Table I. Chemical Analysis of the Prepared Compounds

Compound	% C		% H		% S		% metal	
	Exptl	Theor	Exptl	Theor	Exptl	Theor	Exptl	Theor
Si(IV)	...	49.96	...	3.59	...	38.10	8.51	8.36
Ge(IV)	44.48	44.12	3.07	3.15	32.90	33.66	18.85	19.05
Sn(IV)	33.38	30.81	2.39	2.22	24.88	23.52	43.02	43.51
Pb(IV)	...	32.60	...	2.35	...	24.87	40.00	40.18

Table II

Metal Compd	λ_0, mμ	β (^{1}Ba), mμ
Si(IV)	242.5	232
Ge(IV)	233.5	231
Sn(IV)	237.5	234
Pb(IV)	238.0	237

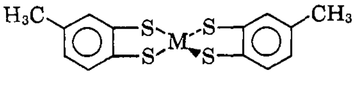
Table III. Infrared Absorptions of Toluene-3,4-dithiol and IV-A Complexes (cm^{-1})

Toluene-3,4-dithiol (in $CHCl_3$)		720–810	867	1050	1130	1285	1392	1470	1600	2570	2900–3100	3670
Si complex		792	856	(1012–1080)		1250						
Ge complex	680	801	860	1025	1099	1251						
Pb complex	680, 741	804	860	1030	1105	1250						

of approximately 10^{-5} *M*, and ultraviolet and optical rotatory dispersion spectra were obtained.

Although rotation was too slight to be measured in the visible portion of the spectrum, it was dramatic in the ultraviolet region. The point at which the sign of rotation changed was in excellent agreement with the $^1B_{ab}$ transition of the ultraviolet absorption spectrum. Molecular rotations up to a magnitude of 10^8 were observed in the ultraviolet region (the ORD attachment to our Cary spectrophotometer was checked *vs.* *d*-camphor). To our knowledge, no previously reported series of optically active compounds have molecular rotations of this magnitude.

The presence of optical activity, chemical analyses, infrared spectra, proton nuclear magnetic resonance spectra, and molecular weight determinations support the model depicted below.



Whereas the aromatic rings are probably too far apart to experience perturbation by the ring substituents which would lead to a coupled oscillator model, another model is then required. It is postulated that the electron cloud around the central atom is asymmetrically distorted and that in the solid state, there is a possibility one could observe four nonequivalent metal to sulfur bonds.

A full paper with experimental detail and discussion will follow shortly.[1] A brief summary of the pertinent data is given in Table I.

The germanium compound was the only one having sufficient solubility for the determination of molecular weight on our Mechrolab osmometer; it was observed at 373 *vs.* a theoretical value of 381. The range of concentrations we could obtain limited our accuracy.

Optical rotatory dispersion data was obtained by use of the Cary 14 recording spectrophotometer equipped with the optical rotatory dispersion attachment. Data are contained in the Table II.

Infrared absorption measurements were made by use of the Beckman IR-8. All compounds prepared except that of tin, plus the ligand, were measured. The data are shown compiled in Table III.

The germanium compound was the only compound possessing sufficient solubility to give proton nuclear magnetic resonance data. Hydrogen absorptions were split into four peaks at 7.25, 7.12, 6.84, and 6.71 ppm in a ratio of 1:3:1:1, respectively.

Ultraviolet absorption data were obtained by use of the Cary 14. All compounds were in acetonitrile; spectra were obtained for solvent, ligand, tetraethyllead, and the four IV-A compounds. Table II shows the correlation of sign of optical rotation inversion with the ultraviolet absorption data.

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(1) The syntheses and optical activity were announced at the combined Southeast–Southwest Regional Meeting of the American Chemical Society, Memphis, Tenn., Dec 2, 1965, paper no. 81.

