Table I. Product Yields Resulting from Direct and Sensitized Excitation of Co(EDTA)$^-$ and Co(HEDTA)X$^-$ [a]

	Direct photolysis				Sensitized photolysis[c]	
	At 254 nm		At 450 nm			
Complex	ϕ_X[b]	$\phi_{Co^{2+}}$	$10^3\phi_X$[b]	$10^3\phi_{Co^{2+}}$	ϕ_X^{lim} [b]	$\phi_{Co^{2+}}^{lim}$
Co(EDTA)$^-$	*d*	0.05 ± 0.005		<0.1	*d*	0.10 ± 0.01
Co(HEDTA)Cl$^-$	0.04 ± 0.01	0.18 ± 0.02	10 ± 1	25 ± 3	0.40 ± 0.06	0.24 ± 0.03
Co(HEDTA)Br$^-$	0.06 ± 0.01	0.12 ± 0.01	30 ± 4	9 ± 1	0.10 ± 0.02	0.8 ± 0.1
Co(HEDTA)NO$_2^-$	~0.01[e]	0.17 ± 0.02	~4 ~10[e]	~4	*f*	0.71 ± 0.09

[a] All studies in water at 25°, pH = 3. [b] Yield for X$^-$ aquation except as indicated. Based on comparison of absorption spectra. [c] The Ru(bipy)$_3{}^{2+}$ sensitizer was irradiated at 450 nm. [d] No detectable spectral change. [e] Approximate linkage isomerization yield. [f] Not known.

mented. This is a particularly good sensitizer for anionic acceptors and this sensitizer has a sufficiently intense, and characteristic, absorption spectrum that chemical or photochemical decomposition of the sensitizer is easily ruled out. Simple Stern–Volmer dependence[2,23] on [Co(HEDTA)X$^-$] of the quenching of Ru(bipy)$_3{}^{2+}$ phosphorescence and of product yields has been observed in each case. The quenching rate constants (calculated assuming a lifetime of 2×10^{-6} sec for the Ru(bipy)$_3{}^{2+}$ triplet)[22] vary, depending on X, in the range 10^8–10^9 M^{-1} sec^{-1}.

We find that a combination, depending again on X, of labilization and oxidation–reduction reactions of Co(HEDTA)X$^-$ accompany direct *and* sensitized excitation. In each case the oxidation–reduction photochemistry involves the production of Co^{2+} and CO$_2$ as the predominant products. In the case of Co(HEDTA)NO$_2^-$ the spectral changes which accompany direct ligand field excitation (at 400 and 540 nm) or CTTM excitation (at 254 nm; correction made for Co^{2+} formation) are most compatible with a combination of NO$_2^-$ aquation and linkage isomerization. Although Co(HEDTA)OH$_2$ is easily prepared and characterized, we have not yet been able to separate and characterize Co(HEDTA)ONO$^-$; our present identification of this species as a reaction product is by analogy with Co(NH$_3$)$_5$ONO^{2+} and will be described in detail elsewhere. It is of considerable significance that, although NO$_2^-$ is appreciably labilized following ligand field excitation, this labilization is not accompanied by the formation of Co^{2+}.

Examination of our observations, summarized in Table I, demonstrates clearly and for the first time that ligand labilization (or aquation) and oxidation–reduction are *not* coupled processes in the photochemistry of cobalt(III). This is also the first demonstration of sensitized ligand labilization reactions in cobalt(III) complexes with relatively low crystal field splitting energy.[24]

It is to be observed that the total limiting yields ($\phi_X^{lim} + \phi_{Co^{2+}}^{lim}$) from our sensitization studies generally are near unity.[25] There seems no reason to question that the mechanism for Co(HEDTA)X$^-$ quenching of the Ru(bipy)$_3{}^{2+}$ phosphorescence involves triplet-to-triplet energy transfer,[2,22] and thus that the triplet states of cobalt(III), whether CTTM *or* ligand field in character, are chemically very reactive. More specifically the implicated ligand field triplet states must have intrinsic yields for product formation greater than or equal to 0.7, 0.5, and 0.3, respectively, for X = Cl, Br, and NO$_2$.

We infer that the simplest (and probably most general) model for the photochemistry of cobalt(III) complexes would have aquation (and other ligand labilization) products produced from some ligand field excited states of triplet spin multiplicity and oxidation–reduction products produced from CTTM excited states of triplet spin multiplicity. Since appreciable yields of both kinds of products result from the sensitization studies, CTTM triplet-to-ligand field triplet internal conversion processes cannot be very efficient compared to reaction processes (the lowest energy ligand field triplet in these complexes must have an energy less than 10^4 cm^{-1}).

