Lactonization of the Acid Anhydrides (VIII) or the Dibasic Acids (VII) into the Paraconic Acids (III).—The refluxing of the acid anhydrides (VIII) or the dibasic acids (VII) with concentrated acid or with hydrobromic acid in aqueous acetic acid afforded the paraconic acids (III) in quantitative yield.

Ethyl γ-Methyl-γ-hexylparaconate.—Refluxing of 4.6 g. of γ-methyl-γ-hexylparaconic acid with 30 ml. of benzene and 10 ml. of ethanol in the presence of a catalytic amount of *p*-toluenesulfonic acid monohydrate gave the ester in a quantitative yield, b.p. 148–149° (1.5 mm.), $n^{21}\text{D}$ 1.4578.

Anal. Calcd. for $C_{14}H_{24}O_4$: C, 65.59; H, 9.44. Found: C, 65.70; H, 9.49.

Decarboxylation of Paraconic Acids (III).—The decarboxylation was carried out following the procedure of Johnson and Hunt.[19] A mixture of 6 g. (0.028 mole) of γ-methyl-γ-pentylparaconic acid (III, $R = CH_3$ and $R' = C_4H_9$) and 0.5 g. of potassium hydrogen sulfate was treated at 220–235° for 2 hr. and there were obtained 2.4 g. of γ-methyl-γ-nonanolactone (II, $R = CH_3$ and $R' = C_4H_9$), b.p. 143° (18 mm.) [reported b.p.[25] 129–131° (13 mm.)], $n^{18}\text{D}$ 1.4527, and 0.8 g. of 4-methyl-3(or 4)-nonenoic acid (X, $R = CH_3$ and $R' = C_4H_9$), b.p. 145° (3 mm.), $n^{18}\text{D}$ 1.4537; infrared: 1695 cm.$^{-1}$ (C=O) and 1625 cm.$^{-1}$ (C=C).

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66. Found: C, 70.61; H, 10.51.

The lacto–enoic tautomerism was observed with these compounds as in the literature.[19]

Cyclodehydration of γ-Methyl-γ-hexylparaconic Acid.—To 6 ml. of polyphosphoric acid warmed on an oil bath at 100–120° was added portionwise 11.4 g. (0.05 mole) of γ-methyl-γ-hexylparaconic acid (III, $R = CH_3$ and $R' = C_4H_9$). After all of the solid had dissolved, the mixture was heated gradually for about 30 min. under reduced pressure to a final temperature of 150°. During this period vigorous evolution of carbon dioxide was observed. After the decomposition reaction subsided, the temperature was raised gradually during about 4 hr. to 190°, when crude cyclopentenone was distilled. From the ethereal solution of this crude cyclopentenone, acidic material was removed with a 5% potassium carbonate solution. The ether layer was washed with water, dried over anhydrous sodium sulfate, and evaporated. On redistillation of the crude cyclopentenone 5.6 g. (67%) of 2-pentyl-3-methyl-2-cyclopentenone-1 (dihydrojasmone) (I, $R = CH_3$ and $R' = C_5H_{11}$) was obtained, b.p. 90–91° (2 mm.) [reported[2] b.p. 91° (2 mm.)], $n^{20}\text{D}$ 1.4855 (reported[5] $n^{20}\text{D}$ 1.4851); semicarbazone, m.p. 173° (lit.[5] m.p. 174°); 2,4-dinitrophenylhydrazone, m.p. 121.5 (lit.[6] m.p. 123°). This ketone, semicarbazone, and 2,4-dinitrophenylhydrazone gave correct analyses. Infrared spectra of this ketone was identical with that of the authentic sample. The higher boiling fraction gave 4 g. of the acid anhydride, b.p. 143° (2 mm.), $n^{21}\text{D}$ 1.4856 (lit.[5] $n^{20}\text{D}$ 1.4851); infrared: 1830 (m) and 1780 (s) cm.$^{-1}$ (C=O).

The combined alkaline extracts were acidified with dilute hydrochloric acid, and the precipitated crystals were recrystallized from water–ethanol (5:1) to give 3.2 g. (28%) of dibasic acids (VII, $R = CH_3$ and $R' = C_5H_{11}$), m.p. 153°; infrared: 1698 cm.$^{-1}$ (C=O); ultraviolet: λ_{max} 223 mμ (ϵ 3000). The alkylidene and alkenyl compounds were calculated[5] as to exist in a ratio of 30:70.

Anal. Calcd. for $C_{12}H_{20}O_4$: C, 61.66; H, 8.47. Found: C, 61.79; H, 8.56.

