

temperatures ($\pm 0.5^\circ$) indicated in Table I for 0.5-hour periods. After cooling, a known volume of chloroform was added and the intensity of the carboxyl carbonyl peak (1736 cm^{-1} in V and 1750 cm^{-1} in VI) in the infrared was measured. The amount of unreacted starting material was determined using a calibration curve prepared from known concentrations of V and VI.

Acknowledgment.—We wish to thank Professor H. W. Walborsky and Professor H. O. House for helpful discussions and Professor House for informing us of his results prior to publication. We also thank Mr. Gerald Caple for determining the n.m.r. spectra.

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Stable Carbonium Ions. IV.^{1a} Secondary and Tertiary Alkyl and Aralkyl Oxocarbenium Hexafluoroantimonates. Formation and Identification of the Trimethylcarbonium Ion by Decarbonylation of the *tert*-Butyl Oxocarbenium Ion

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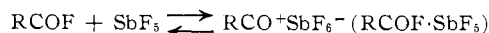
1:1-Addition compounds of di- and trialkyl(aryl)-acetyl fluorides with antimony pentafluoride were prepared and investigated. On the basis of infrared spectra it was found that in the crystalline state the ionic oxocarbenium structure ($\text{RCO}^+\text{SbF}_6^-$) prevails, with minor amounts of donor:acceptor complexes also present. Diphenylacetyl fluoride:antimony pentafluoride is practically exclusively the oxygen coordinated coordination complex. Triphenylacetyl fluoride gives only a very unstable coordination complex decarbonylating to the stable, ionic triphenylcarbonium salt. In solution there is evidence for an increased amount of coordination complex being present in addition to the ionic oxocarbenium salts, according to high resolution nuclear magnetic proton and fluorine resonance spectra. Decarbonylation of *tert*-butyl oxocarbenium hexafluoroantimonate could be followed spectroscopically and the trimethylcarbonium ion was identified. The isolated oxocarbenium salts are reactive acylating agents. Alkylation takes place as well in the case of tertiary and to some degree in secondary alkyl oxocarbenium salts due to prior decarbonylation.

Introduction

As a continuation of previous work^{1a,2} on *n*-alkyl and aryl oxocarbenium salts it was considered that it would be of interest to extend these investigations to secondary and tertiary alkyl (aralkyl) oxocarbenium systems. No previous data were available on any of these ions as stable entities.

Results and Discussion

Preparation of the new oxocarbenium complexes was achieved according to the previously reported "fluoride method."²



Some of the required acyl fluorides were available from previous work^{3,4} and the preparation of others will be reported in a future publication.⁵

The crystalline complexes were found by analytical data to be 1:1 addition compounds of high purity (see Experimental part). Their melting points (in sealed capillary tubes) are listed in Table I and are compared with those of the corresponding primary alkyl (aryl)-acetyl fluoride:antimony pentafluoride complexes.

TABLE I

MELTING POINTS OF SECONDARY AND TERTIARY ALKYL (ARYL)-ACETYL FLUORIDE:ANTIMONY PENTAFLUORIDE COMPLEXES

	M.p., °C.
$\text{CH}_3\text{CH}_2\text{COF}\cdot\text{SbF}_5$	110-112
$(\text{CH}_3)_2\text{CHCOF}\cdot\text{SbF}_5$	95
$(\text{CH}_3)_3\text{CCOF}\cdot\text{SbF}_5$	20 dec.
$\text{CH}_3\text{CH}_2\text{CH}_2\text{COF}\cdot\text{SbF}_5$	58
$(\text{CH}_3\text{CH}_2)_2\text{CHCOF}\cdot\text{SbF}_5$	15 dec.
$(\text{CH}_3\text{CH}_2)_3\text{CCOF}\cdot\text{SbF}_5$	-5 to 0 dec.
$\text{C}_6\text{H}_5\text{CH}_2\text{COF}\cdot\text{SbF}_5$	132-135
$(\text{C}_6\text{H}_5)_2\text{CHCOF}\cdot\text{SbF}_5$	68-69
$(\text{C}_6\text{H}_5)_3\text{CCOF}\cdot\text{SbF}_5$	Dec. to $(\text{C}_6\text{H}_5)_3\text{C}^+\text{SbF}_6^-$, m.p. 211°

(1) (a) Part 111, *Revue de Chimie*, C. D. Nenitzescu's 60th Birthday Issue, 1962. (b) Physical Research Laboratory, The Dow Chemical Co., Midland, Mich.

(2) G. A. Olah, S. J. Kuhn, W. S. Tolgyesi and E. B. Baker, *J. Am. Chem. Soc.*, **84**, 2733 (1962).

(3) G. Olah, S. Kuhn and S. Beke, *Ber.*, **89**, 862 (1956).

(4) G. A. Olah and S. J. Kuhn, *J. Org. Chem.*, **26**, 237 (1961).

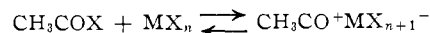
(5) G. A. Olah, S. J. Kuhn and W. S. Tolgyesi, unpublished results.

Spectroscopic Investigations. Infrared Investigations.

—A Perkin-Elmer model 421 grating spectrophotometer was used to record the spectra. Emulsions of the solids in mineral oil (Nujol) and a fluorinated hydrocarbon (Fluorolube, S30, Minnesota Mining and Manufacturing Co.) were pressed between silver chloride or Irtran plates, all operations being carried out in a drybox, as the compounds were extremely sensitive to moisture. No etching of these plates was observed, in marked contrast to the observation when sodium chloride plates were used. Even barium fluoride plates were slightly etched.

The main characteristic data obtained are summarized in Table II. As illustrative examples, the spectra of $(\text{CH}_3)_2\text{CHCO}^+\text{SbF}_6^-$ and $(\text{CH}_3)_3\text{CCO}^+\text{SbF}_6^-$ (as mixed mulls in Nujol-fluorolube) are shown in full in Fig. 1 and 2.

There has been general agreement^{6,7} that the spectra of acetyl halide:Lewis acid metal halide complexes contain a strong band at 2300 cm^{-1} due to the methyl oxocarbenium ion (CH_3CO^+) formed in the process.



Similarly, aromatic acyl halide (benzoyl, etc.) complexes have given spectra containing a strong band at 2200 cm^{-1} , indicating the presence of phenyl oxocarbenium ion.

The lower carbonyl frequency of the phenyl oxocarbenium ion than that of the methyl oxocarbenium ion was attributed to conjugation of the CO group with the ring (an effect often observed in infrared spectroscopy). Similarly, conjugation of the alkyl groups with the CO double bond caused a shift of the C=O stretching frequency to lower values in the secondary and tertiary alkyl substituted oxocarbenium ions.

