

REACTIONS OF THE TIN TETRAHALIDES  
WITH 2,4-PENTANEDIONE IN  
THE PRESENCE OF ORGANIC  
AMINES

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Presented to

The Faculty of the Department of Chemistry  
The College of William and Mary in Virginia

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In Partial Fulfillment

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Master of Arts

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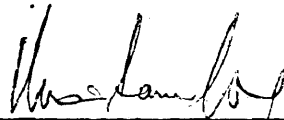
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Kwai-Sam Wong

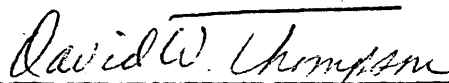
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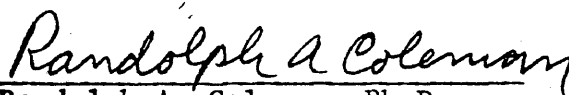
APPROVAL SHEET

This thesis is submitted in partial fulfillment of  
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\_\_\_\_\_  
Author

Approved, August 1976

  
\_\_\_\_\_  
David W. Thompson, Ph.D.

  
\_\_\_\_\_  
Randolph A. Coleman, Ph.D.

  
\_\_\_\_\_  
Cirila Djordjevic, Ph.D.

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To my parents

and

Yin-Ping

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## ABSTRACT

The major goal of this research was to examine the tin tetrahalide ( $\text{SnX}_4$ ,  $\text{X}=\text{Cl, Br, I}$ )—2,4-pentanedione—amine (pyridine, triethylamine) systems with the hope of preparing and characterizing pyridinium and triethylammonium tetrahalo(2,4-pentanedionato)stannate(IV) salts. These salts would be the first examples of anionic  $\beta$ -diketonate tin(IV) complexes.

REACTIONS OF THE TIN TETRAHALIDES  
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## INTRODUCTION AND LITERATURE SURVEY

Although tin is in the fourth period of the group IVB elements, its diffuse empty 5d orbitals in the presence of highly electronegative substituents may contract enough to be used in bond formation and subsequent expansion of its coordination number above four. Indeed, a great many complexes of tin with electronegative ligand donor atoms particularly with coordination number six and the octahedral geometry are known.

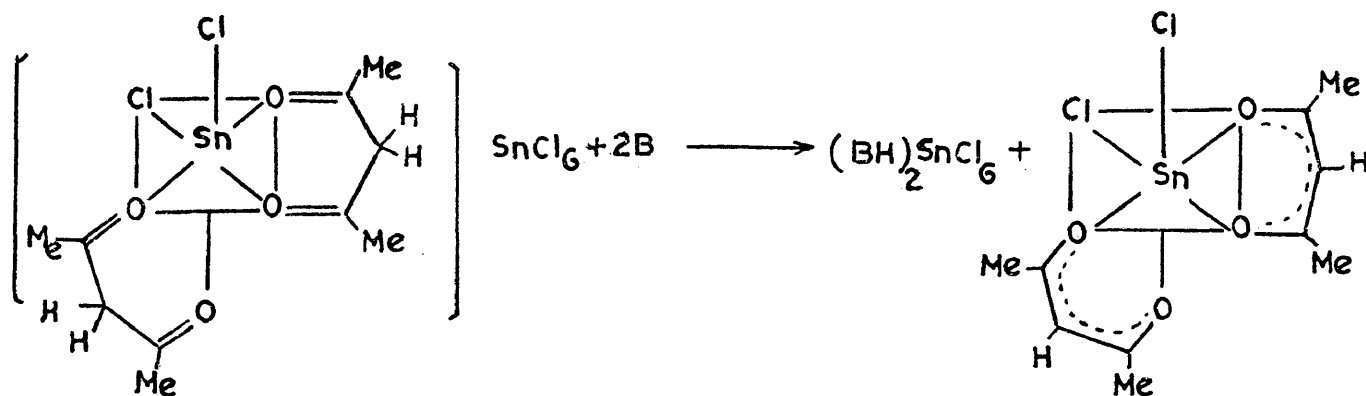
Among the complexes of interest to this thesis as background information are those formed from the interaction of the tin tetrahalides with enolizable  $\beta$ -diketones such as 2,4-pentanedione. In the very early 1900's Dilthey<sup>1,2</sup> and Rosenheim, Loewenstamm, and Singer<sup>3</sup> studied the reaction of tin tetrachloride with 2,4-pentanedione in benzene at the reflux temperature. These workers isolated a product having the following stoichiometry,  $\text{Cl}_2\text{Sn}(\text{C}_5\text{H}_7\text{O}_2)_2$ ,  $\text{C}_5\text{H}_7\text{O}_2$  being the 2,4-pentanedionate ion. Dilthey on the basis of a rather high melting point (202-204°) proposed a salt-like structure for the compound, i.e.  $[\text{Sn}(\text{C}_5\text{H}_7\text{O}_2)_3]_2[\text{SnCl}_6]$  or tris(2,4-pentanedionato)tin(IV) hexachlorostannate(IV). In 1924, Morgan and Drew<sup>4</sup> reported the results of their investigations of the interaction of tin tetrachloride and tin tetrabromide with 2,4-pentanedione. These workers found that the reaction between 2,4-pentanedione and tin tetrachloride at room temperature yields a solid product with the empirical formula  $\text{Cl}_4\text{Sn}(\text{C}_5\text{H}_8\text{O}_2)$ . Morgan and Drew speculated that the room temperature product was a mixture of

Dilthey's complex,  $\text{Cl}_2\text{Sn}(\text{C}_5\text{H}_7\text{O}_2)_2$ , and hexachlorostannic acid,  $\text{H}_2\text{SnCl}_6$ . Upon refluxing the room temperature "mixture" or tin tetrachloride and 2,4-pentanedione in an inert organic solvent, Morgan and Drew isolated a solid identical to Dilthey's  $\text{Cl}_2\text{Sn}(\text{C}_5\text{H}_7\text{O}_2)_2$ . The reaction of tin tetrabromide and 2,4-pentanedione at reflux in dry chloroform led to the isolation of the complex  $\text{Br}_2\text{Sn}(\text{C}_5\text{H}_7\text{O}_2)_2$ . Molecular weight measurements in benzene were consistent with  $\text{Cl}_2\text{Sn}(\text{C}_5\text{H}_7\text{O}_2)_2$  and  $\text{Br}_2\text{Sn}(\text{C}_5\text{H}_7\text{O}_2)_2$  being monomeric. Since a salt-like complex such as that proposed by Dilthey would most likely be highly associated in benzene giving a molecular weight up to three times that of the monomer, Morgan and Drew concluded that the chloro- and bromo-complexes were monomeric six-coordinate dihalobis(2,4-pentanedionato)tin(IV) complexes.

In 1963 Mehrotra and Gupta<sup>5</sup> reexamined the tin tetrachloride-2,4-pentanedione system. These workers attempted to further elucidate the structure of the room temperature "mixture" obtained by Morgan and Drew. The empirical formula was confirmed to be  $\text{Cl}_4\text{Sn}(\text{C}_5\text{H}_8\text{O}_2)$ . However, the presence of hexachlorostannic acid was ruled out by Mehrotra and Gupta because the compound was stable under vacuum ( $10^{-4}$  mm of Hg) at  $55^\circ$ ; hexachlorostannic acid, if present, should have sublimed. On the basis of conductance data in nitrobenzene ( $\Lambda_m = 22 \text{ cm}^2 \text{ mole}^{-1} \text{ ohm}^{-1}$  at  $10^{-3} \text{ M}$ ) and other chemical evidence, they formulated the structure of the room temperature product as a salt,  $[\text{Cl}_2\text{Sn}(\text{C}_5\text{H}_8\text{O}_2)_2][\text{SnCl}_6]$ , containing neutral diketone molecules. The molar conductivity value is, however, only about one-half that expected for a 2:2 electrolyte.<sup>6</sup>

Allred and Thompson<sup>7</sup> studied the interaction of tin tetrachloride with both 2,4-pentanedione and the non-enolizable 3,3-dimethyl-2,4-pentanedione. Reaction of tin tetrachloride with both  $\beta$ -diketones at

room temperature leads to adducts\* of empirical formula,  $\text{Cl}_4\text{Sn}(\beta\text{-diketone})$ . For both adducts no band was found in the infrared spectrum characteristic of the  $\text{SnCl}_6^{2-}$  ion ( $\nu_{\text{Sn-Cl}} \text{ ca. } 320 \text{ cm}^{-1}$ ). Furthermore, when  $\text{Cl}_2\text{Sn}(\text{C}_5\text{H}_7\text{O}_2)_2$  was allowed to react with dry hydrogen chloride at room temperature only  $\text{Cl}_4\text{Sn}(\text{C}_5\text{H}_8\text{O}_2)$  was isolated; no evidence was found for  $[\text{Cl}_2\text{Sn}(\text{C}_5\text{H}_8\text{O}_2)_2]\text{Cl}_2$  as claimed by Mehrotra and Gupta.<sup>5</sup> Also  $\text{Cl}_4\text{Sn}(\text{C}_5\text{H}_8\text{O}_2)$  readily reacts at room temperature with pyridine and triethylamine to form salts of the type  $[\text{M}][\text{Cl}_4\text{Sn}(\text{C}_5\text{H}_7\text{O}_2)]$ .<sup>8</sup> If the room temperature product had the salt-like structure  $[\text{Cl}_2\text{Sn}(\text{C}_5\text{H}_8\text{O}_2)_2][\text{SnCl}_6]$ , reaction with an organic amine should lead to formation of an ammonium hexachlorostannate salt,  $\text{M}_2\text{SnCl}_6$ , and the well-characterized cis-dichlorobis(2,4-pentanedionato)tin(IV),  $\text{Cl}_2\text{Sn}(\text{C}_5\text{H}_7\text{O}_2)_2$ , species.



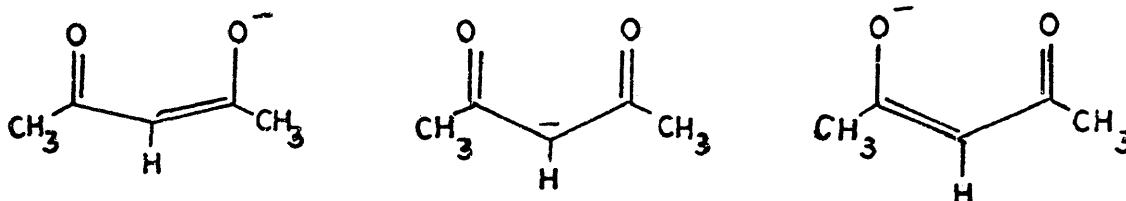
In summary, there is no compelling evidence to believe that the complex formed between tin tetrachloride and 2,4-pentanedione at room temperature is anything but the simple Lewis acid-base adduct. No 2,4-pentanedione adducts are formed with tin tetrabromide and tin tetraiodide.

\*The term adduct is used in this paper to mean a molecular complex formed from interaction of donor and acceptor species such that no bonds are broken in either the donor or the acceptor, although a rearrangement in stereo-chemistry of the interacting species may occur.

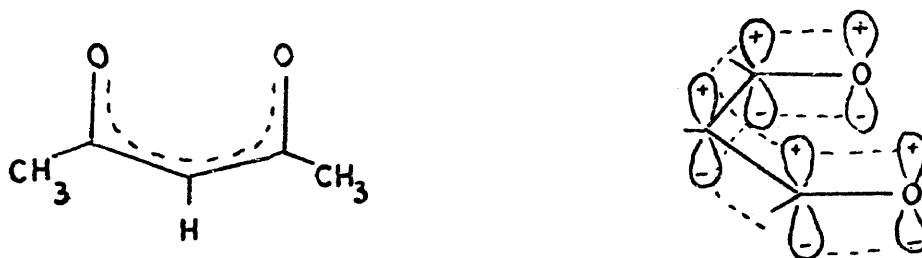
Mehrotra and Gupta also reexamined the product,  $\text{Cl}_2\text{Sn}(\text{C}_5\text{H}_7\text{O}_2)_2$ , obtained from refluxing tin tetrachloride and 2,4-pentanedione in an inert organic solvent. These workers unambiguously showed that the complex was monomeric and non-ionic (via molecular weight and conductivity measurements) as postulated by Morgan and Drew.<sup>4</sup>

Although by 1963 it was conclusively shown that  $\text{Cl}_2\text{Sn}(\text{C}_5\text{H}_7\text{O}_2)_2$  was a monomeric and molecular complex, the structure of the complex was unknown, i.e. the mode of attachment of the 2,4-pentanedionate ion and the geometrical arrangement of the ligands.