On the basis of the present study it appears that the most likely reason for the photoinsensitivity of the ligand field absorption bands of most cobalt(III) complexes must arise from the relatively rapid rate of ligand field excited singlet state-to-ground singlet state nonradiative deexcitation compared to ligand field excited singlet state-to-ligand field excited triplet state intersystem crossing. This may be contrasted to the Rh^{III}(NH$_3$)$_5$X complexes in which the intersystem crossing rate between ligand field states appears to be relatively efficient.[11,26] This contrast in intersystem crossing efficiencies between cobalt(III) and rhodium(III) complexes is a likely manifestation of the larger spin–orbit coupling parameters of the heavier metal.[27] Many of the qualitative features of the excited states of Co(HEDTA)X$^-$ complexes, as discussed above, are very similar to the analogous models inferred from the photochemistry of Rh^{III}(NH$_3$)$_5$X complexes.[26]

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(25) For the Co(HEDTA)X$^-$ complexes ($\phi_X^{lim} + \phi_{Co^{2+}}^{lim}$) averages 0.8. Note that the absorption spectra of Co(EDTA)$^-$ and Co(HEDTA)OH$_2$ are so similar that we would have been unable to detect sensitized aquation of the former.

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Use of the *O*-Trimethylsilyl Group in Conformational Analysis and in Carbon-13 Nuclear Magnetic Resonance Spectroscopy

Sir:

Trimethylsilylation of alcohols is widely used analytically, and the rate of etherification is reported to be

Table I. Carbon-13 Nuclear Magnetic Resonance Shifts[a] of Some Bicyclo[2.2.1]heptyl *O*-Trimethylsilyl Ethers and Shift Differences ($\Delta\nu^b$) between ROH and ROTMS

	C_1	C_2	C_3	C_4	C_5	C_6	C_7
Norbornyl *exo*-2-OTMS	43.8	73.4	41.2	35.5	28.6	24.7	35.5
$\Delta\nu$	−0.2	−0.7	−0.9	0.0	0.0	0.0	−0.1
Norbornyl *endo*-2-OTMS	42.1	71.2	38.4	37.7	29.9	20.1	40.0
$\Delta\nu$	−0.4	−0.8	−0.8	0.0	−0.1	−0.1	+0.4
Norbornyl 7-OTMS	39.7	27.0	27.0	39.7	26.6	26.6	78.2
$\Delta\nu$	−0.3	+0.3	+0.3	−0.3	−0.1	−0.1	−0.6
2-Methylnorbornyl *endo*-2-OTMS	47.0	72.8	45.9	36.8	27.9	21.5	39.0
$\Delta\nu$	−0.5	−3.3	−0.8	−0.1	−0.1	−0.4	+0.7
Isobornyl *exo*-OTMS	48.2	78.4	38.7	45.5	27.1*	33.7*	45.7
$\Delta\nu$	−0.3	−0.6	−1.0	−0.5	−0.3	−0.3	−0.4
Bornyl *endo*-OTMS	49.0†	76.3	38.2	45.0	28.1*	25.9*	48.1†
$\Delta\nu$	+0.2	−0.3	−0.7	−0.2	−0.1	−0.2	+0.3

[a] Parts per million relative to TMS; positive values denote downfield, negative values upfield shifts. The measurements were actually made in *ca.* 50% CCl_4 with $^{13}CH_2Cl_2$ as internal lock and shifts were converted to the TMS scale. Signals denoted by an asterisk or a dagger possibly have to be interchanged. [b] $\Delta\nu = \nu_{ROH} - \nu_{ROTMS}$ (ppm).

sterically controlled.[1] These facts and the known bulk[2a] of the trimethylsilyl group itself make it desirable to provide reliable data on the conformational free energy of the OTMS group[2b] and the rate constants of formation and carbon-13 nuclear magnetic resonance (cmr) spectroscopic properties of these ethers. Hardy and Cumming recently calculated the conformational free-energy difference (*A* value) of the OTMS group by comparison of α-^{1}H nmr shifts of cyclohexyl derivatives as A = 890 cal/mol at room temperature, which they considered to be somewhat higher than that of the OH group.[3] Since the use of model compound shifts can lead to erroneous results,[4] we wish to report measurements by low-temperature pulse–Fourier transform cmr spectroscopy. This method provides several signals of each exchanging conformer for independent measurement and has been found to reproduce the relative populations very accurately (within 0.5% for CH_3 and CH_2 and 4% for CH in the case of *cis*-1,4-dimethylcyclohexane).[5] The spectra were measured at 170°K on 20% solutions in CF_2Cl_2, which also provides the ^{19}F lock signal, with a pulse interval of 0.64 sec, under proton noise decoupling. We find that electronic integration of the C_1, C_2, and C_3 signal pairs of cyclohexyl OTMS shows 10.9, 9.7, and 9.8% "axial" conformer, respectively. The *A* value thus obtained is 735 ± 15 cal/mol[6] and is in fact lower than that of the OH group at comparable temperature (A = 920 cal/mol at 190°K).[7] Explanations for this behavior are that the OTMS group can point away from the ring and that only the alcohol can undergo dimerization, which of course would increase its *A* value.[7]