In addition to the ionic oxocarbenium salts there are present also, but to a lesser extent, the polarized oxygen donor coordination compounds, as shown by the presence of the shifted C=O stretching frequencies. Table II shows the shift of the carbonyl stretching frequency of the donor-acceptor complexes and, as may be seen, the shift increases with the branching of the

(6) B. P. Susz and J. J. Wuhrmann, *Helv. Chim. Acta*, **40**, 971 (1957).

(7) D. Cook, *Can. J. Chem.*, **37**, 48 (1959).

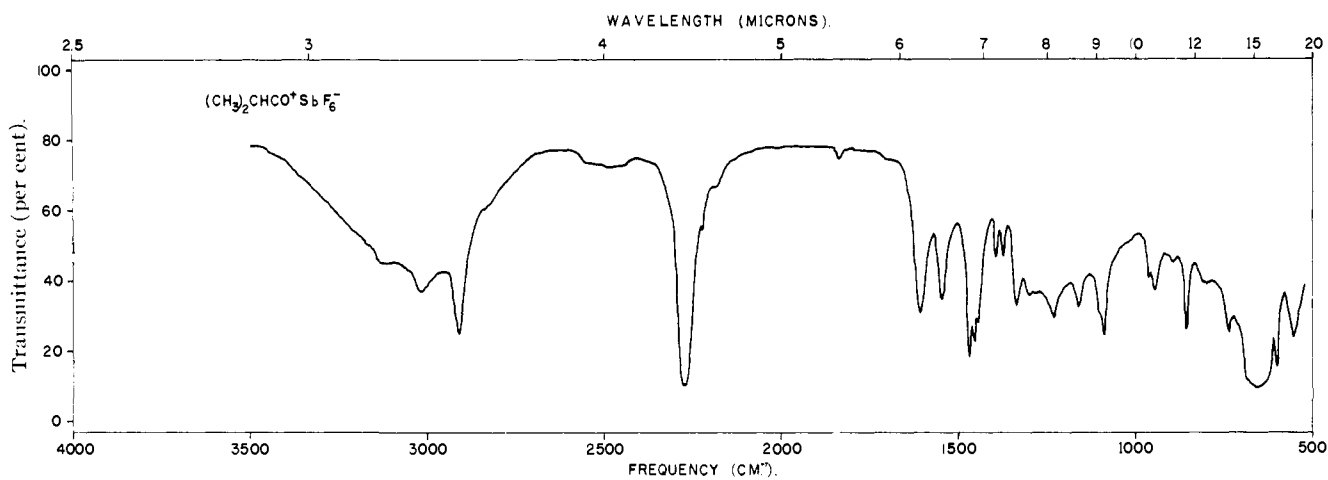


Figure 1.

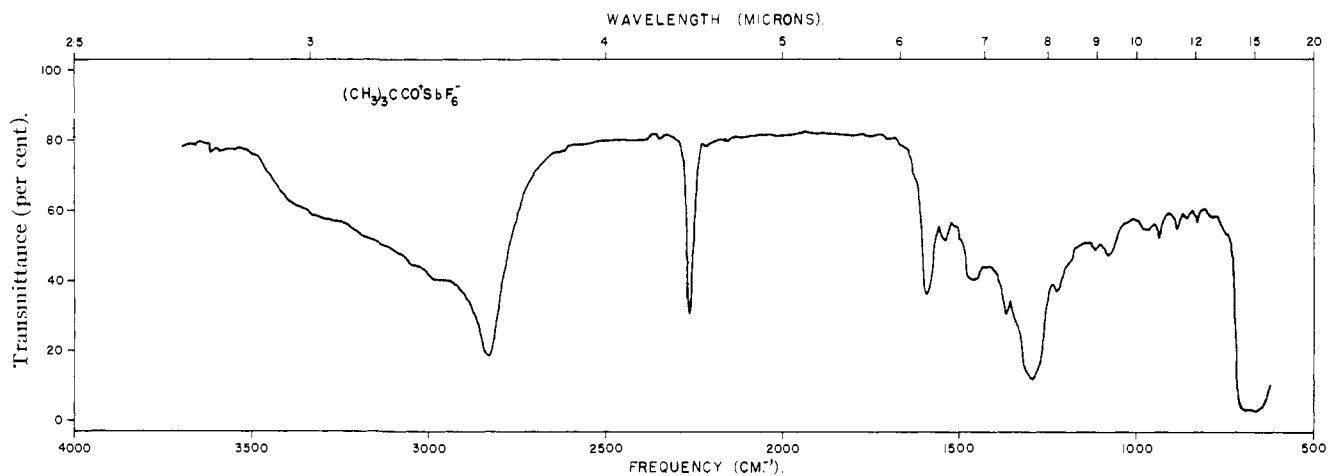


Figure 2.

alkyl group in the acyl fluorides. The sizable carbonyl shifts also indicate the strong Lewis acid nature of antimony pentafluoride.

Of particular interest is the *tert*-butyl oxocarbonium hexafluoroantimonate complex, isolated from pivalyl

fluoride and antimony pentafluoride. The observation of the infrared spectrum at room temperature as a Fluorolube-Nujol mull (Fig. 2) is always accompanied by some decomposition. In preparative runs carbon monoxide was isolated from the decomposition product,

TABLE II

INFRARED FUNDAMENTAL STRETCHING FREQUENCIES OF ACRYL FLUORIDES AND THE CORRESPONDING ACRYL FLUORIDE:SbF₅ COMPLEXES

RCOF	RCOF·SbF ₅	$\nu_{C=O}$	$\nu_{C=O}$	ν_{C-F}	$\nu_{SbF_6^-}$
CH ₃ COF	CH ₃ CO·SbF ₅ ⁻	1848vs	2294vs	826s809s	665s
		1554w			
CH ₂ CH ₂ COF	CH ₂ CH ₂ CO·SbF ₅ ⁻	1845vs	2290vs	1068s	650s
(CH ₃) ₂ CHCOF	(CH ₃) ₂ CHCO·SbF ₅ ⁻	1840vs	2270vs	1065s	650s
(CH ₃) ₃ CCOF	(CH ₃) ₃ CCO·SbF ₅ ⁻	1823vs	2260vs	1060vs	660s
CH ₃ CH ₂ CH ₂ COF	CH ₃ CH ₂ CH ₂ CO·SbF ₅ ⁻	1824vs	2283vs	1073s	655s
		1545w			
(CH ₃ CH ₂) ₂ CHCOF	(CH ₃ CH ₂) ₂ CHCO·SbF ₅	1837vs	2223vs	1070s	661s
(CH ₃ CH ₂) ₃ CCOF	(CH ₃ CH ₂) ₃ CCOF·SbF ₅	1832vs		1065s	
C ₆ H ₅ CH ₂ COF	C ₆ H ₅ CH ₂ CO·SbF ₅ ⁻	1843vs	2279vs	1078vs	650s
		1599m			
		1516m			
(C ₆ H ₅) ₂ CHCOF	(C ₆ H ₅) ₂ CHCOF·SbF ₅	1847vs			
(C ₆ H ₅) ₃ CCOF	(C ₆ H ₅) ₃ CCOF·SbF ₅	1831vs		1052s	
		Decomp. to (C ₆ H ₅) ₃ C·SbF ₅ ⁻			