The electronic structure of the 2,4-pentanedionate ion may be represented by three valence bond structures or by the molecular orbital structure shown below;



Valence-bond structures



Molecular-orbital structure

From the valence bond representations it can be seen that the enolate ion could bond to a positively charged central tin atom through either the  $\gamma$ -carbon or through an oxygen atom. Furthermore, coordination to oxygen could result in either mono- or bidentate attachment. By far, the most common mode of coordination of the 2,4-pentanedionate ion to

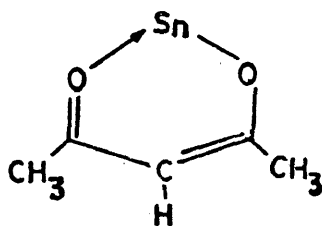
metals is through both oxygen atoms, i.e. the enolate ion functions as a bidentate ligand.

Additionally, all crystallographic data<sup>9</sup> and other spectral data show that the two C—O and two internal C—C bond distances are equal, respectively. Thus, most researchers prefer the molecular orbital representation of the enolate ion. The mode of bonding in metal--2,4-pentanedionate complexes is easily determined from infrared and nmr spectral data. The chelated enolate structure has strong characteristic C≡O and C=C vibrational modes in the 1500-1600 cm<sup>-1</sup> region. Coordination via the  $\gamma$ -carbon would give bands above 1600 cm<sup>-1</sup> characteristic of a  $\gamma$ -substituted diketone (ca. 1700 cm<sup>-1</sup>). Coordination through a single oxygen atom would give the spectrum expected for a conjugated ketone, i.e. a strong C≡O band between ca. 1650 and 1700 cm<sup>-1</sup>. Although useful, the nmr spectra are less definitive than infrared data. However, chelated 2,4-pentanedionates generally exhibit two characteristic resonance peaks. A high-field peak generally 1.85-2.15 ppm downfield from tetramethylsilane and a low-field peak in the region from about 5.40-6.00 ppm. These peaks are assigned to the terminal methyl protons and  $\gamma$ -proton, respectively, with an intensity ratio of 6:1.

In the middle 1960's several groups of workers demonstrated that Cl<sub>2</sub>Sn(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub> contained oxygen-chelated enolate ligands and was a six-coordinate, non-ionic, monomeric tin complex.

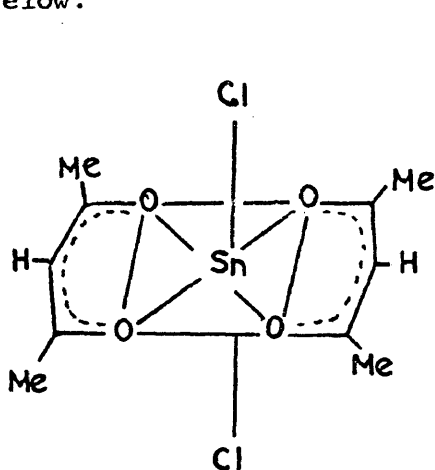
In 1965, Kawasaki and Tanaka<sup>10</sup> reported the 100 MHz nmr spectrum of dichlorobis(2,4-pentanedionato)tin(IV). They found two major peaks in the methyl region of the spectrum and one signal in the  $\gamma$ -proton region. They interpreted the existence of two methyl resonances,

observed by others as well,<sup>11</sup> as arising from the presence of localized double bonds in the chelated ligands, i.e.

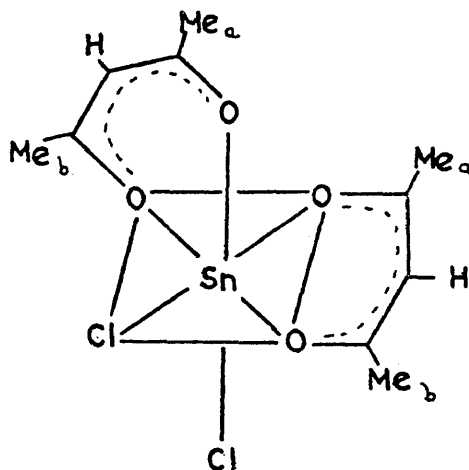


This interpretation seemed tenuous in light of the fact that crystallographic data for several 2,4-pentanedionate complexes always showed the enolate ion to have  $C_{2v}$  symmetry.<sup>9</sup>

A plausible explanation for the existence of the two methyl resonances can be presented in light of different stereochemical possibilities for a six-coordinate  $Cl_2Sn(C_5H_7O_2)_2$  complex. Two geometrical isomers for  $Cl_2Sn(C_5H_7O_2)_2$  are possible. These are illustrated below:



TRANS  $D_{2h}$



CIS-  $C_2$

In the trans isomer (point group  $D_{2h}$ ) the four methyl groups are

symmetry equivalent, i.e. they can be interchanged by a symmetry operation belonging to the  $D_{2h}$  point group; also the  $\gamma$ -protons are symmetry equivalent. Thus one would expect only single terminal methyl and single  $\gamma$ -proton resonance peaks. On the other hand, the cis isomer (point group  $C_2$ ) has two distinct methyl proton ( $CH_{3a}$  and  $CH_{3b}$ ) environments and a single  $\gamma$ -proton environment. Thus one expects a single  $\gamma$ -proton peak and two methyl proton peaks if exchange is slow with respect to the time scale of the nmr experiment. The observation of two methyl resonances by Kawasaki and others, especially in light of the  $C_{2v}$  symmetry for the enolate ion found from crystallographic data, is best explained by the existence of the cis-isomer in solution. Indeed, the existence of the cis configuration in solution has been established subsequently from dipole moment determinations of a wide temperature range. The dipole moment is 6.7 Debyes.<sup>12,13,14</sup> It has also been shown that dibromo- and diiodobis(2,4-pentanedionato)tin(IV) have the cis configuration.<sup>11,12</sup>

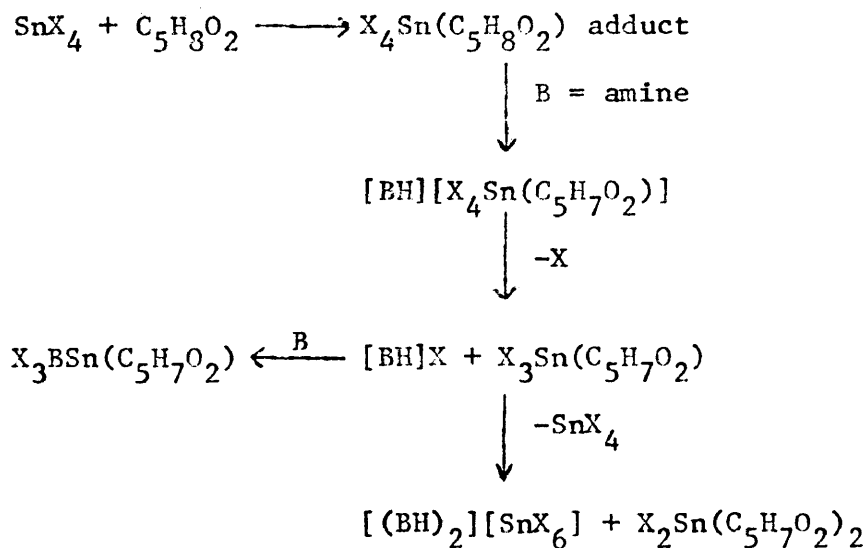
An interesting feature of the nmr spectrum of cis-dichlorobis(2,4-pentanedionato)tin(IV) is the temperature dependence of the spectrum. As already cited at room temperature one  $\gamma$ -proton and two methyl proton peaks are observed. In addition to these peaks, satellites are observed corresponding to the splitting caused by the  $Sn^{117}$  and  $Sn^{119}$  nuclei ( $I = 1/2$  — abundance 8.67% and 8.62%). (See Figure 1.)<sup>10</sup>

As the temperature is raised the two major methyl peaks move closer together, and at ca. 90° complete collapse to a singlet is observed.<sup>15</sup> The coalescence occurs because of rapid interchange of the two distinct types of methyl groups between environments a and b (see previous discussion).



The mechanism for interchange of methyl groups is of fundamental interest. Two general exchange mechanisms are possible: 1) dissociative intermolecular exchange; and 2) intramolecular exchange. For cis-dichlorobis(2,4-pentanedionato)tin(IV) one observes the averaged long-range coupling between the tin nuclei with  $I = 1/2$  persists well above the coalescence temperature. The persistence of the tin-hydrogen coupling is consistent only with an intramolecular exchange mechanism. Unfortunately there is no way of deciding whether the intramolecular exchange involves a dissociative or twisting process.<sup>16</sup>

Although the tin tetrahalide --2,4-pentanedione system was thoroughly characterized by the end of 1968, it was decided that this work would investigate the interaction of the tin tetrahalides with 2,4-pentanedione in the presence of an organic amine. The inclusion of an amine gives several additional reaction possibilities. The most likely of these possibilities are outlined below:



The details of the scheme will be discussed more thoroughly later.

## EXPERIMENTAL

### A. Reagents

Tin tetrachloride was purchased from Fisher Scientific Co. and used without further purification. Tin tetrabromide and tin tetraiodide were purchased from Alfa Inorganics and used without further purification. 2,4-Pentanedione was purchased from Eastman Organics and redistilled before use. Pyridine and triethylamine were purchased from Fisher Scientific Co. and J. T. Baker Chemical Co., respectively. The amines were redistilled before use and stored over 4A Linde molecular sieves. Germanium tetrachloride and phenyltrichlorosilane were purchased from Alfa Inorganics; tetrachlorosilane was purchased from Fisher Scientific. Phenyl germanium trichloride was purchased from Stern Chemical Co. All of these latter reagents were used without further purification.

### B. Solvents

All solvents were obtained from commercial sources and were purified and dried before use by refluxing over either phosphorous pentoxide or calcium hydride under nitrogen and then distilling from the dehydrating agent under nitrogen. The solvents were stored over 4A Linde molecular sieves in flasks, equipped with a side arm stopcock to admit nitrogen. Aliquots of the solvent were transferred from the storage vessel to reaction vessel with a syringe under a stream of nitrogen. Nitrobenzene was purified by the method Fay and Lowry. Nitromethane was distilled from phosphorous pentoxide and stored over Linde type 4A molecular sieves.

## C. Preparations

### 1. General Reaction Procedures

All reactions involving a tin tetrahalide were carried out by first adding 2,4-pentanedione to a tetrahalide and then forming the salt by addition of a nitrogen base. Small round bottoms flasks were equipped with a dropping funnel, nitrogen inlet and magnetic stirrer. (See Figure 2.) Before any reactants were added, the apparatus was thoroughly flamed under a stream of dry nitrogen. Liquid components were transferred with syringes. The tin tetrahalides were added to the solvent (methylene chloride) in the reaction flask, then 2,4-pentanedione was dissolved in the solvent (methylene chloride) and added dropwise to the reaction flask. Finally the amine was added dropwise. The resulting mixture was stirred from 1/2 to one hour, usually at 0°. The resulting solid products were transferred under nitrogen to a filtration apparatus similar to that described in the literature.<sup>16</sup> (See Figures 3 and 4.) After the compounds were washed with solvent, they were dried under vacuum at room temperature. (See Figure 5.) The tin complexes were not sensitive to atmospheric moisture. Nevertheless the compounds were handled under anhydrous conditions using a nitrogen filled glove bag.

Reactions of germanium and silicon Lewis acids were carried out like the reactions involving the tin tetrahalides.