The Crystal Structure of $CH_3CO^+SbF_6^-$

Sir:

The existence of oxocarbonium ions is of interest in Friedel–Crafts acylations,[1] and has been established[2–6] by infrared studies in the solid state and nmr methods in solution. An X-ray structure determination has not hitherto been reported for an oxocarbonium ion, although the structure of an acyl halide–metal halide complex was recently published.[7] Methyloxocarbonium ion (CH_3CO^+) has previously[2] been isolated as the crystalline hexafluoroantimonate salt, and is now shown to have linear geometry. The carbon–methyl bond distance is unusually short and is attributed on the basis of

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(1) For a review of this subject see G. Olah, "Friedel-Crafts and Related Reactions," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1963, pp 91–95, 665–680, and 790–812.

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molecular orbital studies to localization of net positive charge on the carbonyl carbon atom. No association with SbF_6^- ions other than ionic crystal packing is observed, in accord with the infrared spectrum.[2,4]

A sample of $CH_3CO^+SbF_6^-$ as a white solid was obtained from Olah and recrystallized as needles from SO_2 at −40°. The parameters of the monoclinic cell, $a = 5.758 \pm 0.006$, $b = 7.783 \pm 0.008$, $c = 7.879 \pm 0.008$ A, and $\beta = 101° 3'$, give a calculated density of 2.671 g cm^{-3} with two molecules per unit cell. Absence of $0k0$ reflections with k odd indicated the space group to be either $P2_1$ or $P2_1/m$; 968 independent reflections, of which 172 were too weak to be measured, were recorded, with Mo $K\alpha$ radiation by precession methods. Absorption corrections were not made since $\mu R < 0.5$.

The structure was apparent from the Patterson function and indicated a molecular mirror plane corresponding to $P2_1/m$. Refinement was carried out by full-matrix least-squares methods in $P2_1/m$, and after two cycles of anisotropic refinement on the Sb, F, C, and O atoms R_f was 0.074. Attempts at refinement in $P2_1$ failed because of matrix singularities in the vicinity of the centrosymmetric structure. However, normal values of the acylium anisotropic temperature factors perpendicular to the mirror plane suggest no significant deviations out of plane. The H atoms are believed resolved, though subject to errors in position of about 0.3 A. The crystal structure is shown in Figure 1, and final atomic positions, bond distances, and standard deviations are indicated in Table I.

Table I

Atom	Atomic Positions x	y	z
Sb	0.0970	0.2500	0.2323
F(1)	0.9778	0.2500	0.9947
F(2)	0.2231	0.2500	0.4671
F(3)	0.8847	0.0818	0.2663
F(4)	0.3129	0.0848	0.1924
C(1)	0.4481	0.2500	0.8278
C(2)	0.6022	0.2500	0.7137
O	0.7367	0.2500	0.6288
H(1)	0.59	0.2500	0.93
H(2)	0.35	0.15	0.79

	Bond distances, angstroms Uncorrected	Corrected[a]
Sb–F(1)	1.867 ± 0.014[b]	1.918 ± 0.014[b]
Sb–F(2)	1.853 ± 0.014	1.902 ± 0.015
Sb–F(3)	1.845 ± 0.010	1.888 ± 0.010
Sb–F(4)	1.857 ± 0.006	1.892 ± 0.007
C(2)–C(1)	1.378 ± 0.023	1.383 ± 0.024
C(2)–O	1.116 ± 0.021	1.150 ± 0.022
C(1)–H(1)	1.01 ± 0.31	
C(1)–H(2)	1.00 ± 0.17	

[a] Corrected for torsional oscillation assuming the second atom rides on the first. The correction is the same magnitude but opposite in sign assuming the first rides the second. Corrections assuming the ions move as rigid bodies are much smaller. [b] Standard deviations were obtained from the full variance–covariance matrix calculated during the final least-squares refinement.

