_D independent of [H$^+$] requires that $\theta/\theta_0 = \tau/\tau_0$. At high [H$^+$] (>1.5 M), however, our preliminary data suggest that θ/θ_0 decreases somewhat more rapidly than τ/τ_0 (e.g., at [H$^+$] = 1.5 M, $\tau/\tau_0 = 0.62$ while $\theta/\theta_0 = 0.55$). It is currently unclear whether the θ results are due to an artifact in these measurements. Alternatively, an excited state equilibrium may not be established or k_D may be dependent on solution composition.

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Pseudorotation in Diphenyltrifluoroarsorane

Sir:

In two classical papers published in 1963–1964 Muetterties et al.[1,2] showed that fluorophosphoranes of the type R$_2$PF$_3$ were rigid at room temperature; i.e., they do not undergo Berry pseudorotation to any appreciable extent. Their ^{19}F NMR spectra consisted of a doublet of doublets and a doublet of triplets as a result of this rigidity. Much of the work and

thinking on pseudorotation in pentacovalent trigonalbipyramidal molecules has been based on these early papers. Later it was shown[3,4] that ligand exchange occurred when the temperature was raised above room temperature and that the barrier to pseudorotation in compounds such as $(CH_3)_2PF_3$ and $(C_6H_5)_2PF_3$ was in the range 15–20 kcal/mol. Since the appearance of the original two papers from Muetterties' laboratory a large number of papers have appeared on pseudorotation in compounds of the type R_2PF_3 and R_3PF_2.[3-5]

In contrast to the large amount of research on pseudorotation in organophosphorus compounds, very little has been done with organoarsenic compounds. Muetterties[2] reported that the ^{19}F NMR spectrum of $(C_6H_5)_2AsF_3$ in toluene solution consists of a doublet and a triplet of relative intensity 2:1, and that the spectrum was invariant over large changes in temperature and concentration. Unfortunately the preparation of the R_2AsF_3 compounds was not described nor were the compounds characterized other than by their NMR spectra. As far as we are aware no work other than that reported by Muetterties has been performed on the NMR spectra of compounds of the type R_2AsF_3.

A number of attempts to prepare $(C_6H_5)_2AsF_3$ have been made in this laboratory. The two successful syntheses have involved the fluorination of either $(C_6H_5)_2AsH$ or $(C_6H_5)_2AsCl$ with SF_4 by means of standard vacuum line techniques. The product of either synthesis was a white crystalline solid, mp 94–96 °C, in a preheated bath after several recrystallizations from carbon tetrachloride. The carbon, hydrogen, and arsenic analyses agreed closely with the theoretical values. In addition this compound displayed a strong As–F stretching band at 470 cm^{-1} in the IR.

Diphenyltrifluoroarsorane is extremely sensitive to traces of moisture, and all manipulations must be carried out under rigidly anhydrous conditions using either a drybox or Schlenk tube conditions. The solvent (CCl_4) was dried by refluxing over activated molecular sieves and storing the distilled solvent over activated sieves. Exposure to air for even a short time resulted in loss of fluorine as shown by both the NMR spectrum and elemental analysis.

The ^{19}F spectrum of the pure compound in methylene chloride in Teflon tubes,[7] after several recrystallizations under anhydrous conditions, consisted of a slightly broadened singlet at 69.1 ppm upfield from $CFCl_3$. This spectrum was essentially unchanged (except for small chemical shifts) in a wide variety of solvents, nor was it changed by the addition of NaF to the solution. When cooled to −90 °C in methylene chloride the singlet was at least as sharp as at room temperature; no splitting was ever observed. These results suggest that, unlike the analogous fluorophosphorane, the arsenic compound is undergoing fast ligand exchange, both at room temperature and at −90 °C. This may result from a Berry pseudorotation with the larger arsenic atom providing a lower energy barrier, or it may involve an intermolecular exchange process. Moreland and co-workers[6] have demonstrated that exchange in tribenzylarsenic difluoride involves an intermolecular exchange.

While we have taken precautions to exclude moisture and to avoid impurities in our samples there is no guarantee that our results, which differ from those reported earlier by Muetterties, are not caused by catalysis effected by impurities. We have made diphenyltrifluoroarsorane a number of times by two different methods and in none of our products have we ever seen the NMR coupling pattern reported by Muetterties and co-workers. It is obvious that much more work is required on ligand exchange in fluoroarsoranes.

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Oxidation of Ethers via Hydride Abstraction: a New Procedure for Selective Oxidation of Primary, Secondary Diols at the Secondary Position[1]

Sir:

Many new methods have been recently added to the long list of procedures for the oxidation of alcohols to carbonyl compounds. New developments in this area should be designed to effect selective oxidation in polyhydroxylated molecules. We wish to report such a method, namely, the totally selective oxidation of primary, secondary diols at the secondary center by a hydride abstraction process.

Several techniques have been reported in the literature for selective oxidation of a secondary alcohol. Johnson and co-workers[2] reported that treatment of various tricyclic primary, secondary diols with N-bromoacetamide afforded fair yields of the keto alcohols. More recently, Wicha and co-workers[3] have observed that various steroidal diols undergo oxidation only at the most accessible secondary center in preference to primary ones in the presence of chlorine and pyridine. Many other methods have also been reported,[4] including selective protection of the primary hydroxyl function, oxidation, and removal of the protecting group. This three-step method is hampered quite often by the inability to cleanly protect the primary hydroxyl group in the presence of a secondary one, a result which often requires chromatographic separation of the desired material from its by-products.

Our procedure utilizes the oxidation technique we developed recently which involves the treatment of trimethylsilyl or *tert*-butyl ethers of alcohols with triphenylcarbenium (trityl) salts.[5] Doyle has made similar observations in the disproportionation of trityl ethers of alcohols by a cationic chain reaction process.[6] We reasoned that, since these oxidations proceed via initial hydride abstraction followed by loss of the group on oxygen, oxidation at a secondary center should be much faster than at a primary center and our initial studies seemed to corroborate this reasoning.[5] Thus we decided to apply this method to primary, secondary diols.

1,6-Heptanediol could be converted into the bistrityl ether **2a** by treatment with trityl chloride in pyridine in quantitative yield. In a like manner 4-hydroxymethylcyclohexanol (**4**) and 3-(2-hydroxyethyl)cyclopentanol (**7**) could be transformed into the bistrityl derivatives **5a** and **8a**, respectively, in quantitative yield. When the bistrityl ether of 1,6-heptanediol **2a** was treated with trityl tetrafluoroborate in methylene chloride at room temperature for 15 min, the desired product **3**, 7-hydroxy-2-heptanone, was isolated in the pure state in 91% yield.