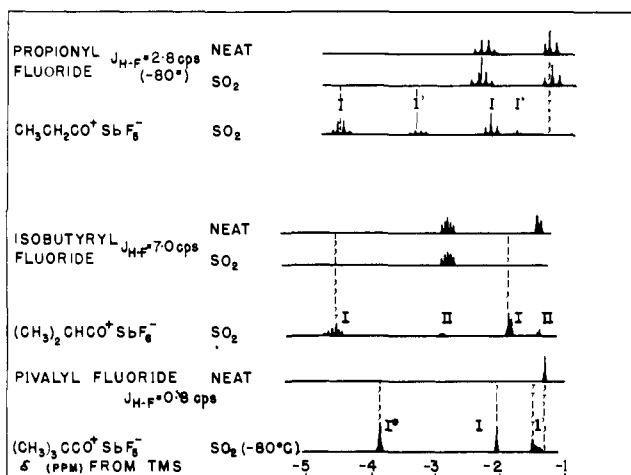


Fig. 3.—H¹ resonance spectra of methylacetyl fluorides and their antimony pentafluoride complexes at 60 Mc.

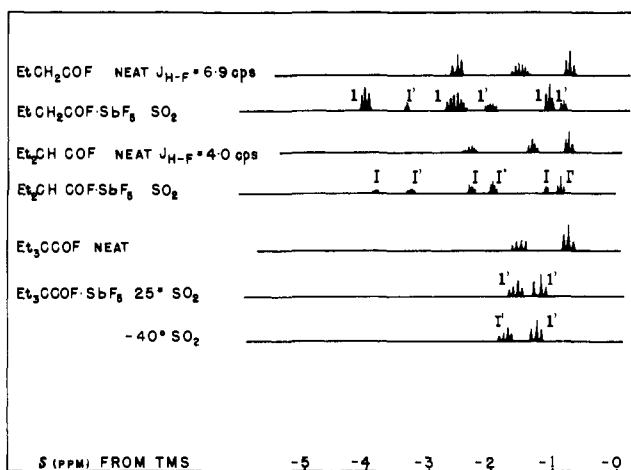
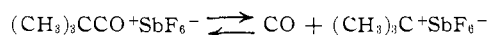


Fig. 4.—H¹ resonance spectra of ethylacetyl fluorides and their antimony pentafluoride complexes at 60 Mc.

together with polyisobutylene and HF. Thus it is believed that partial decarbonylation took place also during the infrared investigations. The strong, broad peak observed in the infrared spectra at 2835 cm^{-1} is unique in that it is not present in the spectra of other alkyl oxocarbenium complexes, pivalyl derivatives, isobutylene or polyisobutylenes.

The CH_3 stretching frequency in isopropyl oxocarbenium hexafluoroantimonate (Fig. 1) is at 2910 cm^{-1} , 75 cm^{-1} higher than that observed for the same vibration in the case of the *tert*-butyl derivative. It therefore is suggested that the peak at 2835 cm^{-1} in the spectrum of the latter represents the methyl stretching frequency in the formed and relatively stable trimethylcarbonium ion.



The corresponding asymmetrical $\text{CH}_3\text{-C}$ deformation vibration is at 1585 cm^{-1} , the symmetrical deformation at 1290 cm^{-1} .

The *tert*-butyl oxocarbenium ion consequently can be considered as a precursor to the trimethylcarbonium ion. Decarbonylation of the former represents a feasible way to generate the latter under moderate, acid-free conditions. The decarbonylation of pivalyl chloride under Friedel-Crafts conditions has been observed by Rothstein,⁸ and by Balaban and Nenitzescu.⁹

(8) E. Rothstein and R. W. Saville, *J. Chem. Soc.*, 1946, 1950, 1954, 1959, 1961 (1949); E. Rothstein, *ibid.*, 1959 (1951); E. Rothstein, *et al.*, *ibid.*, 4558, 4561 (1956); 581 (1958).

(9) A. T. Balaban and C. D. Nenitzescu, *Ann.*, **625**, 60 (1959).

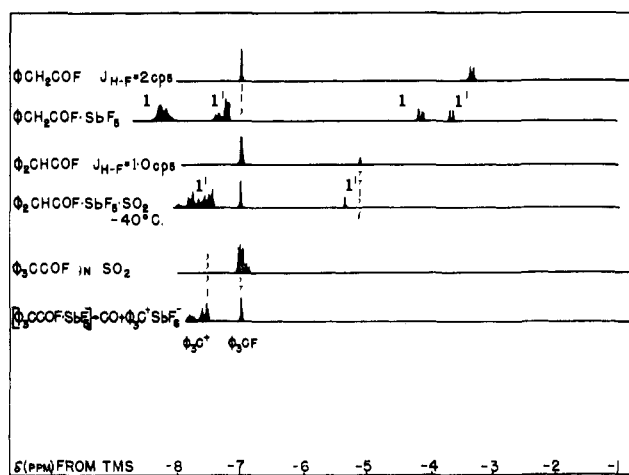


Fig. 5.—Resonance spectra of phenylacetyl fluorides and their antimony pentafluoride complexes at 60 Mc.

High resolution nuclear magnetic proton resonance investigations in sulfur dioxide solutions of the *tert*-butyl oxocarbenium ion, to be discussed later, also show the formation of a second, highly ionic and electron-deficient species, which further substantiates the present observation.

Even more predominant is the decarbonylation of the triethylacetyl fluoride:antimony pentafluoride and triphenylacetyl fluoride:antimony pentafluoride complexes. Although at low temperature 1:1 addition compounds are formed, they lose CO (and HF) so easily that the spectra of the complexes obtained show no carbonyl absorption and were identical with those of 3-ethyl-2-pentene ($(\text{C}_2\text{H}_5)_2\text{C}=\text{CHCH}_3$) and triphenylcarbonium hexafluoroantimonate ($(\text{C}_6\text{H}_5)_3\text{C}^+\text{SbF}_6^-$), respectively.

