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Preparation and Properties of Some Organotin Nitramines[1]

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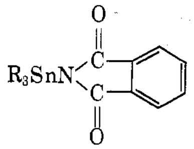
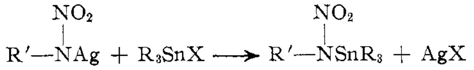
Organotin nitramines, $R_3SnN(NO_2)R$, where R is either a phenyl or an alkyl group, were prepared by metathesis, neutralization, and cleavage reactions. These tin derivatives are colorless to light brown low-melting solids which are stable in air. The infrared and Mössbauer spectra and physical properties suggest that the tin atom exists in a pentacovalent state surrounded by three alkyl groups and a chelated organo nitramine. Chelation of the nitramine probably involves the amino nitrogen and an oxygen.

Articles recently have appeared describing the preparation and properties of compounds containing a tin to nitrogen bond such as the trialkylstannyl dialkylamines $(R_3SnNR'_2)$,[3–6] organotin azides (R_3SnN_3),[6–8] organotin substituted hydrazines $(R_3SnNR'NHR')$,[9] organotin substituted formamides $(R_3SnNR'CHO)$,[10] organotin sulfonamides $(R_3SnNR'SO_2R'')$,[11,12] and organotin carboimides[12]



We have found that a nitrogen to tin bond can be formed by the reaction of nitramines with appropriate organotin compounds. This reaction yields organotin nitramines $(R_3SnN(NO_2)R)$ where R is either phenyl or an alkyl group. The reactivity of these compounds is of interest since organotin amines $(R_3SnNR'_2)$ are quite reactive[3,5,6] toward atmospheric moisture and carbon dioxide, whereas the imidazole derivatives[6] are stable, and yet both of these substances have tin bonded to nitrogen. We have prepared a series of organotin nitramines by three methods.

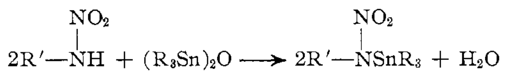
Method A. Metathesis



$$R'\text{—}\overset{NO_2}{\overset{|}{N}}Ag + R_3SnX \longrightarrow R'\text{—}\overset{NO_2}{\overset{|}{N}}SnR_3 + AgX$$

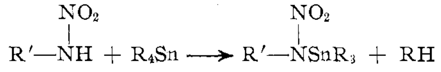
where X = Cl or I; R′, R = C_6H_5 or an alkyl group.

Method B. Neutralization



$$2R'\text{—}\overset{NO_2}{\overset{|}{N}}H + (R_3Sn)_2O \longrightarrow 2R'\text{—}\overset{NO_2}{\overset{|}{N}}SnR_3 + H_2O$$

Method C. Cleavage



$$R'\text{—}\overset{NO_2}{\overset{|}{N}}H + R_4Sn \longrightarrow R'\text{—}\overset{NO_2}{\overset{|}{N}}SnR_3 + RH$$

Experimental

Materials.—Solvents such as hexane, petroleum ether (b.p. 40–60°), and benzene were dried over sodium. Tetraethyltin was obtained from Peninsular ChemResearch, Inc. Triisopropyltin oxide and trimethyltin chloride were kindly furnished by Metal and Thermite Corp. The triphenyltin chloride was Eastman White Label. Triethyltin iodide was prepared from tetraethyltin.[13] The nitrobenzene[14] used for conductivity measurements was chromatographed Fisher reagent grade and had a specific conductance of less than 10^{-10} ohm^{-1} cm.$^{-1}$.

Preparation of the N-Nitroaminoalkanes and Their Silver Salts.—The corresponding alkylamine was converted to the N-nitrocarbamate,[15] which is readily converted to the desired N-nitroaminoalkane according to the procedure of Franchimont.[16] The N-nitroaminoalkanes were purified by vacuum distillation at approximately 10 mm. pressure. N-Nitroaniline was prepared according to the procedure of Bamberger.[17] The alkyl and phenyl nitramines were converted to their silver salts by the procedure of Thomas.[18]

Preparation of N-Trialkylstannyl-N-nitroaminoalkanes and the Corresponding Phenyl Compounds.—Typically, three procedures were employed as reported below (*cf.* Table I).