Both recovered dibasic acid and acid anhydride were repeatedly lactonized by means of hydrogen bromide in acetic acid to γ-methyl-γ-hexylparaconic acid which was subjected to cyclodehydration to give 1.1 g. of the cyclopentenone. After all, 6.7 g. (80%) of 2-pentyl-3-methyl-2-cyclopentenone-1 was obtained.

Other cyclopentenone derivatives are listed in Table II.

Similar treatment of 9.2 g. of γ-methyl-γ-decanolactone (II, $R = CH_3$, $R' = C_5H_{11}$, X = H, and Y = H) with polyphosphoric acid[6] afforded 7.5 g. (90%) of dihydrojasmone. The corresponding ethyl paraconate and Stobbe half-esters gave inferior yields, *i.e.*, 43 and 29%, respectively.

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Formation of an Organotin–Nitrogen Bond. II.[1] Syntheses of Tris(trialkyltin)amines

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Received August 1, 1963

Tris(trialkyltin)amines, $(R_3Sn)_3N$, were prepared by the reaction of lithium amide or sodium amide with trialkyltin halide. Infrared absorption of these compounds at 728–712 cm.$^{-1}$ was assigned to an antisymmetric stretching vibration of an Sn–N–Sn linkage. The decomposition of these compounds in air revealed that tris(trimethyltin)amine was converted to trimethyltin hydroxide, while tris(triethyltin)- and tris(tri-*n*-propyltin)-amines were converted to trialkyltin carbonate *via* bis(trialkyltin) oxide. Except for bis(trimethyltin) oxide, bis(trialkyltin) oxides absorb atmospheric carbon dioxide to afford trialkyltin carbonates.

Bullard, *et al.*,[2] reported a product they assumed to be tris(trimethyltin)amine, $[(CH_3)_3Sn]_3N$, being produced by the reaction of (trimethylstannyl)sodium and bromobenzene in liquid ammonia, but they did not isolate nor characterize the compound.

Recently it has been noted in a short communication that tris(trimethyltin)amine was produced by treatment of trimethyl(dimethylamino)tin with ammonia, but experimental details were not described.[3]

These compounds have now been prepared by the reaction of the corresponding trialkyltin halide with lithium or sodium amide in liquid ammonia or ether and were isolated analytically pure by vacuum distillation in nitrogen atmosphere.

Lithium amide reacts with trialkyltin chloride in liquid ammonia, diethyl ether, and tetrahydrofuran, while sodium amide reacts only in liquid ammonia but not in diethyl ether, tetrahydrofuran, or pyridine at the respective refluxing temperatures.

It is known that the formation of a silicon compound having the structure of $(R_3Si)_3N$ type[3b] is very difficult owing to steric hindrance. In the case of tin compounds, however, owing presumably to the greater radius of the tin atom, the nitrogen atom could find a vacancy among the three tin atoms so that $(R_3Sn)_3N$ type compounds were obtained readily.

Evidence for the $(R_3Sn)_3N$ structure of these compounds is based upon, besides the coincidence of analyses and the absence of an infrared absorption of an N–H bond, the fact that these compounds liberate

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(1) Previous paper: K. Sisido and S. Kozima, *J. Org. Chem.*, **27**, 4051 (1962).

(2) R. H. Bullard and W. R. Robinson, *J. Am. Chem. Soc.*, **49**, 1368 (1927).

(3) (a) K. Jones and M. F. Lappert, *Proc. Chem. Soc.*, 358 (1963); (b) NOTE ADDED IN PROOF.—A silicone compound of the $(R_3Si)_3N$ type was reported by U. Wannagat and O. Brandstätter, *Angew. Chem.*, **75**, 345 (1963); *Angew., Chem. Intern. Ed. Engl.*, **2**, 263 (1963).

ammonia and the respective nitrogen-free organotin compounds on exposure to air, or give trialkyltin chloride and ammonium chloride with hydrochloric acid.

As soon as tris(trimethyltin)amine was exposed to air, ammonia gas was evolved and white crystals of trimethyltin hydroxide were obtained quantitatively. A similar change was noticed in trimethyl(diethylamino)tin to afford diethylamine and trimethyltin hydroxide. The same air exposure of tris(triethyltin)-amine, tris(tri-*n*-propyltin)amine, and trialkyl(diethylamino)tin (where alkyl groups are ethyl, *n*-propyl, or *n*-butyl), however, resulted in the formation of ammonia or amine and trialkyltin carbonates.