Spectroscopic data obtained on crystalline addition compounds, however, cannot be extrapolated to give information on the structure of these compounds in solutions.

Ultraviolet Investigations.—No systematic investigation of the ultraviolet absorption spectra of oxocarbenium complexes has yet been undertaken. However, in view of the particular interest in the possibility of generating trimethylcarbonium ion from the *tert*-butyl oxocarbenium complex, it was felt useful to investigate the ultraviolet absorption of pivalyl halides under conditions allowing ionization and thus subsequent decarbonylation.

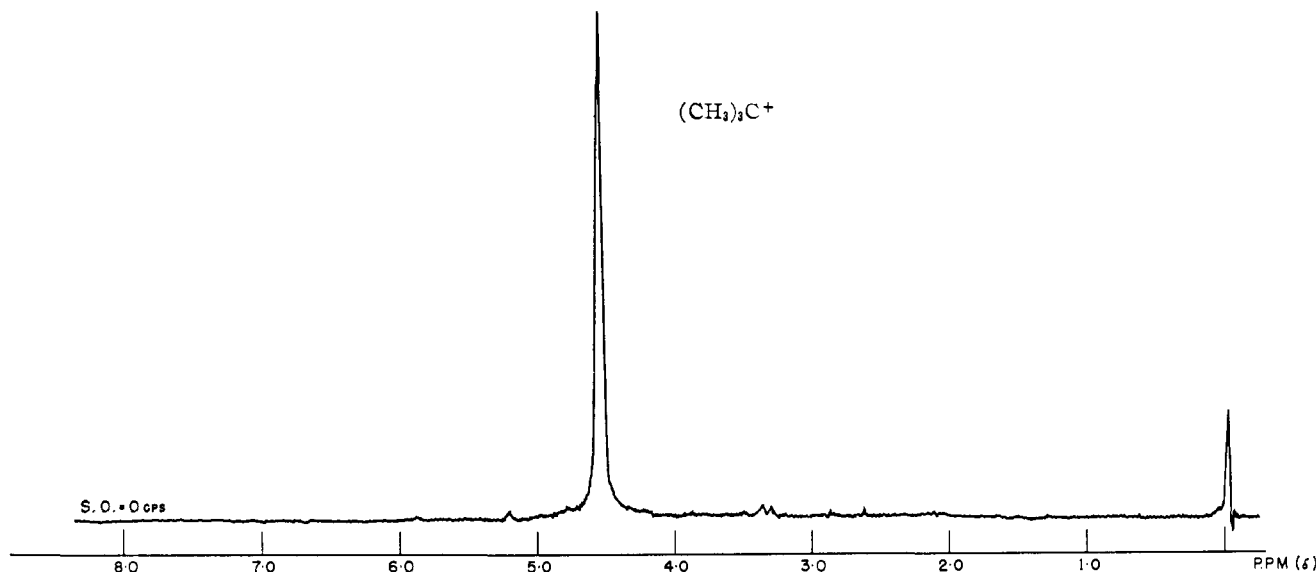
Rosenbaum and Symons¹⁰ have reported the surprising stability of the trimethylcarbonium ion in concentrated sulfuric acid solutions. Solutions of both *tert*-butyl alcohol and isobutene gave in sulfuric acid a single measurable ultraviolet band having $\lambda_{\text{max}} 293 \pm 2\text{ m}\mu$ ($\epsilon 6.4 \times 10^3$) with a half-height width of 490 cm^{-1} .

As an alternate possibility for the absorbing ion, Symons considered the oxidized butenyl cation $\text{CH}_2=\text{C}(\text{CH}_3)\text{-CH}_2^+$.

It has been found now that both pivalyl chloride and fluoride give in 100% sulfuric acid solutions a single ultraviolet band at $292 \pm 1\text{ m}\mu$. The same maximum was observed in antimony pentafluoride solution of pivalyl fluoride or in the same solution of *tert*-butyl fluoride. The observed extinction coefficients were, however, small (~ 500). Deno¹¹ recently questioned the assignment of the $293\text{ m}\mu$ maximum in the sulfuric acid

(10) J. Rosenbaum and M. C. R. Symons, *Proc. Chem. Soc.*, 92 (1959); *Mol. Phys.*, **3**, 205 (1960).

(11) N. C. Deno, Abstr. Papers, p. 77Q, 142nd A.C.S. Natl. Meeting, Atlantic City, N. J., September, 1962; N. C. Deno, H. G. Richey, Jr., J. S. Liu, J. D. Hodge, J. J. Hauser and M. J. Wisotsky, *J. Am. Chem. Soc.*, **84**, 2016 (1962).

Fig. 6.— $(\text{CH}_3)_3\text{CF}$ in SbF_5 at 60 Mc.

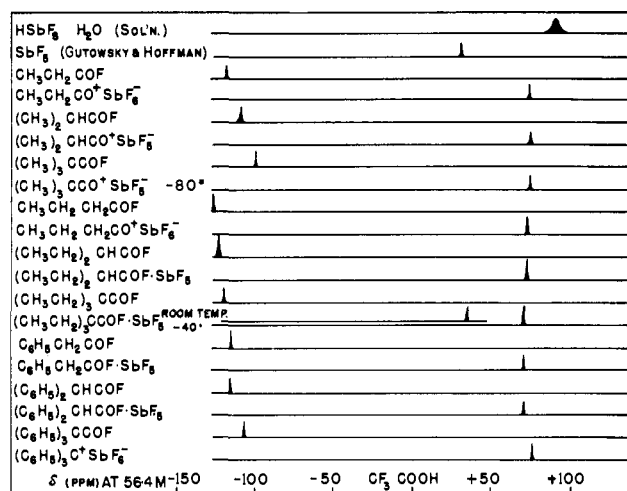
solution of butyl alcohol to be due to the trimethylcarbonium ion or the isobutenyl cation and suggested, based on n.m.r. investigations, that it is entirely that of the heptamethylcyclopentenyl cation. It is difficult from our observation of the ultraviolet spectrum to come at this time to final conclusions. It is possible but not probable to have the oxidized allylic ion in small concentration in our SbF_5 system, not detectable by n.m.r. investigations, but sufficient care was exercised to exclude oxygen from the system. Although our observed extinction coefficient is only 1/10 of that reported by Symons¹² we suggest that the 293 $m\mu$ absorption with the observed small extinction coefficient could be assigned to the electron transfer of the trimethylcarbonium ion involving quasi π -electrons and the vacant p-orbital of the positive carbon. Recovery experiments and other investigations of the *tert*-butyl fluoride: SbF_5 and pivalyl fluoride: SbF_5 systems (to be reported later in detail) gave no evidence of Deno's heptamethylcyclopentenyl ion.