Any strain difference between OTMS and OH is expected to appear also in cmr shifts of γ C atoms, which are known to be sensitive to steric interactions.[8] This effect should be particularly evident for the rigid norbornyl derivatives, where introduction of substituents at C_2 shifts the C_6, and to a lesser degree the C_7, resonance to higher field.[8b,c,9] Inspection of γ shifts in Table I shows clearly that the OTMS group exerts no stronger an interaction on γ-C atoms than the OH group does. It should be noted, however, that in 7-norbornyl-OTMS the C_2–C_3 and C_5–C_6 signals are separated by 0.4 ppm, whereas in 7-norborneol the OH group shifts equally the γ-C atoms in both the syn and the anti position by 3.1 ppm (compared to norbornane), leaving them indistinguishable.[9] Since an *endo*-OTMS group at C_2 causes an upfield shift at C_7, it must be concluded that the OTMS group exerts an anti γ effect (which should be inductive by nature) stronger than the steric syn γ effect. Other than barely affecting γ carbon shifts, the trimethylsilylation produces a downfield shift in the α position of 0.3–0.8 ppm for secondary C atoms (up to 3.3 ppm if the C is tertiary, in accordance with a rationalization as a hidden γ effect for the nontertiary α C atom[10]). β signals are shifted slightly downfield: 0.0–0.2 ppm if the β C atom is quaternary, 0.2–0.4 if it is tertiary, and 0.7–1.0 if it is secondary. The α and β shifts caused by trimethylsilyl substitution are thus helpful in the assignment of ^{13}C signals in alcohols.

In view of the rather bulky trimethylsilyl group the rates of ROTMS formation could be expected to provide a valuable tool for kinetic investigations of the steric environment of an OH group. That the rates of silylation are more sensitive than those of other[11] esterification or saponification reactions seemed to be supported by measurements of per cent conversion *vs.* time with some steroids.[1] Preliminary initial rate measurements with hexamethyldisilazane (HMDS) in pyridine established that this reaction, improperly called noncatalyzed[1]—the rate in cyclohexane is at least 100 times slower than in pyridine—is first order in both HMDS and ROH. Rates were followed by com-

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parison of ROTMS peaks with internal standard hydrocarbon peaks by glpc after work-up of samples with pentane and dilute acetic acid, thus avoiding uncontrolled reactions during glpc analysis. It was secured that there was no measurable reaction during or after work-up by analysis of test mixtures with a known composition of ROH, ROTMS, and hydrocarbon in the absence and in the presence of excess HMDS.

Measurements with 4-*tert*-butylcyclohexanols (Table II) show that an OH group reacts ten times faster in the equatorial than in the axial position, and the rate with *cis*-4-methylcyclohexanol properly reflects the equilibrium with predominantly (92%[5]) axial OH. The rate differences between *exo*- and *endo*-2-norborneol are surprisingly smaller than in the cyclohexyl case, but still high compared to the practically equal succinate saponification rates.[12] That the HMDS reaction is very sensitive to steric hindrance by substituents is shown by the 100-fold rate decrease found for *endo*-fenchol. While it is clear from the cyclohexyl OTMS *A* value and from the cmr shifts that steric interactions are not larger for the OTMS than for the OH group in the ground state, it is evident from the kinetic measurements that the transition states for introduction of a trimethylsilyl group are quite sensitive to the steric environment of the OH group.

Table II. Pseudo-First-Order Rate Constants[a] for the Reaction of ROH with HMDS[b]

ROH	OH position	$k_1 \times 10^5$, sec^{-1}
4-*tert*-Butylcyclohexanol, trans	Eq	13.8 ± 1.2
cis	Ax	1.4 ± 0.1
Cyclohexanol	90 % eq	17.0 ± 2.0
4-Methylcyclohexanol, cis	90 % ax	3.3 ± 0.3
2-Norborneol, exo		18.3 ± 2.0
endo		6.8 ± 0.7
Fenchol, endo		0.07 ± 0.007

[a] The second-order rate constants are: $k_2 = k_1/[\mathrm{HMDS}]$. [b] Reaction conditions: [ROH] = 0.053 *M*, [HMDS] = 0.46 *M* in pyridine at 25.0°.