### 2. Reaction of tin tetrachloride--2,4-pentanedione, and pyridine

Tin tetrachloride (3.0 ml, 6.69 g,  $2.57 \times 10^{-2}$  M) was added to 25 ml of methylene chloride in a 100 ml three-necked round-bottom flask equipped with a dropping funnel and nitrogen inlet adapter. 2,4-

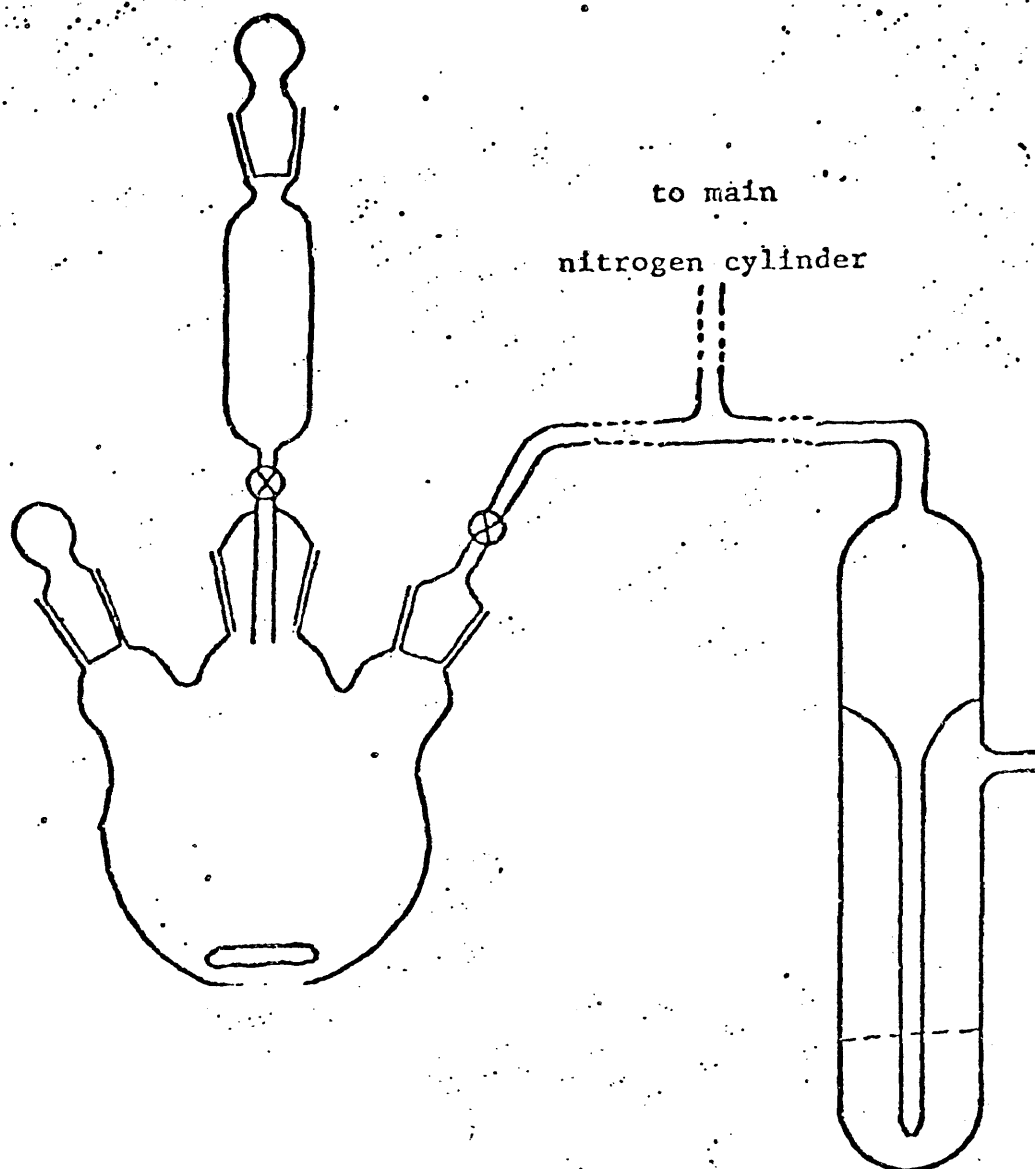


Figure 2.

Diagram of the apparatus for the preparation  
of the

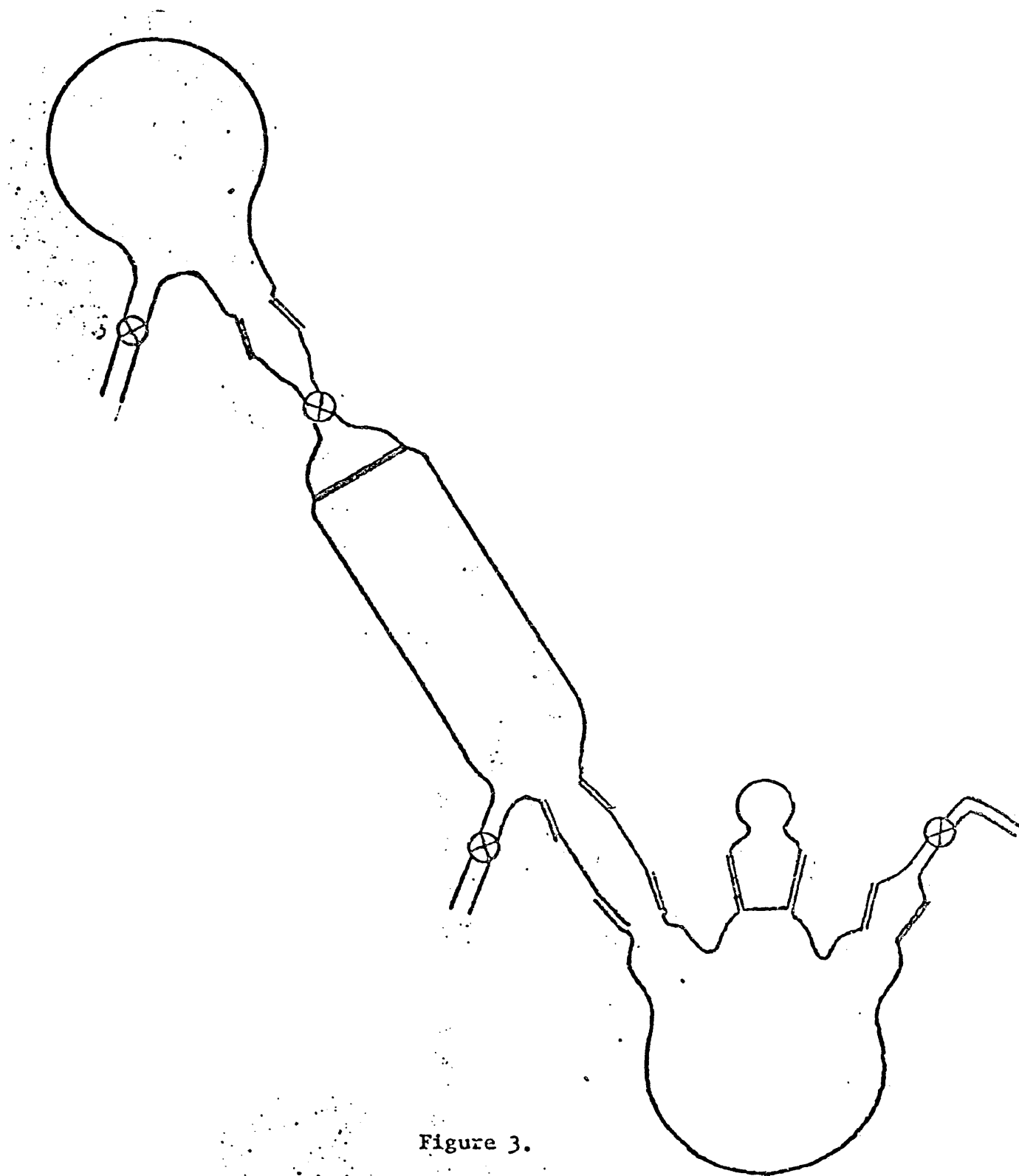


Figure 3.

Diagram of apparatus just before  
filtration of solid products

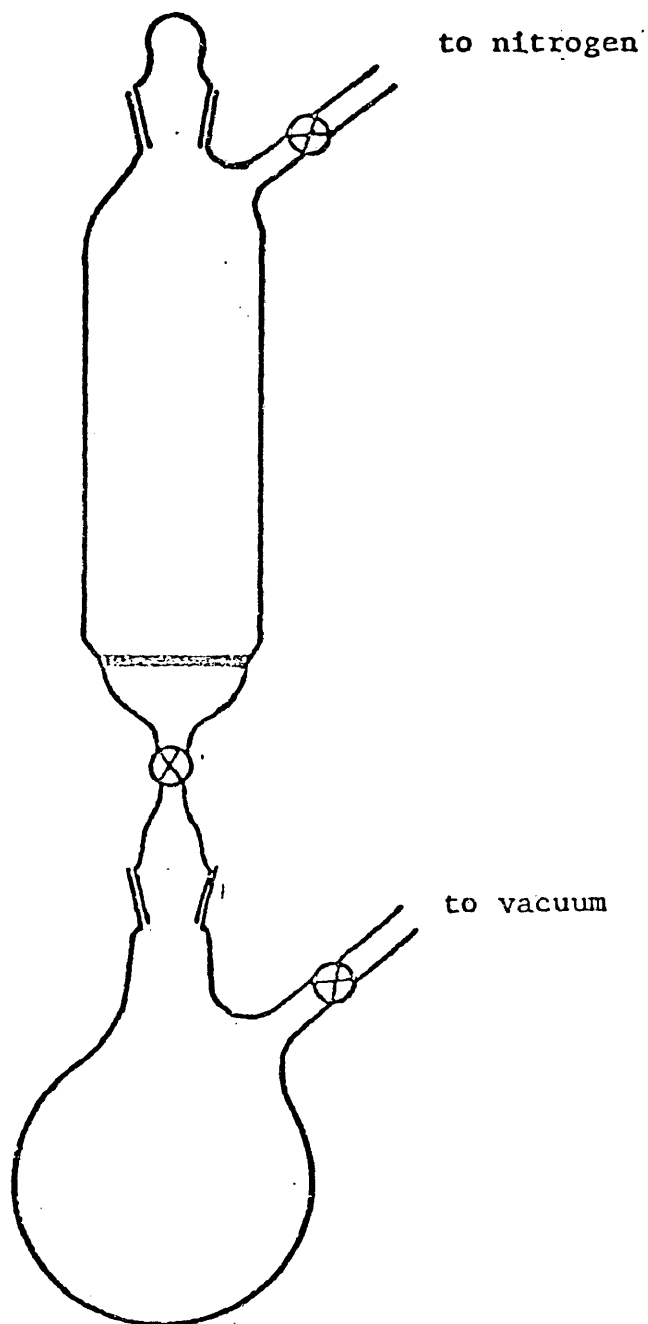


Figure 4.

Diagram of apparatus just after transfer  
from reaction flask to filter flask

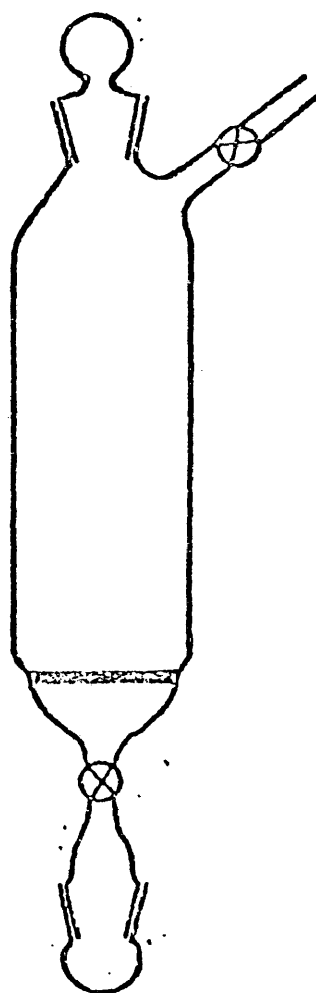


Figure 5.