The formation and decomposition of trialkyltin carbonate have not been described precisely. On exposure of bis(triethyltin) oxide to air or dry carbon dioxide, white crystals of triethyltin carbonate were formed as traced by the quantitative weight increase as well as by the infrared observation following the change. Among the mentioned bis(trialkyltin) oxides, however, only the trimethyltin derivative does not react with atmospheric carbon dioxide.

As to the decomposition of the carbonate,[4] it was found that trialkyltin carbonate gives bis(trialkyltin) oxide almost quantitatively on heating at 140–150° for 5 hr. *in vacuo.*

The tris(trialkyltin)amines had a volatility which showed their monomeric structures, and had higher boiling points compared with the corresponding bis-(trialkyltin) oxides supporting their higher molecular weights.

In the spectra of tris(trimethyltin)-, tris(triethyltin), and tris(tri-*n*-propyltin)amine, strong bands which may be associated with an antisymmetric stretching vibration of an Sn–N–Sn linkage were observed at 728, 712, and 712 cm.$^{-1}$, respectively, but no band at 3300–3500 cm.$^{-1}$ characteristic of N–H stretching was present. In silicon compounds, the band at 934 cm.$^{-1}$ is assigned to the antisymmetric stretching vibration of Si–N–Si for hexamethyldisilazane. This is observed at a frequency lower than that of Si–O–Si for hexamethyldisiloxane at 1055 cm.$^{-1}$.[5] The spectra of bis(trialkyltin) oxide have an intense band at about 775 cm.$^{-1}$ which is assigned to the antisymmetric stretching vibration of Sn–O–Sn link.[6,7] Assuming that antisymmetric stretching vibrations of Sn–N–Sn and Sn–O–Sn linkages for trialkyltin derivatives have a similar relation to these of Si–N–Si and Si–O–Si linkages, and, considering the hydrolytic observations, it may be possible to assign the strong band at 728–712 cm.$^{-1}$ in the spectra of tris(trialkyltin) amines to an antisymmetric stretching vibration of an Sn–N–Sn linkage.

No vibration connected with the symmetric stretching of an Sn–N–Sn linkage was detected in a potassium bromide region. This vibration may be expected to occur at a frequency below 400 cm.$^{-1}$, since a symmetric stretching vibration of Si–N–Si occurs at 566 cm.$^{-1}$.[5]

Existence of C–Sn–C symmetric stretching vibrations[8] in the spectrum of tris(trimethyltin)amine at 503 cm.$^{-1}$ showed that trimethyltin group is not planar[9] in this compound. This fact and their volatility may support the covalent character of organotin–nitrogen bonding.

The air decomposition of tris(trialkyltin)amine was also studied by the infrared spectra. Upon exposure of tris(trialkyltin)amine to air, the strong band at 728–712 cm.$^{-1}$ disappeared, in accordance with the progress of the hydrolysis by the atmospheric moisture. At last, tris(trimethyltin)amine was converted into trimethyltin hydroxide whose spectrum had an Sn–O–H deformation vibration at 917 cm.$^{-1}$,[6,10] while tris(triethyltin)- and tris(tri-*n*-propyltin)amine were converted into the corresponding trialkyltin carbonates having characteristic bands of carbonate.[11] In the course of the air decomposition of trialkyltinamino derivatives which give carbonates, only an antisymmetric stretching band of Sn–O–Sn, but no band of an Sn–O–H, was observed during any stage of the reaction. The carbonates are formed apparently *via* the oxides, which in turn seemed to be produced by the hydrolysis of the starting materials with atmospheric moisture. Presumably the transformation of the hydroxide grouping (Sn–O–H) was so fast that the spectra were not observed.

Experimental

Infrared.—The infrared spectra of the liquid samples which were very sensitive to air were measured in a sealed sodium chloride plate (or potassium bromide plate) by dropping the sample from an injector. The decomposition of the compounds in air was performed by exposing them to air on a sodium chloride or potassium bromide plate.

Tris(trimethyltin)amine, $[(CH_3)_3Sn]_3N$. A.—To a suspension of 2.3 g. (0.06 mole) of sodium amide powder in 40 ml. of liquid ammonia at about −50°, 11.0 g. (0.045 mole) of trimethyltin bromide[12] (b.p. 160–163°) in 30 ml. of anhydrous ether was added dropwise. After stirring for 2 hr. at about −50°, both ammonia and ether were evaporated. The reaction product was distilled *in vacuo* yielding 4.0 g. (53%) of tris(trimethyltin)amine, b.p. 133–134° (20 mm.), m.p. 22–24°, as white crystalline needles which showed a negative Beilstein test for halogen. All procedures were carried out in a nitrogen atmosphere. The product was stored in sealed ampoules under nitrogen. Infrared absorptions (liquid) appeared at 2980 (m), 2910 (m), 1430 (w), 1295 (w), 1285 (m), 760 (sh), 728 (vs), 674 (sh), 524 (s), and 503 (m) cm.$^{-1}$. On exposure to air, the very strong band at 728 cm.$^{-1}$ disappeared and after 30 sec. new bands came out at 917 and 760 cm.$^{-1}$ instead.