Nuclear Magnetic Resonance Investigations.—To obtain further information on the structure of the acyl fluoride:antimony pentafluoride 1:1 addition complexes in solution, high resolution nuclear magnetic proton and fluorine resonance spectroscopic investigations were carried out. A modification of the high resolution n.m.r. spectrograph of Baker and Burd¹³ was used. Part of the proton resonance spectra (when working at slightly elevated temperature, $\sim 40^\circ$) were obtained on a Varian A60 spectrograph. Liquid sulfur dioxide (also anhydrous hydrogen fluoride) was used as solvent, the samples being sealed in quartz probe tubes.

The H^1 and F^{19} spectra obtained are shown in partially schematic form in Fig. 3, 4, 5, 6 and 7. The corresponding acyl fluorides are shown for reference in the same spectrum, and the F^{19} - H^1 splitting (to be discussed later) is removed, for compactness.

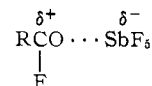
Proton Spectra.—The proton spectra of the complexes obtained at 60 Mc. are displayed in Fig. 3, 4, 5, and 6. The spectra are given in p.p.m. relative to $(\text{CH}_3)_4\text{Si}$ (TMS) as standard.

The acyl fluorides exhibit H^1 - F^{19} coupling of varying magnitude. None of the complexes exhibits H^1 - F^{19} coupling, which would of course not be expected in the ionic forms, but this can hardly be used as conclusive

Fig. 7.— F^{19} resonance spectra of acyl fluoride: SbF_5 complexes in SO_2 solution.

evidence of ionic dissociation, but only as supporting evidence. Fast exchange in a highly polarized donor:acceptor complex could equally well result in the absence of observable H^1 - F^{19} coupling.

The proton spectra of solutions of the acyl fluoride: SbF_5 complexes generally show two species, labeled I and I', with varying chemical shifts to less shielding. Species I, which is the least shielded, is thought to be the ion RCO^+ present, however, as a solvated ion pair (cryoscopic measurements show very little, if any, ion separation). Species I' is suggested to be in all probability the polarized coordination complex



Due to the possible fast fluorine exchange, the H^1 - F^{19} coupling is not observed in the complex and substantial polarization can account for the considerable shift, which is nonetheless smaller than is observed in the case of the truly ionic species I.

The proton resonance spectra of propionyl fluoride and its complex with antimony pentafluoride were discussed previously.²

The proton spectrum of isobutyryl fluoride shows the characteristic separate multiplets for the CH_3 and CH groups. In the spectrum of the SbF_5 complex the

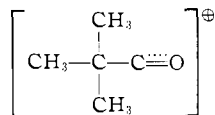
(12) Prof. M. R. C. Symons in a personal communication kindly informed us that his reported extinction coefficient value should be modified, being not more than 2000.

(13) E. B. Baker and L. W. Burd, *Rev. Sci. Instr.*, **28**, 313 (1957).

methyl doublet is at -1.71 p.p.m. and the CH septuplet at -4.33 p.p.m., indicating considerably less shielding of the protons in the complex than in isobutyryl fluoride, in accordance with the ionic isopropyl oxocarbenium structure of the complex.

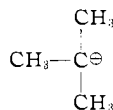
The proton spectrum of pivalyl fluoride shows a methyl line at -1.27 p.p.m., with a small ($J_{\text{HF}} = 0.79$ c.p.s.) coupling by the fluorine. The complex of pivalyl fluoride with SbF_5 shows three methyl lines at -80° , all at lower shielding than with pivalyl fluoride alone. The least shielded is at -3.95 p.p.m., the second at -2.02 p.p.m. and the third at -1.45 p.p.m.

As the positively charged carbon is twice removed from the methyl protons in the *tert*-butyl oxocarbenium ion it cannot be expected that the shift of -3.95 p.p.m.



for the least shielded line corresponds to this ion. In other cases in the present work chemical shifts of protons in methyl groups of secondary and tertiary oxocarbenium ions, in which the electron-deficient carbon is two carbons away, are found to be much smaller—of the order of -0.5 p.p.m. from the parent compound. Even the primary methyl oxocarbenium ion $[\text{CH}_3-\text{C}=\text{O}]^+$, where the positive charge is on the neighboring carbon (see subsequent discussion of the C^{13} -spectrum of this ion) shows a shift of only -1.90 p.p.m.

It therefore is suggested that the chemical shift at -3.95 p.p.m. corresponds to a considerably less shielded electron deficient species, namely the trimethylcarbonium ion



which is formed from the oxocarbenium ion by the loss of CO.

The proton line at -2.02 p.p.m. is assigned to the *tert*-butyl oxocarbenium ion, and the line at -1.45 p.p.m. to the donor:acceptor complex $(\text{CH}_3)_3\text{CCOF} \rightarrow \text{SbF}_5$.

To substantiate that the line at -3.95 p.p.m. is indeed assigned correctly to the trimethylcarbonium ion, we investigated solutions of *tert*-butyl fluoride in excess SbF_5 as solvent.¹⁴ The resulting proton spectrum showed a single line at -4.35 p.p.m. and it thus appears that the trimethylcarbonium ion is formed directly from *tert*-butyl fluoride in excess of the Lewis acid SbF_5 , and is the same species as that formed from pivalyl fluoride by CO elimination (Fig. 6).

Table III summarizes observations of proton resonances relating to the trimethylcarbonium ion. Small differences in chemical shifts are due to the different solvents used (SO_2 and SbF_5). This suggestion was substantiated by observations of the proton magnetic resonance spectrum of $(\text{CH}_3)_4\text{N}^+\text{SbF}_6^-$ in the same solvents, where similar solvent effects were found.

If spectra of the pivalyl fluoride:antimony pentafluoride complex (in SO_2) were obtained at -40° , the amount of the trimethylcarbonium ion present was decreased (as shown by the small -3.95 p.p.m. peak). At room temperature the ion disappears after standing for some hours and a substantially broadened peak indicates polymer formation.

(14) Details to be published in a subsequent paper of this series. Partly presented in talks given by G. A. Olah at the 9th Brookhaven Reaction Mechanism Conference, Upton, N. Y., August, 1962, and at the Stable Carbonium Ion Symposium at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1962.