Diagram of the filter funnel when used  
to dry solid products

Pentanedione (2.9 ml, 2.83 g,  $2.83 \times 10^{-2}$  M) in 10 ml of methylene chloride was added dropwise to the flask at room temperature. A white solid formed, i.e. the tin tetrachloride--2,4-pentanedione adduct. Pyridine (2.4 ml, 2.36 g,  $2.83 \times 10^{-2}$  M) in 10 ml of hexane was added dropwise to the suspension of the adduct. After stirring for ca. 1/2 hour, the resulting white solid was filtered under nitrogen. After the compound was washed with hexane, it was dried under vacuum at room temperature. Mp: 246-248°.

Anal: Calcd for  $[\text{C}_5\text{H}_5\text{NH}][\text{SnCl}_4(\text{C}_5\text{H}_7\text{O}_2)]$ : C, 27.29; H, 2.98; Cl, 32.26. Found: C, 27.48; H, 3.03; Cl, 31.98 and 32.04.

### 3. Reaction of tin tetrabromide, 2,4-pentanedione, and pyridine

Tin tetrabromide (3.0 ml, 10.0 g,  $2.28 \times 10^{-2}$  M) and 2,4-pentanedione (2.6 ml, 2.54 g,  $2.51 \times 10^{-2}$  M) were allowed to react as above. Then pyridine (2.0 ml, 1.96 g,  $2.51 \times 10^{-2}$  M) in 5 ml of hexane was added; a white powdery solid was obtained. The solid was filtered, washed twice with 10 ml portions of hexane, and dried under vacuum. Mp: 242-243°.

Anal: Calcd for  $[\text{C}_5\text{H}_5\text{NH}][\text{SnBr}_4(\text{C}_5\text{H}_7\text{O}_2)]$ : C, 19.47; H, 1.95; Br, 51.85. Found: C, 19.62; H, 2.00; Br, 51.35 and 51.61.

### 4. Reaction of tin tetraiodide, 2,4-pentanedione, and pyridine

Tin tetraiodide (10.6 g,  $1.69 \times 10^{-2}$  M) was suspended in 35 ml of methylene chloride, and 2,4-pentanedione (1.9 ml, 1.85 g,  $1.86 \times 10^{-2}$  M) was added dropwise to the slurry. Pyridine (1.5 ml, 1.47 g,  $1.86 \times 10^{-2}$  M) in 5 ml of hexane was then added dropwise to the mixture. The color of the mixture changed color from dark purple to red-brown. The red solid was filtered, washed, and dried under vacuum. Mp: 166-168°.

Anal: Calcd for  $[\text{C}_5\text{H}_5\text{NH}][\text{SnI}_4(\text{C}_5\text{H}_7\text{O}_2)]$ : C, 14.91; H, 1.49; I, 63.09. Found: C, 14.73; H, 1.58; I, 64.83, 64.31, and 63.49.

5. Reaction of tin tetrachloride, 2,4-pentanedione, and triethylamine

Tin tetrachloride (3.0 ml, 6.68 g,  $2.57 \times 10^{-2}$  M) and 2,4-pentanedione (2.9 ml, 2.83 g,  $2.83 \times 10^{-2}$  M) were allowed to react as in the analogous pyridine system. Triethylamine (3.9 ml, 2.83 g,  $2.83 \times 10^{-2}$  M) in 10 ml of hexane was added dropwise to the suspension of the adduct. Hexane (25 ml) was added to the yellow solution; it separated into two layers. The lower layer appeared to be a yellow oil; the upper layer was turbid and white. The solution was cooled in an ice bath and another 25 ml portion of hexane was added; no crystals were obtained. Methylene chloride was boiled off and two phases still remained. Methylene chloride added until the two liquid phases disappeared. After heating gently for 5 minutes, the solvents were removed under vacuum. A light colored solid product was obtained. After recrystallization from a methylene chloride-hexane mixture, an off-white solid was isolated and treated as before. Mp: crude product--99-100°; recrystallized product--123-125°.

Anal: Calcd for  $[(\text{C}_2\text{H}_5)_3\text{NH}][\text{SnCl}_4(\text{C}_5\text{H}_7\text{O}_2)]$ : C, 28.61; H, 5.02; Cl, 30.71. Found: C, 28.77; H, 5.15; Cl, 30.19, 29.95.

6. Reaction of tin tetrabromide, 2,4-pentanedione, and triethylamine

Tin tetrabromide (3.0 ml, 10.0 g,  $2.28 \times 10^{-2}$  M) and 2,4-pentanedione (2.6 ml, 2.54 g,  $2.51 \times 10^{-2}$  M) were mixed together with 35 ml of methylene chloride. Triethylamine (3.5 ml, 2.53 g,  $2.51 \times 10^{-2}$  M) in 5 ml hexane was added dropwise to the solution. After cooling the mixture in ice bath and stirring for about 5 minutes, a white precipitate

was obtained. The solid was filtered off and dried under vacuum. Mp: 174-177°.

Anal: Calcd for  $[(C_2H_5)_3NH][SnBr_4(C_5H_7O_2)]$ : C, 19.48; H, 1.96; Br, 51.84. Found: C, 19.79; H, 3.53; Br, 50.12, 50.60.

#### 7. Reaction of tin tetraiodide, 2,4-pentanedione, and triethylamine

Tin tetraiodide (17.0 g,  $2.71 \times 10^{-2}$  M) and 2,4-pentanedione (3.1 ml, 2.98 g,  $2.98 \times 10^{-2}$  M) were mixed in 35 ml of methylene chloride at room temperature. Triethylamine (4.2 ml, 3.01 g,  $2.98 \times 10^{-2}$  M) in 5 ml of hexane was added dropwise to the mixture. After prolonged stirring, a red solid was isolated. Mp: partially melted at about 129°; completely melted at 131-134°.

Anal: Calcd for  $[(C_2H_5)_3NH][SnI_4(C_5H_7O_2)]$ : C, 15.98; H, 2.68; I, 61.40. Found: C, 15.86; H, 2.71; I, 60.55 and 60.86.

### D. Physical Measurements

#### 1. Infrared Spectra

The infrared spectra reported were taken with a Perkin-Elmer 457 instrument. The solid state spectra were run as Nujol mulls using KBr cells. Calibration was effected with polyethylene (thin film).

#### 2. Halide Determinations

Per cent halogen was determined potentiometrically with silver nitrate using a Fisher Accumet Model 210 pH meter with a glass electrode as the reference electrode and a silver indicate electrode. The samples were decomposed in aqueous potassium hydroxide solution. The solution was acidified with 6M nitric acid and titrated against standard silver nitrate solution.

### 3. Melting Points

All melting points were taken in sealed capillaries in a Hoover-Thomas melting point apparatus and are uncorrected.

### 4. Conductance Measurements

Conductivities were measured in nitrobenzene at room temperature with an Autobalance B642 Wayne Kerr Universal Bridge in a Freas-type conductivity cell with bright platinum electrodes operating at 1591.5 Hz.

### 5. Nuclear Magnetic Resonance Spectra

The spectra reported were run on a Hitachi-Perkin-Elmer R-20 B Spectrometer.

### 6. Mössbauer Spectra\*

The spectra were obtained with a constant acceleration velocity drive system similar to that developed at the National Bureau of Standards (U.S.).<sup>17a</sup> Velocity calibration of the instrument was accomplished with an iron source of  $\text{Co}^{57}$  diffused into a chromium matrix and absorbers of iron foil and sodium nitroprusside. A  $\text{BaSnO}_3\text{Sn}^{119\text{m}}$  source at room temperature with a palladium filter was used to obtain spectra of the samples which were held at the liquid nitrogen temperature. The tin isomer shifts are reported with respect to the centroid of the  $\text{BaSnO}_3$  spectrum.

### 7. Analyses

Carbon and hydrogen analyses were done by Alfred Bernhardt Mikro-analytisches Laboratorium, West Germany.

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\*These spectra were obtained by Dr. J. F. Lefelhocz at Virginia Commonwealth University, Richmond, Virginia.

## RESULTS AND DISCUSSION

Addition of 2,4-pentanedione to tin tetrachloride in methylene chloride at room temperature yields the simple 1:1 diketone adduct of tin tetrachloride. This adduct has been fully investigated.<sup>4,5,7</sup> This work reports studies to determine whether the acidic proton of the diketone ligand of the simple 1:1 adducts can be eliminated to form anionic 2,4-pentanedionato-tin(IV) complexes by means of the presence of an organic base. Indeed, when either pyridine or triethylamine is added to the tin tetrachloride-2,4-pentanedione adduct, a new compound of the type  $[M][Cl_4Sn(C_5H_7O_2)]$  is formed where  $M = C_5H_5NH$  or  $(C_2H_5)_3NH$ . With tin tetrabromide and tin tetraiodide analogous complexes are isolated although no evidence for a solid diketone-tin tetrahalide adduct is observed. In the case of pyridine, interaction of 2,4-pentanedione with the tin tetrahalides apparently enhances the acidity of the enolizable proton ( $pK_a \sim 8.8$  in water) to the point where transfer to pyridine ( $pK_a \sim 5.2$ ), a weaker base than the enolate ion, occurs. For triethylamine ( $pK_a \sim 10.7$ ), which is a stronger base than the 2,4-pentanedionate ion, complex formation may be interpreted in terms of proton transfer to the amine from an activated diketone or in terms of adduct formation between the enolate anion and the  $SnX_4$  Lewis acid. The tin salts prepared in this work are summarized in Table I.

The infrared spectra for the six tetrahalo(2,4-pentanedionato)tin(IV) salts are shown in Figures 6-11. Spectra in the  $3300-3000\text{ cm}^{-1}$  region