Anal.[1] Calcd. for $C_9H_{27}NSn_3$: N, 2.77; Sn, 70.45. Found: N, 2.77; Sn, 70.53.

As soon as 2.53 g. (0.050 mole) of the substance was exposed to air on a watch glass, ammonia gas was evolved, and 2.70 g. (0.149 mole) of white crystals were obtained. These crystals were identified as trimethyltin hydroxide[10,13] by identical infrared spectra and a mixture melting point. On addition of dilute hydrochloric acid to an ethereal solution of the methyltinamine, trimethyltin chloride and ammonium chloride were obtained from ethereal and aqueous layer, respectively.

B.—A lithium amide suspension prepared from 0.56 g. (0.08 g. atom) of lithium metal and 0.01 g. of ferric nitrate in 50 ml. of liquid ammonia was diluted with 50 ml. of anhydrous ether. The

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[12] S. N. Naumov and Z. M. Manulkin, *J. Gen. Chem. USSR*, **5**, 281 (1935); *Chem. Abstr.*, **29**, 5071 (1935).

[13] C. A. Kraus and R. H. Bullard, *J. Am. Chem. Soc.*, **51**, 3605 (1929).

suspension was kept at room temperature to evaporate the ammonia and finally was refluxed for 1 hr. to remove a trace of ammonia. To this lithium amide suspension in ether 12.1 g. (0.05 mole) of trimethyltin bromide in 30 ml. of anhydrous ether was added. Refluxing for 3 hr. followed by vacuum distillation gave 7.0 g. (83%) of white crystals, b.p. 130° (14 mm.), m.p. 22–24°.

Tris(triethyltin)amine and Tris(tri-*n*-propyltin)amine were prepared also in about 70% yields by an analogous method.

Tris(triethyltin)amine was obtained from triethyltin chloride,[14] b.p. 86–88° (9 mm.), as white crystalline needles, b.p. 192–194° (4 mm.), redistillation, m.p. 21–22°.

Anal. Calcd. for $C_{18}H_{45}NSn_3$: N, 2.22; Sn, 56.38. Found: N, 2.23; Sn, 56.48.

As soon as 2.52 g. (0.0400 mole) of the substance was exposed to air, ammonia was evolved and 2.81 g. (0.0596 mole) of white crystals were obtained. These crystals were identified as triethyltin carbonate by the infrared spectra (1540, 1370, 1070, and 833 cm.$^{-1}$ [11]) and analyses. During air decomposition, a strong band at 775 cm.$^{-1}$ (Sn–O–Sn) appeared, but this disappeared in several minutes.

Tris(tri-*n*-propyltin)amine, prepared from tri-*n*-propyltin chloride,[14] b.p. 122–123° (10 mm.), was a colorless liquid, b.p. 143–145° (0.6 mm.), on redistillation.

Anal. Calcd. for $C_{27}H_{63}NSn_3$: N, 1.85; Sn, 46.98. Found: N, 1.94; Sn, 46.79.

On similar air exposure, from 1.06 g. (0.0140 mole) of the substance, 1.15 g. (0.0207 mole) of pasty viscous oil was obtained. This was identified as tri-*n*-propyltin carbonate by an analogous method.

Trimethyl(diethylamino)tin.[15]—An ether solution of diethylaminolithium prepared from 0.76 g. (0.11 g.-atom) of lithium metal and 6.9 g. (0.05 mole) of *n*-butyl bromide and 4.0 g. (0.055 mole) of diethylamine in 30 ml. of anhydrous ether was added dropwise to a solution of 7.3 g. (0.03 mole) of trimethyltin bromide[12] in 30 ml. of ether. After refluxing for 3 hr., the solvent was distilled and the reaction product was fractionated under atmospheric pressure. A fraction boiling at 156–162°, lit.[15] b.p. 162°, was collected, yielding 4.3 g. (61%). The infrared spectrum of this compound had the characteristic absorptions of the diethylaminotin grouping at 1455, 1372, 1290, 1185, 1170, 1150, 1116, 1075, 1048, 1007, and 872 cm.$^{-1}$. All these bands immediately disappeared on exposure to air and a characteristic band of trimethyltin hydroxide at 917 cm.$^{-1}$ appeared.