TABLE III
PROTON MAGNETIC RESONANCE INVESTIGATION OF THE TRIMETHYLCARBONIUM ION

	Solvent	δ (p.p.m. TMS)	J_{HF} (c.p.s.)
$(\text{CH}_3)_3\text{CCOF}$	Neat	-1.27	0.7
$(\text{CH}_3)_3\text{CCOF} + \text{SbF}_5$	SO_2	-3.95	..
$(\text{CH}_3)_3\text{CF}$	Neat	-1.30	20
$(\text{CH}_3)_3\text{CF} + \text{SbF}_5$	SbF_5	-4.35	..

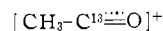
F^{19} Spectra.—The F^{19} spectra were obtained at 56.5 Mc. and are shown in p.p.m. (parts per million of applied frequency or field) relative to external CF_3COOH (Fig. 7). The antimony pentafluoride complexes were reasonably soluble in both solvents (HF and SO_2) and the spectra indicated only the ion SbF_6^- in all cases. In the HF solutions, exchange of fluorine from SbF_6^- to HF is slow enough to give separate lines. However, there is no evidence to exclude the possibility of an exchanging, highly polarized $-\text{F} \rightarrow \text{SbF}_5$ system. The HF lines are quite broad in some cases. There is a large solvent effect for the SbF_6^- ion in SO_2 of 17.6 p.p.m. from that in H_2O , and -3.8 p.p.m. in HF, or a difference of 13.8 p.p.m. of HF solutions relative to SO_2 solutions.

The possibility of fluorine exchange in a highly polarized complex of the type $\text{RCO} \rightarrow \text{SbF}_5$, where the C-F

band must be considerably weakened (and in the limiting case ionized) must be considered. There is also a possibility of exchange involving solvent HF and SbF_6^- ions. Fluorine resonance probably cannot differentiate between the SbF_6^- line and the one corresponding to an exchanging $\text{F}-\text{SbF}_5$ system. Attempts were made to see if at lower temperature, due to the decreased exchange, differences are observable, but this was not the case.

C^{13} Resonance Investigation of $\text{CH}_3\text{C}^{13}\text{O}^+\text{SbF}_6^-$.—To further substantiate that in the ionic oxocarbenium complexes the positive charge is at least partially located on the carbon atom (and not—as alternatively possible—entirely on the oxygen), the complex $\text{CH}_3\text{C}^{13}\text{O}^+\text{SbF}_6^-$ was prepared and investigated. Due to the fact that the solubility of the complex in the used solvent employed (anhydrous HF) is less than 10% , it was necessary to prepare the complex with the highest C^{13} isotopic concentration (53%) available to use, as the sample is tenfold diluted in solution.

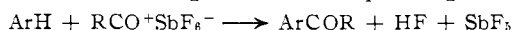
Owing to the low concentration of the complex in the solution it was not possible to observe the C^{13} resonance directly on a 4-mm. sample, even though enriched. However, this resonance was observable indirectly by the INDOR (internuclear double resonance) method¹⁵ and showed a 1:3:3:1 quartet at 15.09231 Mc. with the proton methyl resonance centered at 60.009769 Mc. The coupling of the enriched carbonyl carbon to the methyl protons was $J_{\text{CCH}} = 6.0$ c.p.s. The C^{13}O is shifted -30.9 p.p.m. relative to C^{13} in $\text{CF}_3\text{C}^{13}\text{OOH}$, or -45.4 p.p.m. relative to C^{13} in acetyl fluoride, $\text{CH}_3\text{C}^{13}\text{OF}$. A direct C^{13} spectrum of an enriched sample of $\text{CH}_3\text{C}^{13}\text{OF}$ consisted of a pair of quartets with $J_{\text{CCH}} = 7.6$ c.p.s. and $J_{\text{CF}} = 355.2$ c.p.s. Thus the C^{13}O in the complex is considerably less shielded than in acetyl fluoride, which is consistent with at least a partial positive charge on the carbonyl carbon atom in the ion



Chemical Reactivity.—The isolated oxocarbenium complexes are highly effective acylating agents in C-, O-, N- and S-acylations of a variety of organic compounds.

(15) E. B. Baker, *J. Chem. Phys.*, **37**, 911 (1962).

Aromatic hydrocarbon when allowed to react with oxocarbonium hexafluoroantimonates, preferably in nitromethane solution, gave the corresponding ketones



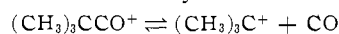
Yields of ketones obtained are listed in Table IV.

TABLE IV
C-ACYLATION OF AROMATICS WITH OXOCARBONIUM HEXAFLUOROANTIMONATES

Aromatic compound	Yield ketone, %		
	$\text{CH}_3\text{CH}_2\text{CO}^+\text{SbF}_6^-$	$(\text{CH}_3)_2\text{CHCO}^+\text{SbF}_6^-$	$(\text{CH}_3)_3\text{CCO}^+\text{SbF}_6^-$
Benzene	93	87	3
Ethyl-	96		3
<i>tert</i> -Butyl-			27
Fluoro-	93	90	
Chloro-	89	68	
Toluene	92	89	2

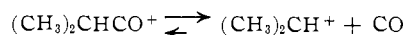
All yields reported were obtained from preparative runs. Although acylations seem to give high yields, data do not necessarily represent optimum conditions, owing to losses during preparative operations.

Reaction of *tert*-butyl oxocarbonium hexafluoroantimonate with benzene yielded predominantly *tert*-butylbenzene. The reactions with toluene, ethylbenzene and *tert*-butylbenzene gave varying amounts of pivalophenones and *tert*-butylated products. *tert*-Butylations are believed to take place through primary decarbonylation of the *tert*-butyl oxocarbonium ion



as no decarbonylation of pivalophenones was observed under the reaction conditions used. These data are in accordance with previous observations on the Friedel-Crafts reaction of pivalyl halides with aromatics, investigated by Rothstein⁸ and Balaban and Nenitzescu.⁹

It was interesting to observe that in the reaction of isopropyl oxocarbonium hexafluoroantimonate with toluene and benzene, although the corresponding isopropyl ketones were predominantly formed, there was a smaller amount (3.5% in the case of the reaction of benzene, 1.5% in the case of toluene) of isopropylated hydrocarbons formed (as analyzed by gas-liquid chromatography, using a Golay-type capillary column and hydrogen flame ionization detector). Thus a limited decarbonylation of the isopropyl oxocarbonium ion according to



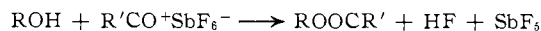
was taking place.

Table V summarizes the ratios of acylations compared with alkylations in the reactions of isobutyryl and pivalyl fluoride complexes with aromatics.