(A) In a 250-ml. round-bottom flask equipped with a condenser were placed 6.67 g. (33.8 mmoles) of the N-nitroaminoethane silver salt and 11.30 g. (33.9 mmoles) of triethyltin iodide and 100 ml. of benzene. This heterogeneous mixture was heated under reflux for 13 hr. and filtered while hot, and the benzene was removed by distillation to yield 9.25 g. of crude product (m.p. 109–111°). The product was purified by sublimation at 80–90° (0.1 mm.); yield 6.31 g., 21.4 mmoles, 63.3%; m.p. 112–113.5°. Some of the products were purified by recrystallization (*cf.* Table I).

(B) To 2.31 g. (19.6 mmoles) of 2-methyl-N-nitro-2-aminopropane was added 5.00 g. (9.78 mmoles) of triisopropyltin oxide in 50 ml. of dry benzene. This mixture was heated under reflux in a 100-ml. round-bottom flask equipped with a Dean–Stark trap and condenser until 0.12 ml. of water was collected. The solution was filtered and solvent was removed by distillation, yielding 6.83 g. of crude product. Upon sublimation at 70° (1 mm.), 6.46 g. (91% yield) of material was collected; m.p. 78–82°.

(C) Tetraethyltin (2.37 g., 10.0 mmoles) was boiled under reflux with 1.00 g. (9.6 mmoles) of N-nitro-2-aminopropane for

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TABLE I

ORGANOTIN NITRAMINES

Compound $R_3SnN(NO_2)R'$		Elemental analysis, %								Yield,	Equiv. wt.[b]		M.p.,[c]
		C		H		Sn[a]		N		%			°C.
R	R'	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found		Calcd.	Found	
CH_3	CH_3[e]	20.1	20.9	5.1	5.1	49.7	49.5	11.7	12.1	71[g,j]	238.9	238.5	155–156
C_2H_5	CH_3	29.9	30.1	6.5	6.2	42.3	42.1	10.0	10.0	10[i,k] 66[g,k]	280.9	280.5	109.5–110.5
C_2H_5	C_2H_5[d]	32.6	32.4	6.8	6.9	40.2	40.3	9.5	9.3	63[g,k]	294.9	294.1	108–109.5
C_2H_5	i-C_3H_7	35.0	34.9	7.2	7.1	38.4	38.2	9.1	8.8	89[g,k] 10[i,l]	308.9	309.0	144–144.5
C_2H_5	t-C_4H_9	37.2	37.1	7.5	7.5	36.7	36.9	8.7	9.2	80[g,j]	323.0	325.5	179–180.5
C_2H_5	C_6H_5	42.0	40.1	5.9	6.0	34.6	34.7	8.2	8.4	48[g,m]	343.0	344.9	138–139
i-C_3H_7	CH_3	37.2	37.8	7.5	7.5	36.7	36.6	8.7	8.9	68[h,k]	323.0	324.0	69–72
i-C_3H_7	t-C_4H_9[e]	42.8	42.8	8.3	8.3	32.5	32.6	7.7	7.4	91[h,k]	365.1	373.5	77–81
C_6H_5	CH_3[e]	53.7	53.5	4.3	4.4	27.9	27.6	6.6	6.7	63[g,m]	425.1	424.0	142–144
C_6H_5	C_6H_5	59.2	59.2	4.1	4.2	24.4	24.6	5.8	6.2	10[g,m]	487.1	484.0	138–139[f]

[a] Tin determined as stannic oxide after use of fuming nitric and sulfuric acids on sample. [b] Titration with standard ethanolic sodium hydroxide with phenolphthalein indicator. Method suggested by Dr. H. H. Anderson. [c] All melting points are uncorrected. [d] Determined cryoscopic molecular weight using camphor (305) and benzene (304). [e] Cryoscopic molecular weight using camphor agreed with theoretical within ±5%. [f] Melts with decomposition. [g] Method A was used for preparation. [h] Method B was used for preparation. [i] Method C was used for preparation. [j] Product was recrystallized from benzene for purification. [k] Product was sublimed for purification. [l] Product was recrystallized from petroleum ether for purification. [m] Product was recrystallized from hexane for purification.

15 min., cooled, and refluxed for an additional 5 min. The mixture was cooled and the solid collected. The crude N-triethylstannyl-N-nitro-2-aminopropane was recrystallized from dry low-boiling (40–60°) petroleum ether (yield 0.24 g., 10%); m.p. 144–144.5°.

All of the compounds isolated were colorless solids, except N-triphenylstannyl-N-nitroaniline, which was light brown.