Decomposition of Bis(triethyltin) Oxide by Exposure to Air.—On exposing 2.97 g. (0.00694 mole) of bis(triethyltin) oxide[16] (b.p. 142–143° at 13 mm., $n^{20}{}_D$ 1.5005) to air for 12 hr., 3.26 g. of white crystals were obtained. The weight increase of 0.29 g. corresponds to the 0.0066 mole of carbon dioxide. These crystals were identified also as triethyltin carbonate by infrared spectrum, analysis, and decomposition point.

Bis(triethyltin) Oxide from Triethyltin Carbonate.—Upon heating 3.2 g. of triethyltin carbonate at 140–150° *in vacuo*, the white crystals melted with evolution of carbon dioxide. After an additional heating for 5 hr., the product was distilled at 155–156° (20 mm.) to obtain 2.7 g. (93%) of bis(triethyltin) oxide, $n^{20}{}_D$ 1.4990. The infrared spectrum had a strong band at 775 cm.$^{-1}$, but no bands at 1540, 1370, 1070, and 833 cm.$^{-1}$.

Decomposition of Bis(tri-*n*-propyltin) Oxide by Exposure to Air.—On exposing 1.45 g. (0.00283 mole) of bis(tri-*n*-propyltin) oxide[17] (b.p. 161–166° at 5 mm., $n^{20}{}_D$ 1.4917) to air for 12 hr., 1.56 g. of viscous pasty oil was obtained. The weight increase of 0.11 g. corresponds to 0.0025 mole of carbon dioxide. This was identified as tri-*n*-propyltin carbonate by infrared spectrum.

Bis(tri-*n*-propyltin) Oxide from Tri-*n*-propyltin Carbonate.—A 2.9-g. sample of tri-*n*-propyltin carbonate was heated for 5 hr. at about 150° under diminished pressure and the content was distilled at 161–165° (5 mm.) when bis(tri-*n*-propyltin) oxide, $n^{20}{}_D$ 1.4911, was obtained, yielding 2.4 g. (90%). The infrared spectrum had a strong band at 775 cm.$^{-1}$, but no bands at 1540, 1370, and 833 cm.$^{-1}$.

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Condensation of Halophenols with Formaldehyde and Primary Amines[1]

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Received August 22, 1962

The reaction of *o*- and *p*-halogen-substituted phenols with formaldehyde and representative primary aliphatic amines was studied. The number of halogen substituents on the phenol and the specific amine used were found to be important factors in determining both the course of the condensation and the stability of the benzoxazines, which were obtained with substituted N,N-bis(hydroxybenzyl)amines and substituted 2-aminomethylphenols.

The Mannich reaction involving phenols, formaldehyde, and primary amines has been used as a convenient source of a variety of compounds. The course of this generally facile condensation is, however, greatly influenced by a number of reaction variables.[4,5] In particular, the size of the *ortho* substituent on the phenol has been shown to play an important role. For example, by merely utilizing the calculated quantities of reactants in the condensation of 2,4-dimethylphenol with formaldehyde and cyclohexylamine, high yields (70–90%) of either 2-cyclohexylaminomethyl-4,6-dimethylphenol (Ia), or 3-cyclohexyl-3,4-dihydro-6,8-dimethyl-2*H*-1,3-benzoxazine (IIa), or bis(3,5-dimethyl-2-hydroxybenzyl)cyclohexylamine (IIIa) can be obtained.[4] Use of 4-*t*-butylphenol in place of 2,4-dimethylphenol, however, resulted in a high yield of a benzoxazine (II) even when the molar ratio of reactants was that calculated for the formation of a bis(hydroxybenzyl)amine (III). In contrast, efforts to prepare benzoxazines (II) from a phenol having an *o*-*t*-butyl substituent were unsuccessful, and only the bis(hydroxybenzyl)amine (III) was obtained.[4]

In view of the striking manner in which the course of the condensation can be shifted by steric factors, it was of interest to determine the effect of varying the electrophilic character of substituents on the phenol. A comparison of *o*-chloro- and *o*-methylphenols in such studies appeared to have attractive possibilities for substantially eliminating steric factors since the chloro and methyl groups are approximately equivalent in size.

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(1) This investigation was supported in part by Research Grant CY-5211 from the National Cancer Institute of the Public Health Service. We are also indebted to the University of Utah Research Committee for a research fellowship to E. L. Mortenson.

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(3) This paper was abstracted in part from a dissertation presented to the faculty of the University of Utah by E. L. Mortenson in partial fulfillment of the requirements for the Ph.D. degree.

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