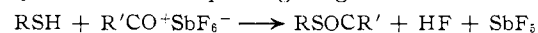
TABLE V
RATIO OF ACYLATION TO ALKYLATION IN THE REACTIONS OF METHYL- AND ETHYLACETYL FLUORIDE COMPLEXES WITH AROMATICS

Aromatic	Substitut. agent RCOF·SbF ₅ , R =	ArCOR:ArR
Benzene	(CH ₃) ₂ CH	29.8
Toluene	(CH ₃) ₂ CH	82.2
Benzene	(CH ₃) ₃ C	0.1
Toluene	(CH ₃) ₃ C	.03
Ethylbenzene	(CH ₃) ₃ C	.09
<i>tert</i> -Butylbenzene	(CH ₃) ₃ C	.67
Benzene	(CH ₃ CH ₂) ₂ CH	2.3
Toluene	(CH ₃ CH ₂) ₂ CH	14.2
Benzene	(CH ₃ CH ₂) ₃ C	0.01
Toluene	(CH ₃ CH ₂) ₃ C	0.01

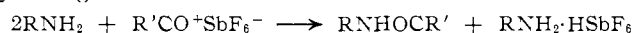
Oxocarbonium salts are also highly effective acylating agents for O-acylation of alcohols giving esters



for acylation of mercaptans giving thioesters



and for N-acylation of primary and secondary amines yielding amides



Results of acylations are shown in Tables VI, VII and VIII, respectively.

TABLE VI
O-ACYLATION OF ALCOHOLS WITH OXOCARBONIUM SALTS

Alcohol	Yield alkyl ester, %		
	$\text{CH}_3\text{CH}_2\text{CO}^+\text{SbF}_6^-$	$(\text{CH}_3)_2\text{CHCO}^+\text{SbF}_6^-$	$(\text{CH}_3)_3\text{CCO}^+\text{SbF}_6^-$
Methanol	65	70	53
Ethanol	74	78	58
1-Propanol	72		63
1-Butanol	80	79	
<i>tert</i> -Butyl alcohol	84		
1-Octanol	82		

TABLE VII
S-ACYLATION OF MERCAPTANS WITH OXOCARBONIUM SALTS

Mercaptan	Yield thioester, %		
	$\text{CH}_3\text{CH}_2\text{CO}^+\text{SbF}_6^-$	$(\text{CH}_3)_2\text{CHCO}^+\text{SbF}_6^-$	$(\text{CH}_3)_3\text{CCO}^+\text{SbF}_6^-$
Methanethiol	52	57	47
Ethanethiol	50	59	51
<i>n</i> -Octanethiol	70	62	48

TABLE VIII
N-ACYLATION OF AMINES WITH OXOCARBONIUM SALTS

Amine	Yield amide, %		
	$\text{CH}_3\text{CH}_2\text{CO}^+\text{SbF}_6^-$	$(\text{CH}_3)_2\text{CHCO}^+\text{SbF}_6^-$	$(\text{CH}_3)_3\text{CCO}^+\text{SbF}_6^-$
Ammonia	90	81	
Ethylamine	89	87	63
Diethylamine	84	90	70
Aniline	90	82	

Experimental

Acyl fluorides were prepared by the method earlier described.⁴ Antimony pentafluoride was obtained from the Harshaw Chemical Co., Cleveland, O., and was freshly distilled before use. $\text{BaC}^{13}\text{O}_3$ was obtained from Merck, Sharp and Dohme Lt., Montreal, Que.

Preparation of Oxocarbonium Hexafluoroantimonates.—Acyl fluoride (0.2 mole) was dissolved in 70 ml. of 1,1,2-trifluoroethane (Freon 113) and the solution was allowed to react at -5 to 0° with an equimolar solution of freshly distilled antimony pentafluoride, adding this solution to the stirred cold acyl fluoride solution. After half an hour of continued stirring, the white, crystalline precipitate that formed was filtered, washed with cold Freon 113 and dried under vacuum.

All operations were carried out under the usual conditions for excluding moisture, preferably in vacuum systems. Yields are generally close to quantitative.

The prepared oxocarbonium salts could be recrystallized from liquid SO_2 solutions and were obtained as colorless crystalline compounds with high purity. Melting points (in sealed tubes) are given in Table I. Elementary analysis of the complexes are summarized in Table IX. The fluoride analyses were carried out by neutron activation, in sealed polyethylene sample tubes. This method is particularly recommended for the analysis of hydrolytically sensitive or otherwise not too stable complexes.

$\text{CH}_3\text{C}^{13}\text{OF}$.— $\text{CH}_3\text{C}^{13}\text{OONa}$ (1.66 g., 0.02 mole) with 53% C^{13} content (obtained from Merck, Sharp and Dohme of Canada Ltd., Montreal, Que.) was placed in a semimicro distillation apparatus, provided with a 10 ft. Vigreux column and protected in the usual way from atmospheric moisture. Benzoyl fluoride (25 g., 0.2 mole) was added through a dropping funnel to the reaction flask, which was gently heated to regulate a smooth evolution of the $\text{CH}_3\text{C}^{13}\text{OF}$. When the distillation stopped (b.p. 20 – 21°) the collected acetyl fluoride (cooled receiver) was found (infrared and n.m.r. spectra, gas-liquid chromatography) to be of sufficient purity to be used without further purification in the preparation of the antimony pentafluoride complex.

$\text{CH}_3\text{C}^{13}\text{O}^+\text{SbF}_6^-$.—The preparation of the labeled methyl oxocarbonium salt was carried out under identical conditions as

TABLE IX

	Mol. wt.	Fluorine, %		Carbon, %		Hydrogen, %	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
CH ₃ CH ₂ CO+SbF ₆ ⁻	293	38.93	38.59	12.30	12.18	1.72	1.79
(CH ₃) ₂ CHCO+SbF ₆ ⁻	307	37.15	37.07	15.65	15.78	2.30	2.27
(CH ₃) ₂ CCO+SbF ₆ ⁻	321	35.52	35.44	18.71	^a	2.82	^a
CH ₃ CH ₂ CH ₂ CO+SbF ₆ ⁻	307	37.15	37.03	15.65	15.39	2.30	2.21
(CH ₃ CH ₂) ₂ CHCO+SbF ₆ ⁻	335	34.03	33.87	21.51	21.18	3.31	3.17
C ₆ H ₅ CH ₂ CO+SbF ₆ ⁻	355	32.12	31.98	27.07	26.80	1.98	1.78
(C ₆ H ₅) ₂ CHCO+SbF ₆ ⁻	431	26.45	26.13	39.01	38.28	2.57	2.39

^a Not determined due to relative instability of complex at room temperature.

described previously for CH₃CO+SbF₆⁻ and CD₃CO+SbF₆⁻,² by treating Freon 113 solutions of CH₃C¹³OF and SbF₆ at -5 to -10° and subsequently isolating the stable, crystalline oxocarbenium salt.