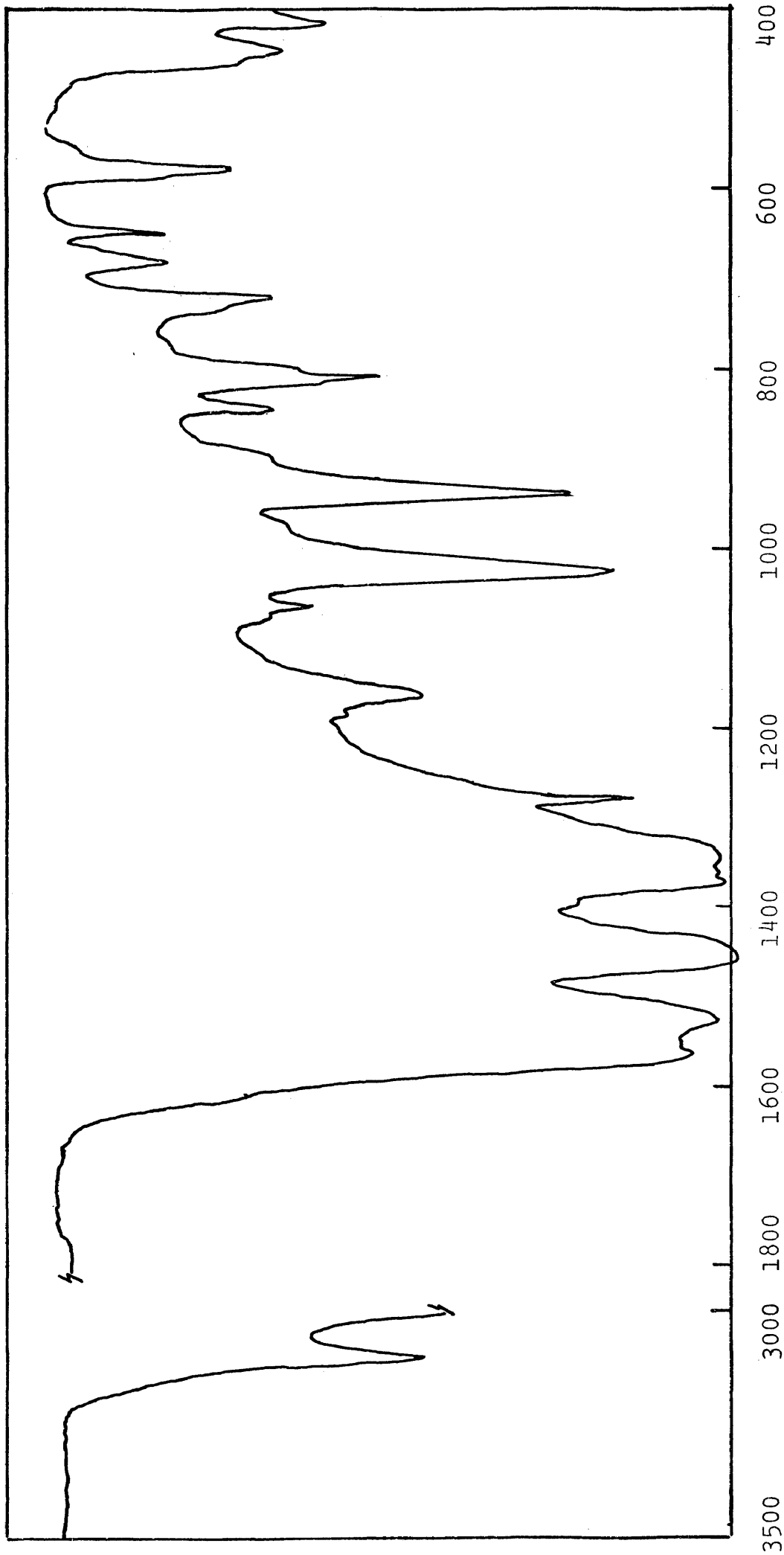
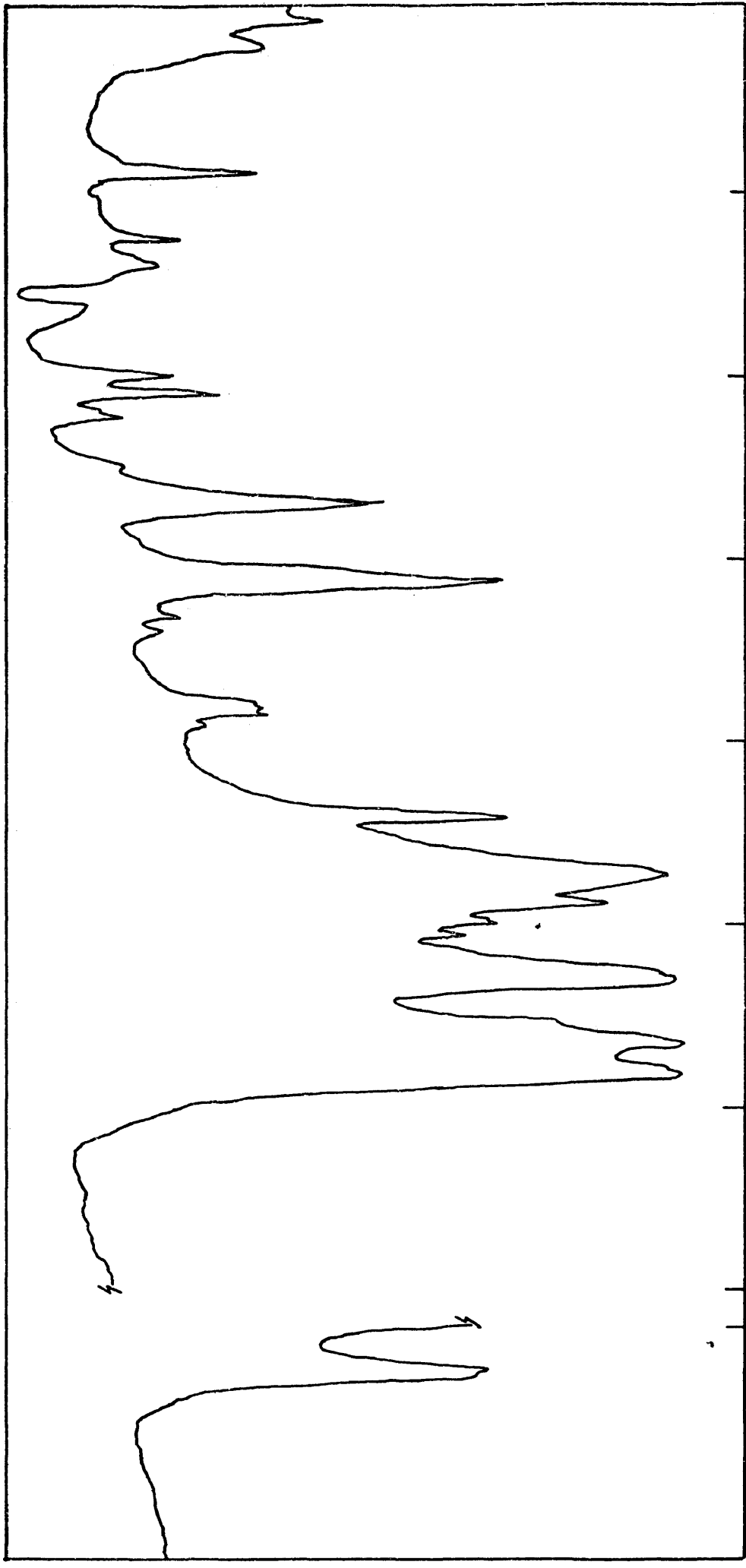


Figure 6.

Infrared spectrum of triethylammonium  
tetrachloro(2,4-pentanedionato)stannate(IV)  
as a Mull in Nujol



3500 3000 1800 1600 1400 1200 1000 800 600 400

Figure 7.

Infrared spectrum of triethylammonium  
tetrabromo(2,4-pentanedionato)stannate(IV)  
as a Mull in Nujol

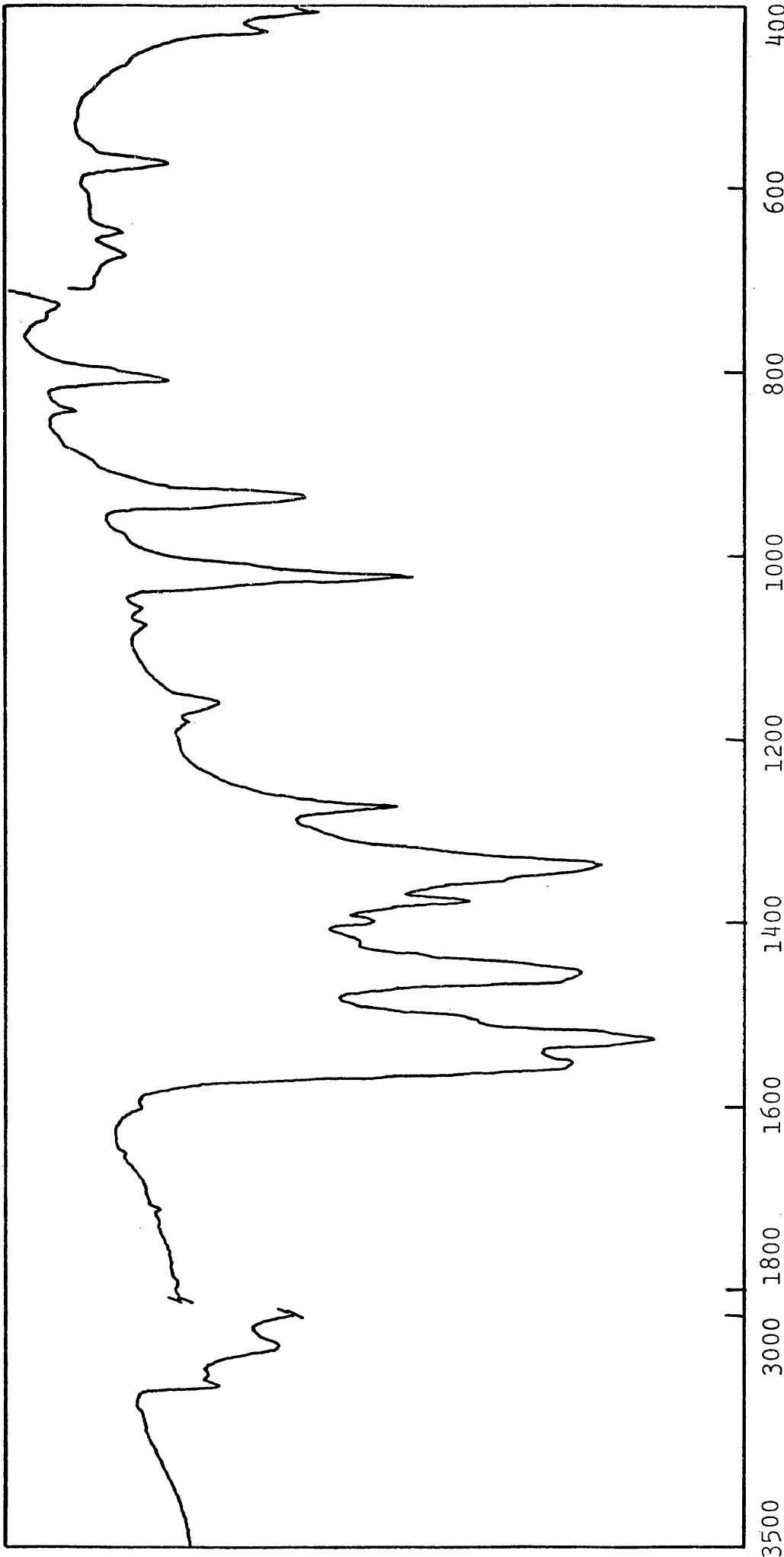


Figure 3.  
Infrared spectrum of triethylammonium  
tetraiodo(2,4-pentanedionato)stannate(IV)  
as a Kull in Nujol

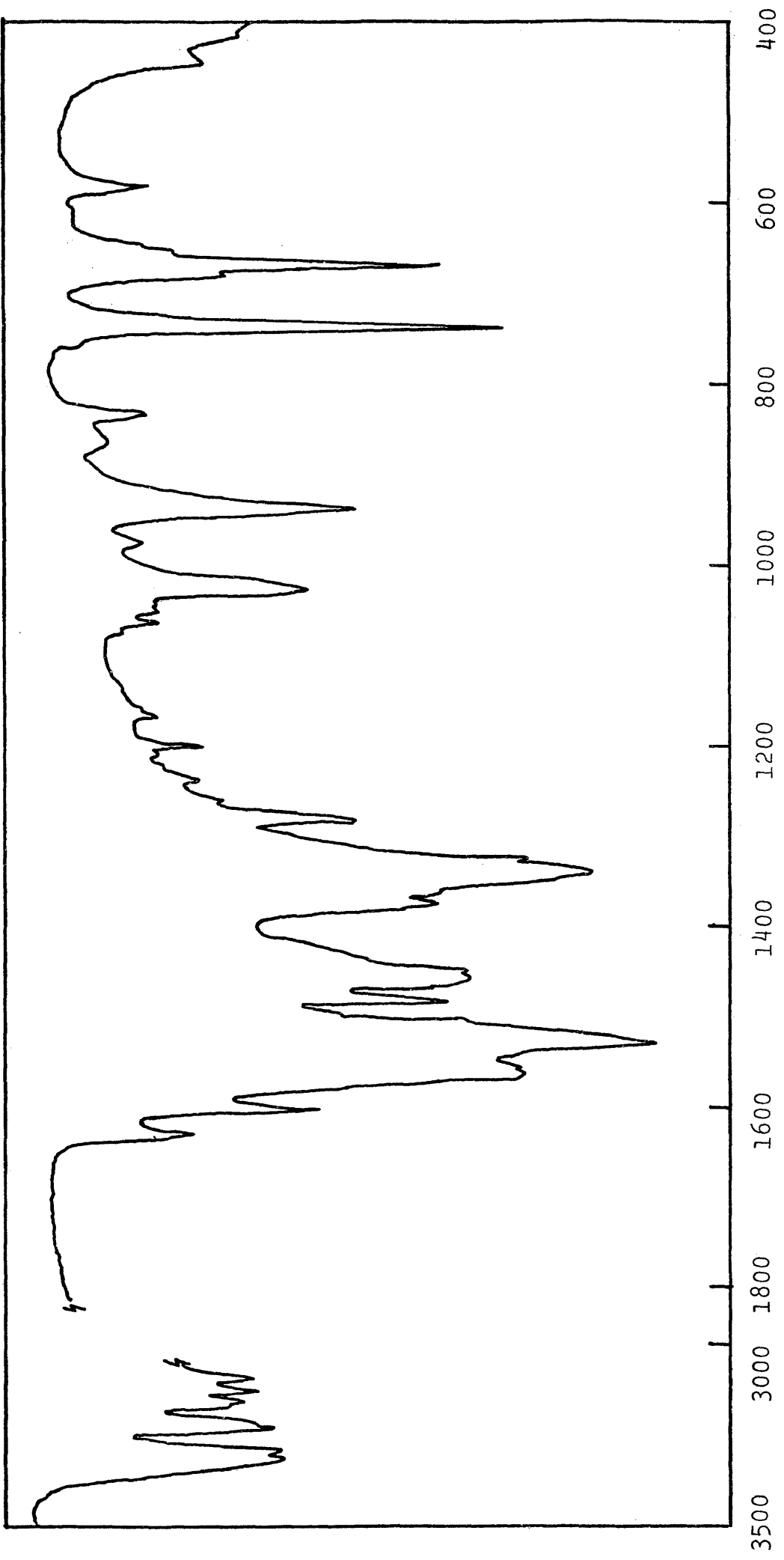


Figure 9.