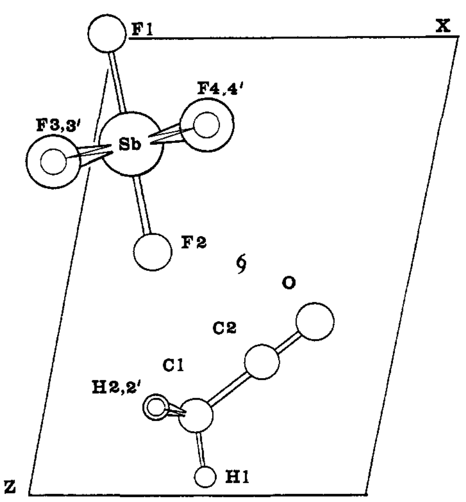

Figure 1. The structure of $CH_3CO^+SbF_6^-$ showing the ions on the mirror plane at $y = {}^1/_4$. The 2_1 axis generating the rest of the unit cell appears at $x = {}^1/_2$, $z = {}^1/_2$. Hydrogen atoms are drawn at chemically reasonable positions. The C(2)–F(2) distance of 2.63 A indicates a shortened C van der Waals radius of 1.3 A, in accord with localization of positive charge on C(2).

The C(1)–C(2) distance of 1.378 ± 0.023 A is considerably shorter than the corresponding bond distances of 1.458 and 1.460 in the isoelectronic species $CH_3C{\equiv}N$ and $CH_3C{\equiv}CH$, respectively. The C–O distance of 1.116 A is close to the $C{\equiv}O$ distance of 1.128 A in carbon monoxide and somewhat shorter than the $C{=}O$ distances of about 1.20 A in aldehydes and ketones. While the standard deviations are perhaps larger (because of the presence of the heavy Sb atom) than desirable for theoretical purposes, additional shortening of the C–C single bond beyond that required by sp hybridization[8] is indicated.

A molecular orbital calculation by the NEMO method[9] indicates a net Mulliken charge[10] of −0.11 on the methyl carbon, +1.18 on the carbonyl carbon, −0.35 on the oxygen, and +0.09 on each hydrogen.

The shortening of the C–C single bond may be attributed to the carbonyl carbon atom being present as a carbonium ion C^+, with a concomitant shortening of its bonding radius. The amount of shortening from a normal single bond sp carbon is about the same as that for an sp^2 carbon atom in triphenylmethyl carbonium ion,[11] although the two cases are not precisely analogous. Because the net positive charge does not appear on the oxygen atom and the hydrogens are not much more positive than in ethane (+0.07), the contribution of the valence structures $H_3{\equiv}C{-}C{\equiv}\ddot{O}^+$ and $H_3^+{=}C{=}C{=}\ddot{O}$: should not be substantial. Since the ion is linear the carbonyl π bond must have nearly cylindrical symmetry (*i.e.*, both of the π orbitals perpendicular to the principal axis are necessarily equivalent). The detailed population analysis indicates that the electron density in the π system is concentrated on the O 2p atomic orbitals (about ${}^3/_2$e each) rather than in C 2p orbitals (about ${}^1/_2$e each), and as a result the bonding is not as strong as in a "pure" triple bond.

Parameters for the MO calculation were obtained from SCF calculations[12] on CO and C_2H_6 using Slater-

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(11) A. H. Gomes de Mesquita, C. H. MacGillavry, and K. Eriks, *Acta Cryst.*, **18**, 437 (1965).

(12) M. D. Newton and W. E. Palke, private communications.

type basis sets. A detailed report on the crystallographic and molecular orbital studies is in preparation.

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Nucleophilic Substitution at the Alkoxyl Carbon of Imidates[1]

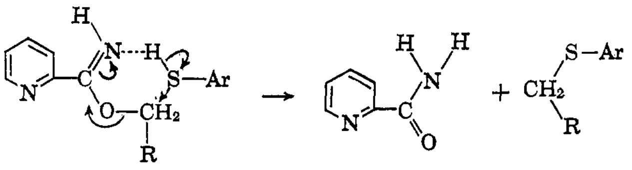
Sir:

It is well known that, generally speaking, substitution in derivatives of carboxylic acids, such as esters and imidates, tends to occur at the central sp^2 carbon rather than at the sp^3 carbon of the alkoxyl group. Exceptions to this trend are the thermal decomposition of imidate hydrochlorides (Pinner cleavage),[2] the alkyl–oxygen fission of esters of tertiary alcohols,[3] and the nucleophilic substitution reactions of esters in which a highly electron-withdrawing substituent (*i.e.*, N-phthalimido)[4] is present at the α-carbon of the alkoxyl group.