Conductance.—The conductance of N-trimethylstannyl-N-nitroaminomethane at 25.5 ± 0.5° in nitrobenzene was determined using a Wayne–Kerr Type B-221 Universal Bridge.

Infrared Spectra.—Infrared spectra reported in this paper were of solids in potassium bromide disks using a Beckman Model IR-7 spectrophotometer. A Perkin-Elmer Model 421 spectrophotometer was used for the 650 to 400 cm.$^{-1}$ region of N-trimethylstannyl-N-nitroaminomethane, N-triethylstannyl-N-nitro-2-methyl-2-aminopropane, and N-triethylstannyl-N-nitroaminomethane. The infrared spectrum of N-trimethylstannyl-N-nitroaminomethane also was determined in Nujol; the region from 2000 to 650 cm.$^{-1}$ was similar to that obtained in potassium bromide except for slight band shifts. In the 650 to 400 cm.$^{-1}$ region, the spectra were very similar except that a strong band appears at 628 cm.$^{-1}$ in Nujol, whereas only a possible shoulder at 630 cm.$^{-1}$ was found in the potassium bromide disk.

N-Triethylstannyl-N-nitroaminomethane: 1585 w, 1467 v, 1440 s, 1424 sh, 1375 v, 1327 s, 1263 sh, 1232 m, 1187 m, 1108 v, 1012 s, 951 s, 768 m, 720 m, 680 s, 660 w, 639 s, 530 m, 515 s, 489 m, 400 w (br) cm.$^{-1}$.

N-Triethylstannyl-N-nitroaminoethane: 1486 v, 1458 m, 1435 m, 1419 m, 1382 m, 1378 sh, 1335 s, 1260 v, 1250 sh, 1228 m, 1187 m, 1145 w, 1107 m, 1082 m, 1015 sh, 995 s, 965 m, 956 m, 912 m, 726 s, 676 v cm.$^{-1}$.

N-Triethylstannyl-N-nitro-2-aminopropane: 1477 v, 1455 sh, 1419 s, 1384 m, 1378 w, 1363 m, 1325 s, 1280 sh, 1259 v, 1247 v, 1229 v, 1185 w, 1166 m, 1129 m, 1033 v, 1018 sh, 965 m, 955 m, 920 m, 868 w, 732 m, 676 s cm.$^{-1}$.

N-Triethylstannyl-N-nitro-2-methyl-2-aminopropane: 1478 v, 1452 s, 1418 s, 1392 w, 1375 w, 1362 s, 1330 v, 1290 sh, 1262 v, 1235 sh, 1222 s, 1195 sh, 1185 s, 1050 s, 1013 v, 965 w, 955 m, 928 m, 907 w, 795 w, 735 s, 682 s, 675 sh, 665 sh, 592 sh, 517 s, 526 sh, 492 w, 477 m, 385 w, 358 m cm.$^{-1}$.

N-Triethylstannyl-N-nitroaniline: 1590 w, 1587 w, 1580 w, 1575 w, 1497 sh, 1482 s, 1457 v, 1450 m, 1445 v, 1432 m, 1415 s, 1377 m, 1313 v, 1310 sh, 1280 sh, 1257 s, 1245 s, 1230 s, 1220 sh, 1210 m, 1205 m, 1192 m, 1170 m., 1157 sh, 1076 w, 1042 w, 1022 sh, 1012 sh, 1002 s, 993 sh, 988 s, 965 m, 932 m, 912 w, 901 w, 775 m, 765 s, 745 w, 735 m, 725 m, 693 sh, 688 s, 677 s, 669 s cm.$^{-1}$.

N-Triisopropylstannyl-N-nitroaminomethane: 1497 v, 1458 v, 1428 v, 1404 v, 1380 v, 1364 s, 1326 v, 1305 sh, 1266 v, 1206 s, 1155 s, 1139 s, 1090 w, 1069 m, 992 m, 978 w, 932 m, 920 w, 875 m, 772 m, 735 w, 710 m, 670 w cm.$^{-1}$.

N-Triisopropylstannyl-N-nitro-2-methyl-2-aminopropane: 1480 v, 1468 v, 1444 s, 1412 sh, 1382 w, 1360 s, 1355 sh, 1318 w, 1290 sh, 1260 v, 1230 sh, 1221 m, 1207 sh, 1190 v, 1155 w, 1090 v, 1080 w, 1057 sh, 1047 m, 1020 sh, 1002 v, 990 s, 925 w, 917 m, 872 m, 789 w, 737 m, 729 s cm.$^{-1}$.