Infrared spectrum of pyridinium tetrachloro-(2,4-pentanedionato)stannate(IV) as a Mull in Nujol

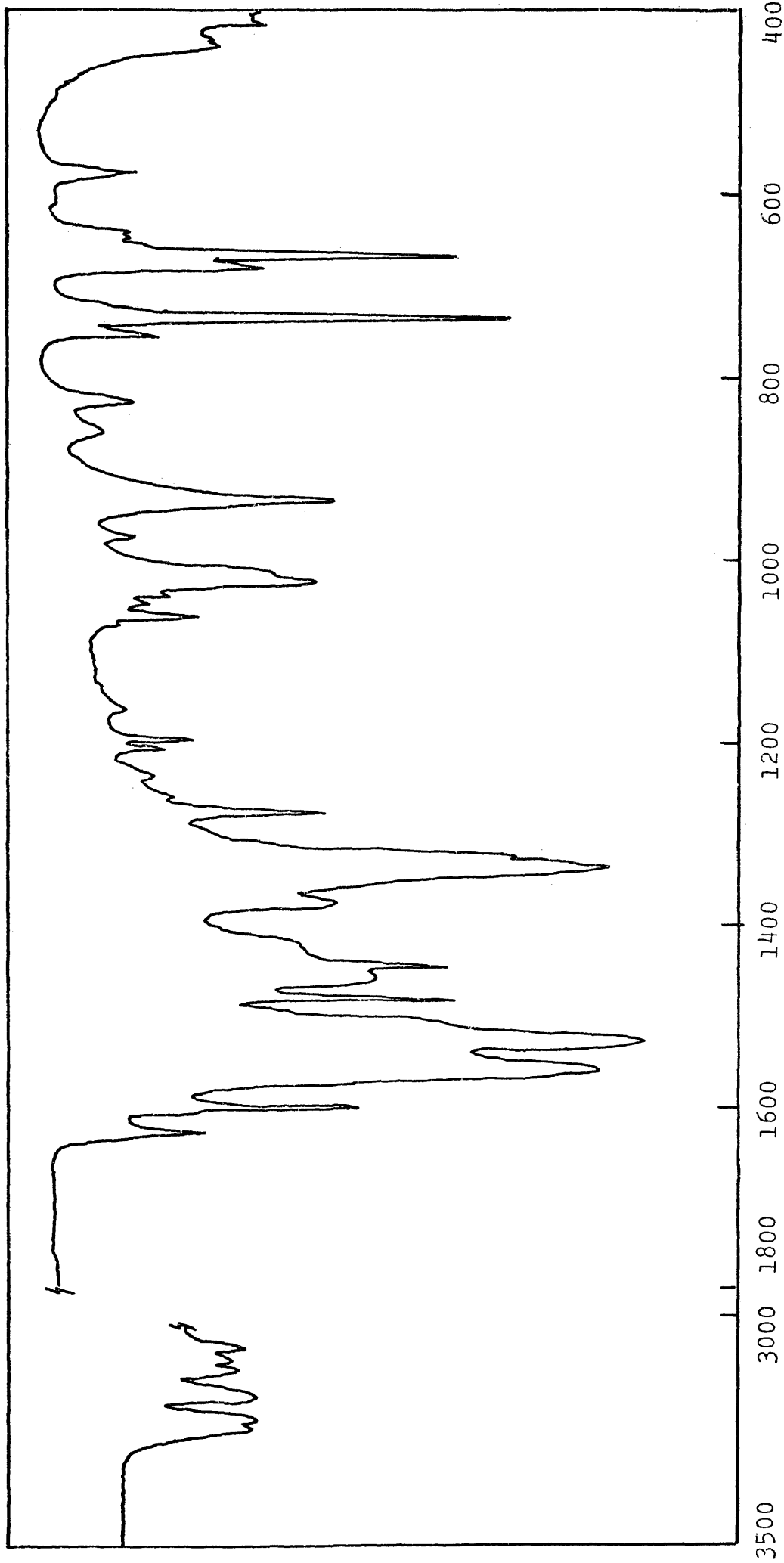


Figure 10.  
Infrared spectrum of pyridinium tetrabromo-  
(2,4-pentanedionate)stannate(IV) as a  
Mull in Nujol

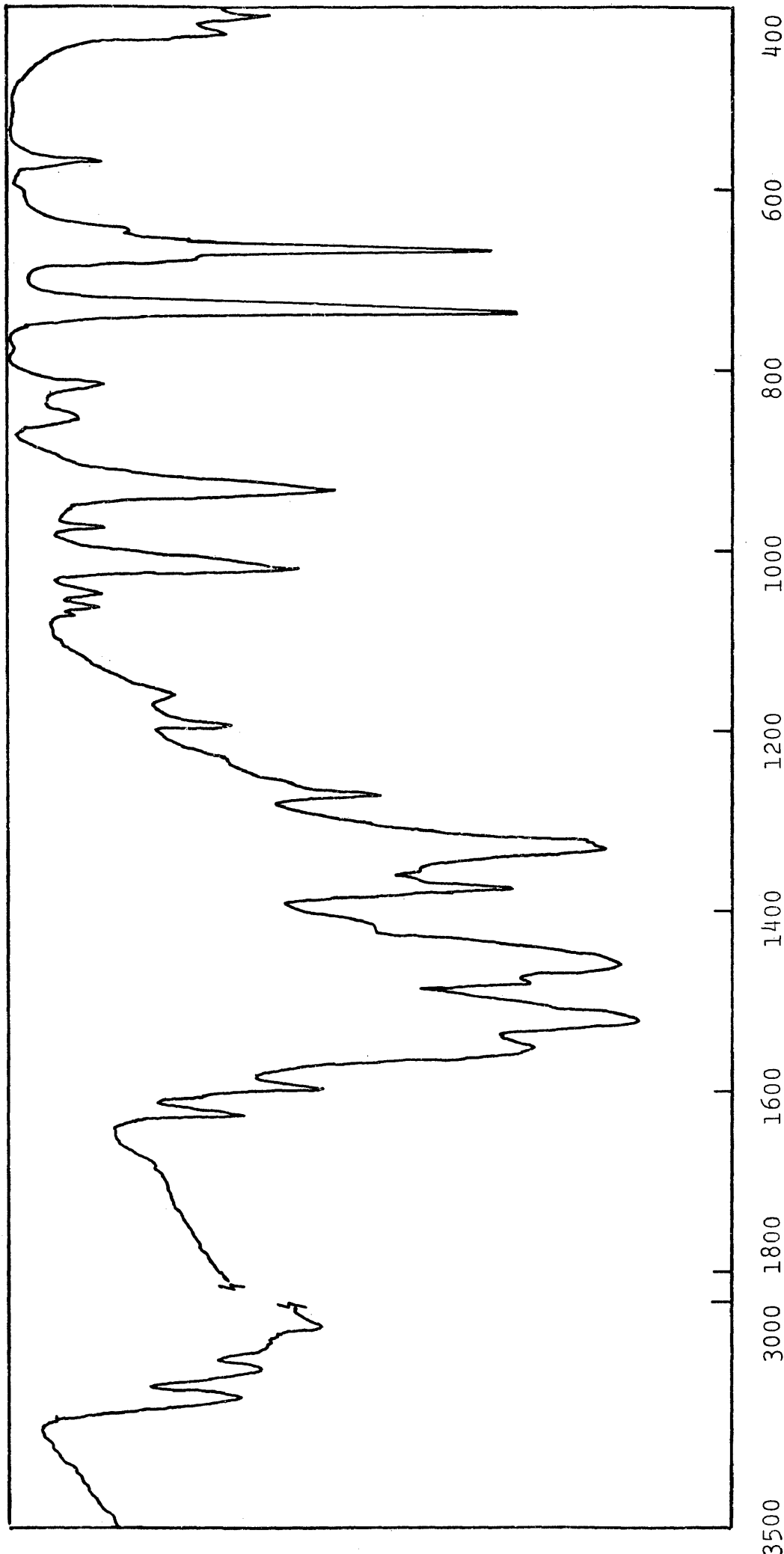


Figure 11.

Infrared spectrum of pyridinium tetraiodo-  
(2,4-pentanedionato)stannate(IV) as a  
Mull in Nujol

Table I  
Some Properties of the Tin Salts

Complex	Mp, °C	Color
Pyridinium Salts		
$[\text{Cl}_4\text{Sn}(\text{C}_5\text{H}_7\text{O}_2)]$	248-252	white
$[\text{Br}_4\text{Sn}(\text{C}_5\text{H}_7\text{O}_2)]$	242-244	off-white
$[\text{I}_4\text{Sn}(\text{C}_5\text{H}_7\text{O}_2)]$	164-168	red-orange
Triethylammonium Salts		
$[\text{Cl}_4\text{Sn}(\text{C}_5\text{H}_7\text{O}_2)]$	122-125	white
$[\text{Br}_4\text{Sn}(\text{C}_5\text{H}_7\text{O}_2)]$	174-177	off-white
$[\text{I}_4\text{Sn}(\text{C}_5\text{H}_7\text{O}_2)]$	131-134	red-orange

Table II

## Nmr and Mössbauer Spectral Data

Complex	Nmr Data <sup>a</sup> (ppm)		Mössbauer Data <sup>b</sup> (mm/sec)	
	<u>-CH<sub>3</sub></u>	<u>=CH-</u>	<u>isomer shift</u>	<u>line width</u>
<b>Pyridinium Salts</b>				
[Cl <sub>4</sub> Sn(C <sub>5</sub> H <sub>7</sub> O <sub>2</sub> )]	-2.06	-5.70	0.47	0.80
[Br <sub>4</sub> Sn(C <sub>5</sub> H <sub>7</sub> O <sub>2</sub> )]	-2.04	-5.71	0.70	0.90
[I <sub>4</sub> Sn(C <sub>5</sub> H <sub>7</sub> O <sub>2</sub> )]	-2.01	-5.77	1.10	0.85
<b>Triethylammonium Salts</b>				
[Cl <sub>4</sub> Sn(C <sub>5</sub> H <sub>7</sub> O <sub>2</sub> )]	-2.06	-5.69	0.43	0.80
[Br <sub>4</sub> Sn(C <sub>5</sub> H <sub>7</sub> O <sub>2</sub> )]	-2.05	-5.70	0.70	0.90
[I <sub>4</sub> Sn(C <sub>5</sub> H <sub>7</sub> O <sub>2</sub> )]	-2.00	-5.74	1.10	0.90

a: Solvent---nitromethane. Concentration ca.  $5 \times 10^{-2}$  M, shifts relative to measure with internal TMS.  
 b: respect to the centroid of the BaSnO<sub>2</sub> peak---mm.