In search of a selective method for the replacement of a hydroxyl in polyfunctional alcohols by a suitable nucleophile, the polyfunctional alcohol was first converted to the monoimidate by reaction with 2-cyanopyridine under base-catalyzed conditions,[5] and the resulting imidate was then treated at *ca.* 150° with arylthiols to give the products of the desired nucleophilic substitution reaction at the sp^3 carbon of the alkoxyl group, namely, hydroxyalkyl aryl sulfides, and the novel "leaving group," namely, 2-pyridinecarboxamide.

Thus, the monoimidate of ethylene glycol, upon treatment with *o*- or *p*-thiocresol, *p*-*t*-butylthiophenol, and *p*-bromothiophenol, gave the corresponding 2-hydroxyethyl aryl sulfides in yields as high as 64% of theoretical. The products gave the correct microanalytical results and infrared spectra identical with those of authentic samples prepared by the reaction of the thiols with ethylene chlorohydrin.[6]

The reaction can be carried out in excess of the thiol, or by using diethylbenzene or dimethylformamide as solvent. The yields of the reaction improved when nonpolar solvents were employed, and this observation, as well as the failure of the desired nucleophilic substitution when the hydrochloride or picrate of the imidate was treated with sodium thiocyanate, potassium iodide, or sodium mercaptides, suggest that the reaction occurs in the complex of the imidate and the conjugated acid of the nucleophile by an intramolecular mechanism.



Ar = *o*- or *p*-$CH_3C_6H_4$, *p*-*t*-BuC_6H_4, *p*-BrC_6H_4; R = $HOCH_2$

In accord with the postulated mechanism is the observation that the reactions of benzylamine, piperidine, and morpholine with the imidate derived from 2-cyanopyridine and ethylene glycol produce the conventional attack at the sp^2 carbon. This course of the substitution reaction was proven by the isolation of the N-benzylamide and the N-piperidino- or N-morpholinoamidines (the latter in the form of the picrates), respectively, derived from 2-pyridinecarboxylic acid. Also, the recent report[7] of the formation of thiono esters by the base-catalyzed reaction of imidates with hydrogen sulfide indicates that strong bases, or anionic nucleophiles, react preferentially at the sp^2 carbon, while nucleophiles capable of hydrogen bonding with the imidate favor the intramolecular reaction path leading to the SN reaction at the sp^3 carbon of the alkoxyl group.

The novel substitution reaction is being extended to more complex polyfunctional alcohols and to nucleophiles other than thiols. Also, the optimum conditions for the reaction are being determined.

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(1) This investigation was supported in whole by Public Health Service Research Grant GM 09481-04, from the National Institutes of Health.

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Physical Theory of Chemiluminescence in Systems Evolving Molecular Oxygen[1]

Sir:

Chemiluminescence of organic molecules is a frequently observed phenomenon in liquid reaction systems and most often accompanies oxidation in the presence of hydrogen peroxide or molecular oxygen. An inorganic chemiluminescent reaction system which has been extensively investigated recently[2,3] involves the reaction in alkaline solution of H_2O_2 with either Cl_2 gas or OCl^- (hypochlorite ion). It is now generally agreed that the observed red (and infrared) chemiluminescence in this inorganic case arises from metastable excited states of molecular oxygen produced in the reaction. These observations and interpretations extend the much earlier ones made by Groh and Kirrmann.[4] New observations made in this laboratory now permit the projection of a general theory of chemiluminescence which unites these two classes of phenomena, *i.e.*, organic molecule chemiluminescence in oxidation reactions in solution and excitation of metastable states of molecular oxygen in peroxide systems.

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(1) Work supported in part by a contract between the Division of Biology and Medicine, U. S. Atomic Energy Commission, and the Florida State University, and in part by a contract between the Physics Branch, Office of Naval Research, and the Florida State University.

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