N-Triphenylstannyl-N-nitroaminomethane: 1578 w, 1570 w, 1482 s, 1465 v, 1442 m, 1430 s, 1377 v, 1363 sh, 1338 s, 1323 v, 1319 v, 1304 s, 1261 w, 1195 sh, 1185 w, 1157 w, 1100 s, 1075 m, 1065 w, 1020 m, 997 m, 955 m, 914 w, 761 m, 732 v, 719 m, 697 v cm.$^{-1}$.

N-Triphenylstannyl-N-nitroaniline: 1592 w, 1585 w, 1578 w, 1487 v, 1481 s, 1474 v, 1455 sh, 1430 v, 1375 sh, 1335 m, 1308 sh, 1300 s, 1254 s, 1242 sh, 1235 s, 1224 s, 1192 m, 1170 w, 1160 w, 1075 s, 1067 m, 1036 w, 1021 m, 994 s, 973 w, 925 m, 912 w, 895 w, 879 w, 853 w, 770 m, 762 m, 759 m, 740 sh, 730 v, 722 s, 718 s, 696 v, 688 s, 668 m, 662 w cm.$^{-1}$.

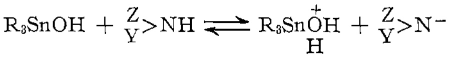
Discussion

In terms of yield (Table I) the metathesis and neutralization reactions are the preferred means of synthesis. There is no apparent effect upon the yield when one varies the structure of the alkyl groups. When the alkyl groups are replaced by a phenyl group a noticeable drop in yield occurs. Several unsuccessful attempts were made to prepare N-triphenylstannyl-N-nitro-2-methyl-2-aminopropane by the metathesis and neutralization reactions.

The neutralization reaction between compounds containing an acidic proton attached to nitrogen and organotin oxides is considered to be general and provides a route to compounds containing a tin to nitrogen bond. Examples of acidic nitrogen compounds forming stable derivatives with bis(trialkyltin) oxides and hydroxides are phthalimide,[12] *p*-toluenesulfonamide,[12] pyrrole,[6] and imidazole and its derivatives.[6] A plausible mechanism for this type of reaction might be

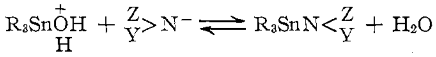
$$(R_3Sn)_2O + {}^{Z}_{Y}{>}NH \rightleftharpoons \underset{\text{I}}{(R_3Sn)_2\overset{+}{O}H} + \underset{\text{II}}{{}^{Z}_{Y}{>}N^-}$$

$$(R_3Sn)_2\overset{+}{O}H + {}^{Z}_{Y}{>}N^- \longrightarrow R_3SnN{<}^{Z}_{Y} + R_3SnOH$$



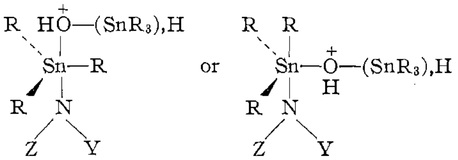
$$R_3SnOH + {}^{Z}_{Y}{>}NH \rightleftharpoons R_3Sn\overset{+}{\underset{H}{O}}H + {}^{Z}_{Y}{>}N^-$$

III



$$R_3Sn\overset{+}{\underset{H}{O}}H + {}^{Z}_{Y}{>}N^- \rightleftharpoons R_3SnN{<}^{Z}_{Y} + H_2O$$

The reaction between the conjugate base of the amine (II) and the protonated trialkyltin oxide (I) or protonated trialkyltin hydroxide (III) can be considered to be a simple nucleophilic displacement or possibly could involve formation of an intermediate pentacovalent species (IV). A similar mechanism has been



IV

suggested for the solvolysis of trialkyltin chlorides.[19]

The cleavage of an ethyl group from tetraethyltin is quite facile. The reported yields are relatively low, but no attempt was made to determine the optimum reaction conditions. This is the first reported case where a compound with an acidic hydrogen bonded to a nitrogen participates in this type of reaction.

The products isolated by the different methods of synthesis proved to be identical as determined by infrared spectra and mixture melting points.