Table III

## Conductivity Measurements

Compounds	Concentration (mole lit <sup>-1</sup> )	$\Lambda_m$ (cm <sup>2</sup> mole <sup>-1</sup> ohm <sup>-1</sup> )
[SnCl <sub>4</sub> (acac)]C <sub>5</sub> H <sub>5</sub> NH	$0.99 \times 10^{-2}$	17.148, 19.852, 25.455, 26.917,
	$9.88 \times 10^{-4}$ , $3.95 \times 10^{-3}$ , $1.98 \times 10^{-3}$ , $9.88 \times 10^{-5}$ , $9.88 \times 10^{-5}$	29.566
[SnBr <sub>4</sub> (acac)]C <sub>5</sub> H <sub>5</sub> NH	$9.23 \times 10^{-3}$	16.983, 21.517, 23.458, 26.901,
	$7.39 \times 10^{-5}$ , $1.85 \times 10^{-6}$ , $3.69 \times 10^{-4}$ , $7.39 \times 10^{-5}$ , $7.39 \times 10^{-5}$	26.924
[SnI <sub>4</sub> (acac)]C <sub>5</sub> H <sub>5</sub> NH	$0.52 \times 10^{-2}$	13.326, 14.324, 15.718, 16.812,
	$5.24 \times 10^{-4}$ , $2.09 \times 10^{-3}$ , $1.05 \times 10^{-5}$ , $5.24 \times 10^{-4}$ , $1.05 \times 10^{-4}$ , $1.05 \times 10^{-5}$	20.504, 29.685
[SnCl <sub>4</sub> (acac)](C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> NH	$1.40 \times 10^{-2}$	14.766, 22.517, 25.343, 24.477,
	$1.13 \times 10^{-4}$ , $2.81 \times 10^{-3}$ , $5.63 \times 10^{-4}$ , $1.13 \times 10^{-4}$ , $2.25 \times 10^{-5}$	26.445
[SnBr <sub>4</sub> (acac)](C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> NH	$9.44 \times 10^{-3}$	17.767, 23.234, 24.402, 27.553,
	$7.55 \times 10^{-5}$ , $1.89 \times 10^{-5}$ , $3.78 \times 10^{-4}$ , $7.55 \times 10^{-5}$ , $1.51 \times 10^{-5}$	28.822
[SnI <sub>4</sub> (acac)](C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> NH	$8.52 \times 10^{-3}$	16.994, 22.039, 24.927, 27.369,
	$6.82 \times 10^{-5}$ , $1.71 \times 10^{-5}$ , $3.41 \times 10^{-4}$ , $6.82 \times 10^{-5}$ , $1.36 \times 10^{-5}$	36.642

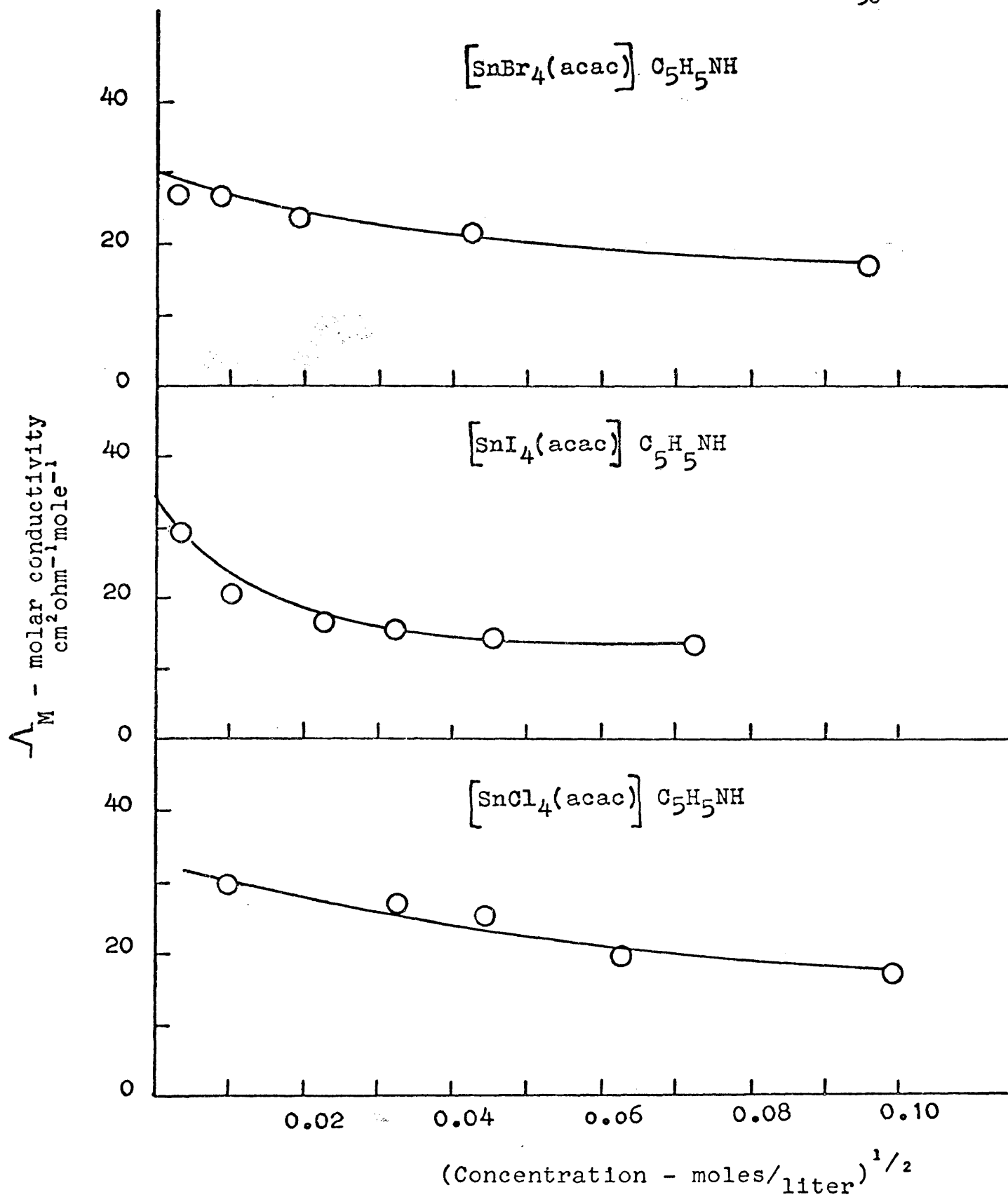


Figure 12.--Molar conductance of pyridinium tetrahalo(2,4-pentanedionato)stannate(IV) salts in nitrobenzene