Reaction of Oxocarbenium Salts with Aromatic Compounds. (a) **Without Solvent.**—The appropriate oxocarbenium salt (0.2 mole) was added into 0.5 mole of well-stirred aromatic. The complex salts are generally not soluble in the aromatics. In most cases gentle heating was necessary to start the reaction. The formed ketones give complexes with the by-product Lewis acids and separate from the excess aromatic as a lower layer. After washing the reaction mixtures, they were dried over Na₂SO₄ and the products isolated (fractionation or crystallization).

(b) **In Solution.**—In these experiments the reaction was carried out in nitromethane solutions in which the aromatics and the oxocarbenium salts are both soluble. The reactions are much slower in solvent, and owing to the partial decomposition of the oxocarbenium salts in nitromethane the yields are lower.

Reaction of Oxocarbenium Salts with Alcohols.—Oxocarbenium salt (0.3 mole) was added as nitromethane solution or in

small portions as a solid into 0.6 mole of the appropriate stirred and cooled alcohol. A fast reaction takes place. The resulting mixture was washed with water, dried over Na₂SO₄ and fractionated.

Reaction of Oxocarbenium Salts with Mercaptans.—Oxocarbenium salt (0.3 mole) was added in nitromethane solution or in small fractions as a solid to 0.6 mole of well stirred and cooled mercaptan. The reaction is very fast. After completion of the reaction, the mixture was washed with water, dried over Na₂SO₄ and fractionated.

Reaction of Oxocarbenium Salts with Amines.—The solution of 0.3 mole of oxocarbenium salt in nitromethane or SO₂ solution was added to 0.6 mole of the stirred and cooled primary or secondary amine. The products, after water washings, were isolated either by distillation or crystallization.

Acknowledgments.—Dr. O. U. Anders, Radiochemistry Laboratory, The Dow Chemical Company, Midland, Mich., is thanked for neutron activation fluorine analyses.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF CLARK UNIVERSITY, WORCESTER, MASS., AND ILLINOIS INSTITUTE OF TECHNOLOGY, CHICAGO, ILL.]

Pyridoxine and Pyridoxal Analogs. VIII. Synthesis and Infrared Spectra of Metal Chelates¹

BY DIETRICH HEINERT² AND ARTHUR E. MARTELL²

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The preparation and purification of a number of metal chelates derived from the amino acid Schiff bases of pyridoxal analogs 3-hydroxypyridine-4-aldehyde and 3-hydroxypyridine-2-aldehyde are described. Copper(II) chelates containing a 1:1:1 molar ratio of Cu(II):hydroxypyridinealdehyde:amino acid and iron(III) and nickel(II) chelates having a 1:2:2 molar ratio of constituents were synthesized. Glycine, glutamic acid and valine were employed as the amino acids. Probable structures of these compounds were deduced from their stoichiometry, properties and infrared spectra.

This paper describes the synthesis and properties of Fe(III), Cu(II) and Ni(II) chelates of the 3-hydroxy-4-pyridinealdimines (XVI) and 3-hydroxy-2-pyridinealdimines (XVII) containing residues of the natural amino acids glycine, valine, phenylalanine and glutamic acid. Interest in such metal chelate compounds arises from their analogy to pyridoxylideneimine chelates, whose role in vitamin B₆ catalyzed reactions has been the subject of considerable investigation. The role of metal chelates of pyridoxal derivatives of the natural amino acids has been reported by Metzler and Snell³ and a general mechanism for a wide variety of reactions catalyzed by these compounds was described by Metzler, *et al.*⁴ The first crystalline metal chelate of pyridoxal Schiff bases reported was the 1:1 Cu(II) chelate of pyridoxylidenetyrosine described by Baddiley.⁵ Christensen isolated and measured spectrophotometrically the formation in solution of the Cu(II), Mn(II), Ni(II), Zn(II), and Mg(II) chelates of pyridoxylidene-glycine,⁶ containing a 1:1 molar ratio of

ligand to metal ion, and the Mn(II), Ni(II), Zn(II), Fe(II) and Fe(III) chelates of a number of other amino acid-pyridoxal Schiff bases⁷ containing a 2:1 molar ratio of ligand to metal ion. The formation constants of a number of 1:1 metal pyridoxylideneimine chelates have been reported,^{8,9} but little evidence was found for the formation of 2:1 chelates in aqueous solution.⁹

The purpose of the present investigation was to prepare and study metal chelates of amino acid Schiff bases derived from the pyridoxal analogs described in previous communications.^{10,11}

Experimental

General Synthesis of Hydroxypyridylmethylene Amino Acid Metal Chelates.—Two mmoles of anhydrous reagent grade amino acid is converted to the potassium salt by the slow addition with stirring of a 0.10 M solution of potassium hydroxide in absolute methanol. For the preparation of the Cu(II) and Ni(II) chelates, two equivalents of base was added to one and two equivalents of the amino acid, respectively. For the preparation of the 2:1 Fe(III) chelate, three equivalents of base was added to two equivalents of the amino acid. The methanol solution containing the potassium salt of the amino acid with or without excess base was cooled and combined with an equimolar amount of the hydroxyaldehyde in anhydrous methanol. The resulting yellow Schiff base solution was then slowly combined with the

(1) This investigation was supported by research grants A-1307 and A-5217 from the National Institute of Arthritis and Metabolic Diseases, U. S. Public Health Service.

(2) Department of Chemistry, Illinois Institute of Technology, Chicago 16, Ill.

(3) D. E. Metzler and E. E. Snell, *J. Am. Chem. Soc.*, **74**, 979 (1952).

(4) D. E. Metzler, M. Ikawa and E. E. Snell, *ibid.*, **76**, 648 (1954).

(5) J. Baddiley, *Nature*, **170**, 711 (1952).

(6) H. N. Christensen and S. Collins, *J. Biol. Chem.*, **220**, 279 (1956).

(7) H. N. Christensen, *J. Am. Chem. Soc.*, **79**, 4073 (1957).

(8) H. N. Christensen, *ibid.*, **80**, 2305 (1958).

(9) L. Davis, F. Roddy and D. E. Metzler, *ibid.*, **83**, 127 (1961).

(10) D. Heinert and A. E. Martell, *ibid.*, **84**, 3257 (1962).

(11) D. Heinert and A. E. Martell, *Tetrahedron*, **3**, 49 (1958).