Structure of N-Trialkylstannyl-N-nitroaminoalkanes.—The infrared absorption spectra in the 2000 to 650 cm.$^{-1}$ range of the solid derivatives show the characteristic absorption of an ionic N-nitroaminoalkane salt, such as the silver and ammonium salts of N-nitroaminomethane (*cf.* Table II).[20] The stretching vibrations associated with the ionic (NNO_2) grouping are designated as $\nu'_{as}(NNO_2)$, $\nu''_{as}(NNO_2)$, and $\nu_{sym}(NNO_2)$ and appear for the silver salt at 1359, 1310, and 946 cm.$^{-1}$ (ammonium salt 1351, 1274, and 985 cm.$^{-1}$). These bands also are exhibited by N-trialkylstannyl and N-triphenylstannyl-N-nitroaminoalkanes. In N-methylstannyl-N-nitroaminomethane these absorptions appear at 1373, 1319, and 950 cm.$^{-1}$. The infrared spectra do not show the typical covalent alkyl nitramine absorption.[20,21] The infrared spectra seem to indicate either a trialkyltin cation or pentacovalent tin such as is found in the trialkyltin carboxylates[22] rather than a simple covalent structure.

TABLE II

INFRARED SPECTRA (CM.$^{-1}$) OF N-TRIMETHYLSTANNYL-N-NITROAMINOMETHANE AND THE SILVER SALT OF N-NITROAMINOMETHANE

Assignments	$(CH_3)_3SnN(NO_2)CH_3$[a]	$Ag(NO_2)\cdot NCH_3$[b]
	1592 w[c]	
CH_3 asym. deform.	1470 v	1466
CH_3 sym. deform.	1443 m	1420 s
NNO_2 asym. str. ($\nu'_{as}NNO_2$)	1375 v	1359 v
CH_3 sym. deform.	1358 sh	
NNO_2 asym. str. ($\nu''_{as}NNO_2$)	1319 v	1307 v
	1250 sh	1255 m
CH_3 (–Sn) sym. deform.	1198 w	
CH_3 (–N) rock	1189 m	1172 m
C–N str.	1103 s	1060 s
NNO_2 sym. str. ($\nu_{sym}NNO_2$)	949 s	945 m
CH_3 (–Sn) rock	775 v	
NNO_2 wag	764 s	734 s
	714 m	
NO_2 def.	709 m	722 m
	700 w	
NO_2 rock	644 s	642
	630 sh	
Sn–C str.	556 m	
	541 m	
	512 w	
	395 w[d]	

[a] Abbreviations: v, very strong; s, strong; m, medium; w, weak; sh, shoulder. [b] N. Jonathan, *J. Mol. Spectry.*, **5**, 101 (1960). [c] Very weak, probably an impurity. [d] Broad band with several small peaks.

A distinction between an ionic or pentacovalent structure of these compounds may be made from conductivity measurements in nitrobenzene. The specific conductivity of N-trimethylstannyl-N-nitroaminomethane was determined to be 1.394×10^{-6} and 6.949×10^{-7} ohm^{-1} cm.$^{-1}$ for solutions of 0.48926 g. in 47.585 ml. and in 67.958 ml., respectively. An approximate specific conductance of a 0.1 *M* solution was 6.1×10^{-6} ohm^{-1} cm.$^{-1}$. The low conductivity suggests this substance has very little tendency to ionize in a solvent of relatively high dielectric constant, and therefore it is probably not ionic. This view is corroborated by the fact that these organotin derivatives possess relatively low melting points.

The Mössbauer spectrum[23] of N-triethylstannyl-N-nitroaminomethane at 78°K. *vs.* $Sn^{119m}O_2$ at 296°K. shows two well-resolved peaks separated by 3.53 mm. sec.$^{-1}$ which were shifted 1.49_0 mm. sec.$^{-1}$ from zero velocity. The ρ value, which is the ratio of quadrupole splitting to the isomer shift as calculated from these quantities, is 2.37_3. No resonant absorption was detected at room temperature. These factors suggest the tin atom is five-coordinate.