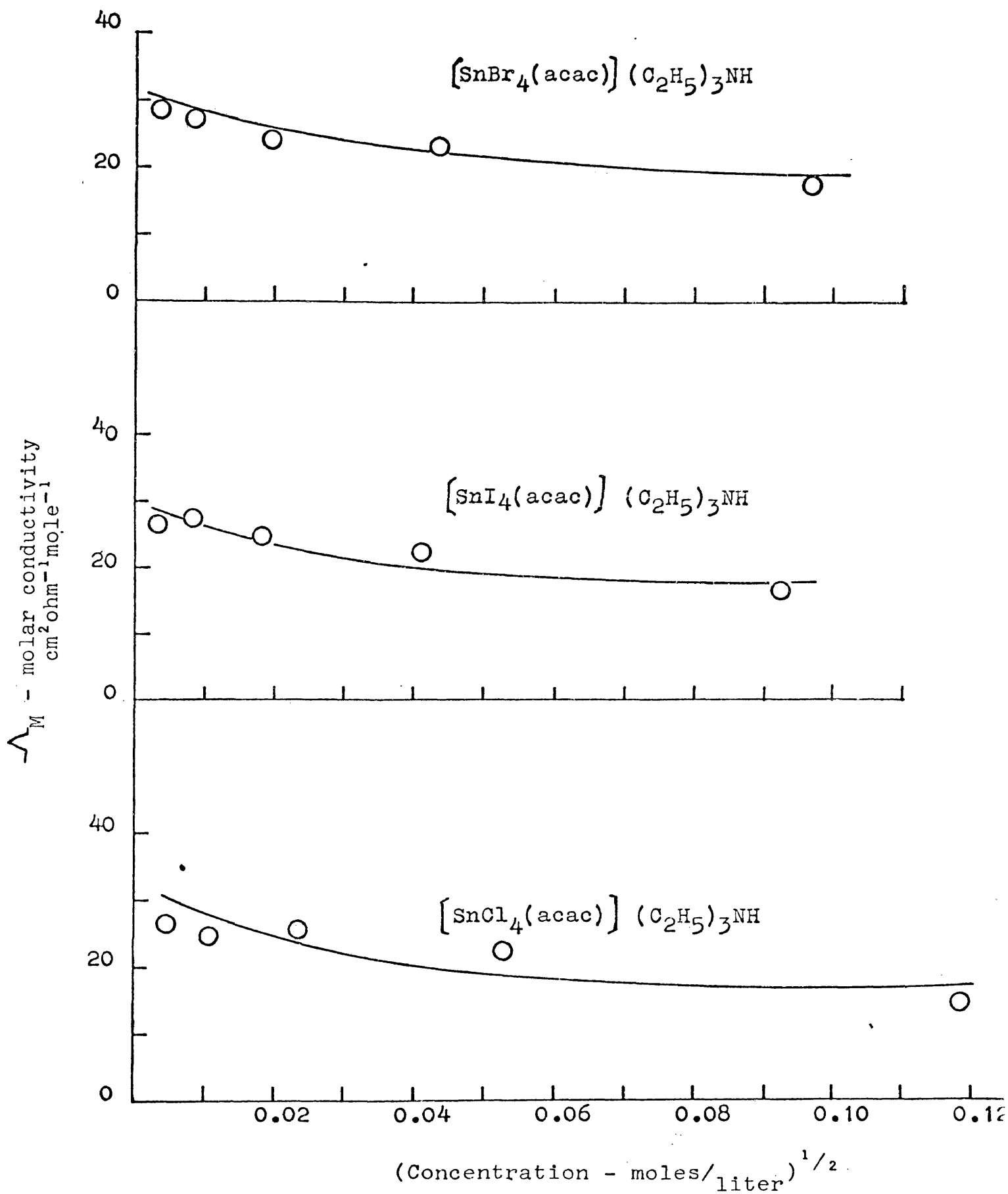


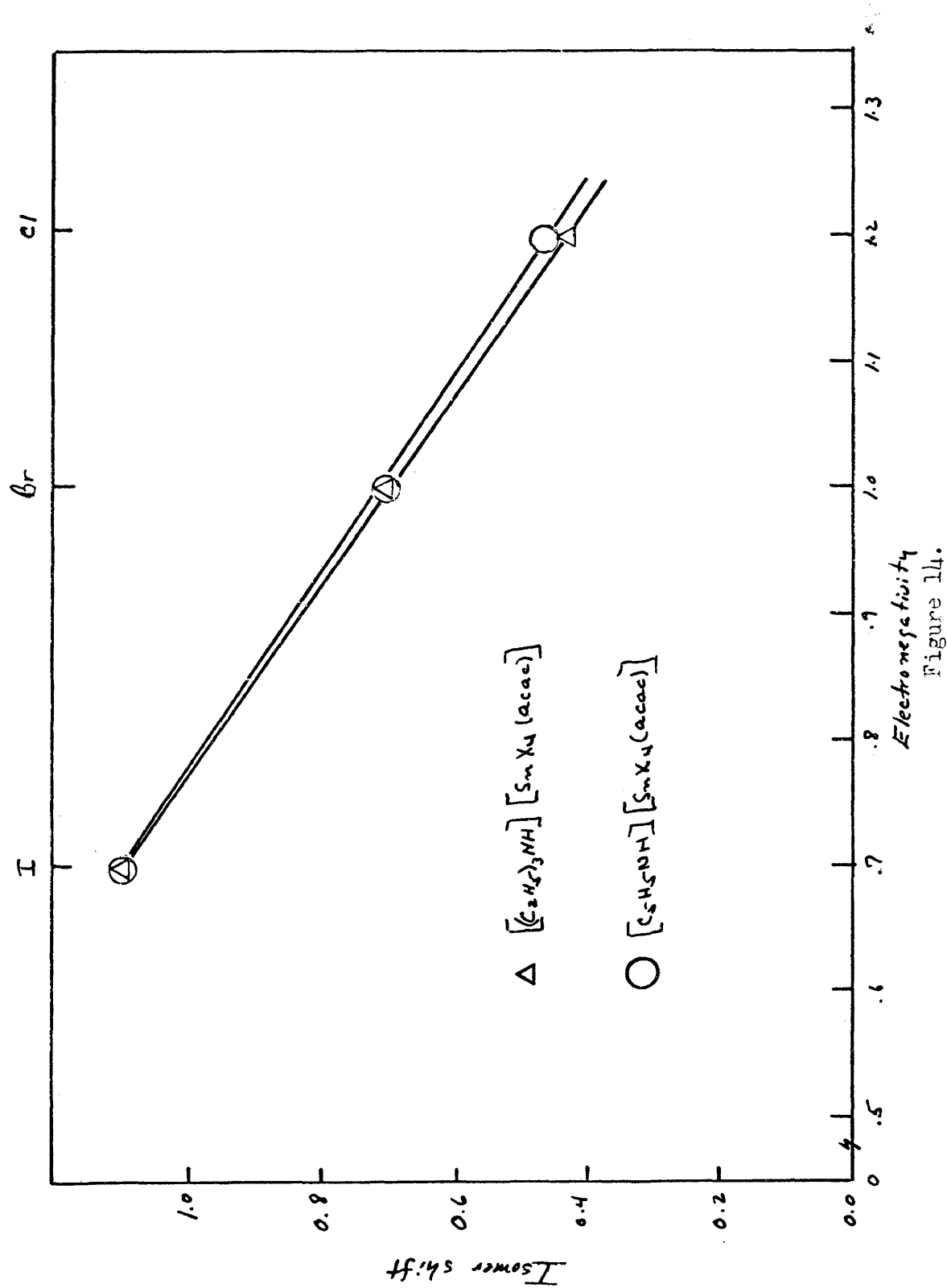
Figure 13.--Molar conductance of triethylammonium tetrahalo(2,4-pentanedionato)stannate(IV) salts in nitrobenzene.

( $\nu_{\text{N-H}}$ ) clearly show the presence of pyridinium and triethylammonium ions. Characteristic enolate bands in the 1600-1500  $\text{cm}^{-1}$  region ( $\nu_{\text{C}=\text{O}}$  and  $\nu_{\text{C}=\text{C}}$ ) unambiguously indicate the presence of oxygen-chelated 2,4-pentanedionate ligand.

Nmr spectra obtained in studying the tin tetrachloride-2,4-pentanedione-amine systems are set out in Table II. The spectra were run as dilute ( $5 \times 10^{-2}$  M) solution in nitromethane, if the compound is soluble in the solvent, or saturated solutions in nitromethane, if the compound is not quite soluble, at room temperature. The nmr data of these compounds are also consistent with the presence of the enolate ligands. For the  $\text{CH}_3$ - and =CH- protons each exhibits one peak.

All conductivity measurements which were made in nitrobenzene at room temperature presented in Table III. Figures 12 and 13 are consistent with the complex being a 1:1 electrolyte. All data are consistent with the formulation of the six compounds of empirical formula  $[\text{M}][\text{X}_4\text{Sn}(\text{C}_5\text{H}_7\text{O}_2)]$  as pyridinium or triethylammonium tetrahalo(2,4-pentanedionato)stannate(IV) salts.

Tin-119 Mössbauer spectral data are presented in Table II. Although the complexes do not have cubic symmetry, no quadrupole splittings were observed. This fact is consistent with the observations of other workers that octahedrally coordinated nitrogen, oxygen, and halide atoms are not sufficiently different in electrical properties so as to generate significant electrical asymmetry at the tin nucleus.<sup>17b</sup> The observed isomer shifts correlate well with the Pauling electronegativity values for the halogens, i.e. a linear increase in chemical shift with decrease in electronegativity (Figure 14). For the pyridinium series a least square analysis generates an equation  $I_s = -1.26X + 4.46$ <sup>18</sup>; for



Plots of isomer shifts versus Pauling electronegativity values for the pyridinium and triethylammonium tetrahalo(2,4-pentanedionato)-stannate(IV) salts

Figure 14.

the triethylammonium series the equation is  $I_s = -1.34X + 4.66$ .

Besides the formulation of the six compounds of empirical formula  $[M][X_4Sn(C_5H_7O_2)]$  as pyridinium or triethylammonium tetrahalo(2,4-pentanedionato)stannate(IV) salts, several products which hypothetically could be obtained from the tin tetrahalide -2,4-pentanedione-amine systems are illustrated at following page (Figure 15).

The possibility that  $[M][X_4Sn(C_5H_7O_2)]$  ( $M = B-H$ ) complexes were stoichiometric mixtures of either  $MCl$  and  $X_3Sn(C_5H_7O_2)$  or  $[M_2][SnX_6]$  and the well-known disubstituted derivatives  $X_2Sn(C_5H_7O_2)_2$  was rejected for several reasons. The possibility of having isolated an  $X_3Sn(C_5H_7O_2)$  complex seems remote since no success has been reported in obtaining the mono-substituted derivative by direct reaction of tin tetrachloride and 2,4-pentanedione.<sup>19</sup> Furthermore, two of the complexes (see Table I) isolated have melting points substantially higher than what is expected for the ammonium halides, e.g.  $C_5H_5NHCl$  melts ca.  $140^\circ$ --the chloro complex melts at ca.  $250^\circ$ . Also for a mixture of  $MX$  and  $X_3Sn(C_5H_7O_2)$ , the molar conductivity values should be approximately one-half those expected for 1:1 electrolytes; all values appear to be in the expected range.<sup>20</sup> The possibility that the new compounds are stoichiometric mixture of  $[M_2][SnX_6]$  and  $X_2Sn(C_5H_7O_2)_2$  complexes can be rejected for the following reasons. First, several of the compounds have relatively sharp melting points well above the melting points of the disubstituted product (e.g. the pyridinium salt of tetrachloro(2,4-pentanedionato)stannate(IV) melts at  $248-252^\circ$ , but the disubstituted  $Cl_2Sn(C_5H_7O_2)_2$  has been found to melt at  $203-204^\circ$ ). Secondly, only a single enolate methyl resonance was observed for each complex in the nmr spectra; all of the disubstituted products (except dimethylbis(2,4-pentanedionato)-

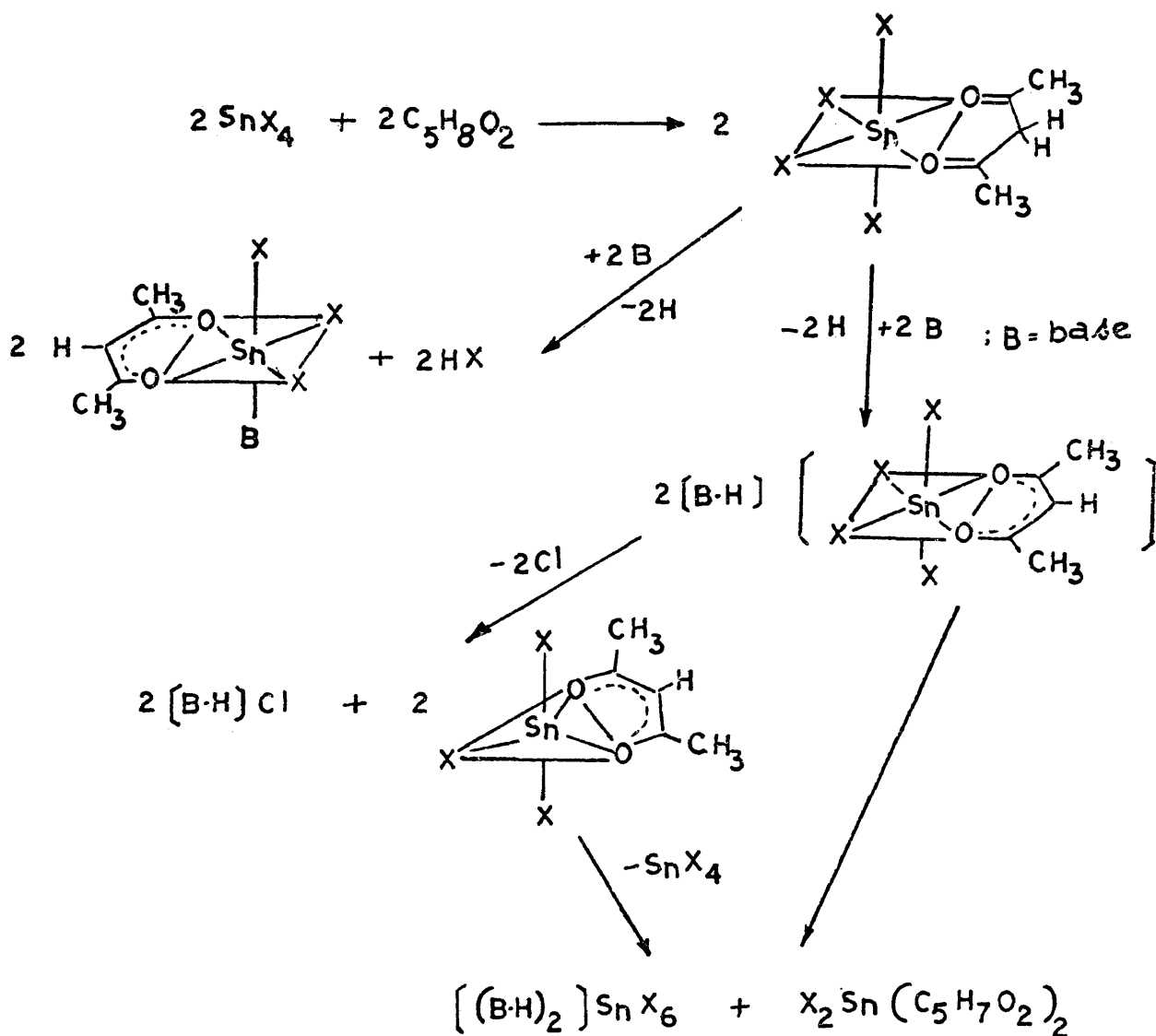


Figure 15.

The possible scheme reactions of tin tetrahalides-2,4-pentanedione-amine system.

tin(IV)). have the cis-configuration and exhibit two enolate methyl resonances at room temperature. Thirdly, the  $\text{Sn}^{119}$  Mössbauer spectra show only a single line of relatively narrow width (see Table II). The  $\text{Cl}_2\text{Sn}(\text{C}_5\text{H}_7\text{O}_2)_2$  compound would consist of a single line with line width 1.15 mm/sec and chemical shift 0.25 mm/sec.<sup>17c</sup>

Attempts were made to extend the reactions of the tin series to germanium and silicon. The analogous anionic complexes were not obtained. Reaction of germanium tetrachloride, phenyltrichlorogermane, and phenyltrichlorosilane with 2,4-pentanedione and pyridine only led to the isolation of the already characterized disubstituted enolate complexes, i.e.  $\text{Cl}_2\text{Ge}(\text{C}_5\text{H}_7\text{O}_2)_2$ <sup>11b,21</sup>  $\text{Cl}(\text{C}_6\text{H}_5)\text{Ge}(\text{C}_5\text{H}_7\text{O}_2)_2$ <sup>22</sup> and  $\text{Cl}(\text{C}_6\text{H}_5)\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_2$ <sup>23</sup>.

The reaction of tetrachlorosilane with 2,4-pentanedione and pyridine yielded the well-known tris(2,4-pentanedionato)silicon(IV) chloride.<sup>21</sup> Thus the formation of the anionic tetrahalo(2,4-pentanedionato) complexes appears to be specific for tin.

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## VITA

KWAI-SAM WONG

Born in Sinhui, Kwangtung, China, July 19, 1946. Graduated from Pui-Ching Middle School, Macao, in June 1965, B.S., Hong Kong Baptist College, Hong Kong, in June 1969. Entered the College of William and Mary in Virginia, September 1970. With the course requirements completed, became a M.A. candidate, May 1971.