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Unexpected Conformational Stability of Poly(2′-azido-2′-deoxyuridylic acid)

Sir:

Although the conformational stability of polyribonucleotides and polydeoxyribonucleotides differs markedly, no satisfactory theory has been developed for this phenomenon. Intramolecular hydrogen bonding through the 2′-hydroxyl cannot be the reason for the greater stability of polyribonucleotides, because poly(2′-*O*-methyluridylic acid) (poly $\mathrm{U_m}$)[1] and poly(2′-*O*-adenylic acid) (poly $\mathrm{A_m}$)[2] are thermally more stable than poly U or poly A. The most recent variation, *viz.*, poly(2′-chloro-2′-deoxyuridylic acid) (poly $\mathrm{U_{Cl}}$),[3] is unusual in that it has no stable secondary structure as a single strand, but forms a stable double-stranded complex with poly A. We now wish to report on poly(2′-azido-2′-deoxyuridylic acid) (poly $\mathrm{U_z}$) which, quite unexpectedly, possesses a highly ordered structure both in the single- and double-stranded forms.

Tritylation of 2′-azido-2′-deoxyuridine[4] (I) gave II[5] (glass; mp 89–91°; $\nu_{\max}$ 2120 cm^{-1} (N_3); pmr ($CDCl_3$) δ 9.60 (s, 1, N*H*), 7.83 (d, 1, *J* = 8 Hz, H-6), 7.33 (br s, 15, trityl H), 5.94 (d, 1, *J* = 3 Hz, H-1′), 5.37 (d, 1, *J* = 8 Hz, H-5), 4.50 (br m, 1, H-3′), 4.12 (br m, 2, H-2′ and H-4′), 3.55 (br s, 2, H-5′), 3.08 (d, 1, *J* = 6 Hz, 3′-OH)). Reaction of II with acetic anhydride in dry pyridine for 12 hr at 0° gave III (85%; glass; mp 87–89°; $\nu_{\max}$ 2120 (N_3) and 1740 cm^{-1} (OAc); pmr ($CDCl_3$) δ 9.07 (s, 1, N–H), 7.75 (d, 1, *J* = 8 Hz, H-6), 7.36 (br s, 15, trityl H), 6.04 (d, 1, H-1′), 5.45 (d, 1, *J* = 8 Hz, H-5), 5.25 (br m, 1, H-3′), 4.24 (br m, 2, H-2′ and H-4′), 3.56 (br s, 2, H-5′), 2.24 (s, 3, acetate–CH_3)). Hydrolysis of III in 80% HOAc gave IV (88%; prisms; mp 189–191°; $\nu_{\max}$ 2120 (N_3) and 1750 cm^{-1} (OAc); uv $\lambda_{\max}^{\mathrm{CH_3OH}}$ 260 nm). Phosphorylation of IV by a modification of the cyanoethyl phosphate procedure[6] gave 2′-azido-2′-deoxyuridine 5′-monophosphate (V; 55%; $\nu_{\max}$ 2120 cm^{-1} (N_3); $R_{f(\mathrm{UMP})}$ = 2.0 (system A, isobutyric acid–1 *M* NH_4OH–0.2 *M* EDTA, 100:60:0.8)). Bacterial alkaline phosphatase digestion of V gave I quantitatively. The phosphate V was converted, *via* the morpholidate,[7] to 2′-azido-2′-deoxyuridine 5′-diphosphate (VI; 60%; $\nu_{\max}$ 2120 cm^{-1} (N_3); uv $\lambda_{\max}^{\mathrm{H_2O}}$ 262 nm ($\epsilon_{\max}$ 10,000); $R_{f(\mathrm{UDP})}$ = 1.75 (system A)). Treatment of VI with alkaline phosphatase gave I quantitatively. The diphosphate VI was polymerized by polynucleotide phosphorylase[8] (*M. luteus*) with Mg^{2+} as cofactor. After deproteinization with Genetron 113, the polymer was isolated in 30% overall yield by gel filtration on a Sephadex G-100 column from which the polymer was excluded in the void volume. Use of Mn^{2+} as cofactor[9] raised the yield by 10–20%, but was not necessary for *de novo* synthesis. This contrasts sharply with the behavior of other nucleoside diphosphates modified in the 2′ position,[1,3,10] since such substrates usually require Mn^{2+} for polymerization.

Poly $\mathrm{U_z}$ prepared in this manner (as Dr. C. B. Klee of this Institute kindly determined) had $s_{20,\mathrm{w}}$ = 8.0 S (0.1 *M* NaCl, 0.01 *M* NaH_2PO_4, 0.001 *M* EDTA, pH 6.5) and gave only I upon hydrolysis with a mixture of

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