Examination of the infrared spectra in the 650 to 400 cm.$^{-1}$ region of several compounds shows at least three absorption bands. The simplest compound, N-trimethylstannyl-N-nitroaminomethane, has bands at 556, 541, and 512 cm.$^{-1}$. Typical assignments for tin–methyl asymmetric and symmetric stretching vibrations as found in trimethyltin chloride are 545 and 514 cm.$^{-1}$, respectively.[24] These are in good agreement with obtained values. The observed spectra are therefore not consistent with an ionic structure; the peak corresponding to the symmetric stretching frequency at approximately 514 cm.$^{-1}$ should be absent.[25,26]

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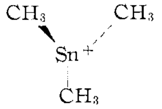
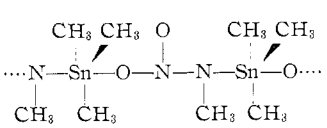
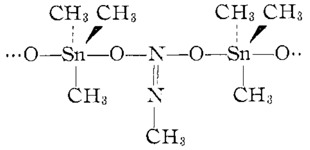
Since we have observed the symmetrical stretching frequency, the compound does not possess a symmetrical planar trimethylstannyl species. This eliminates from consideration a planar trimethyltin cation (V) and any polymeric structure (VI) and VII) where the trimethylstannyl moiety is planar.

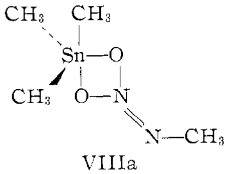

V

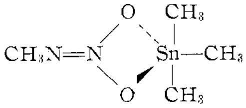

VI

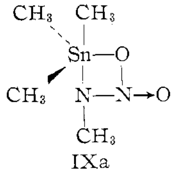

VII

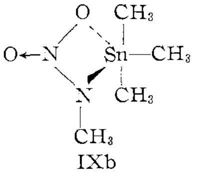
The trimethylstannyl moiety in the polymer-like structure VI could be nonplanar due to the different substituents joined to the tin atom. This model would be very similar in symmetry to trimethyltin chloride and therefore only two infrared absorption peaks would be expected in the 600–500 cm.$^{-1}$ range. The third absorption peak that is observed could be a result of a tin to nitrogen or tin to oxygen stretching vibration, but there seems to be no strong precedence for either of these assignments. In addition, it seems unlikely that the trimethylstannyl species would be nonplanar in this model because it is known[19,27] that this moiety is essentially planar in the trimethyltin chloride–pyridine adduct. The results of the cryoscopic molecular weight determination in benzene of N-triethylstannyl-N-nitroaminoethane (*cf.* Table I) are also not consistent with a polymeric structure.

Two possible structures can be formulated in agreement with a nonplanar trimethylstannyl moiety and an ionic nitramine. These would involve a trigonal bipyramid tin atom with the nitramine acting as a chelating group. In the structures (VIIIa and VIIIb) involving the two oxygens of the nitro group the nitrogen to nitrogen bond should have double bond character and therefore show an infrared absorption peak at approximately 1570 cm.$^{-1}$.[28] No infrared absorption peak was observed in this region.


VIIIa


VIIIb


IXa


IXb

The trigonal bipyramid structures (IXa and IXb) involving the amino nitrogen and the oxygen of the nitro group are compatible with the infrared spectra. An absorption due to a >N→O grouping is expected to be present at approximately 1270 cm.$^{-1}$.[29] We have observed an infrared absorption band in all of our compounds in this region which could be ascribed to this group.

The chelated structures (IXa and IXb) also are consistent with the observed infrared spectra in the 600–500 cm.$^{-1}$ region. The appearance of three absorption peaks at 556, 541, and 512 cm.$^{-1}$ instead of two peaks is most likely due to the lower symmetry (C_s) in comparison to a tetrahedral arrangement of the trimethyltin group (C_{3v}). The asymmetric tin to carbon stretching vibration which is doubly degenerate in trimethyltin chloride is probably split into two absorption peaks by this change in symmetry.

Stability.—The organotin nitramines are stable in air like the trialkyltin imidazoles. They dissolve slowly in water to form an acidic solution which can be titrated with standard base.

The stability of the tin to nitrogen bond in the nitramine derivatives can be related to structure. The organotin nitramines are considered to contain pentacovalent tin similar to the imidazole derivatives.[6] On the other hand, the N-trialkyltin amines such as $R_3SnNR'_2$ or R_3SnNHR' most likely possess a tetrahedral tin atom and are very reactive toward atmospheric moisture and carbon dioxide.[3–6] It is concluded the stability of the tin to nitrogen bond is enhanced when the tin atom changes from a tetracovalent to a pentacovalent state.

Unlike the imidazole derivatives the pentacovalent nitramines probably do not exist in the polymeric structure. Instead the nitramine portion of the molecule is chelated to the tin atom to form a four-membered ring.

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[27] I. R. Beattie and G. P. McQuillan, *J. Chem. Soc.*, 1519 (1963).

[28] Reference 21, p. 273.

[29] Reference 21, p. 307.