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# Synthesis of Tribromoacetic Anhydride and Its Reaction with Dimethyltin(IV) Oxide

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**Synopsis.** The synthesis of previously unknown tribromoacetic anhydride and its reaction with dimethyltin(IV) oxide is reported. The compounds were characterized by analytical methods, IR, $^1$H, $^{13}$C, $^{119}$Sn NMR, and MS (EI) spectral studies.

Conventional method of preparing carboxylic anhydrides by heating the respective carboxylic acid with $P_4O_{10}$ and subsequent distillation of the anhydride formed, even under reduced pressure, lead to partial decomposition of the product in certain cases.[1] Consequently, a few halo carboxylic anhydrides were yet to be synthesized.[2–4] In continuation of the synthesis of dibromoacetic anhydride in these laboratories,[1] preparation of previously unknown tribromoacetic anhydride is reported by a similar method. Its reaction with dimethyltin(IV) oxide and the structural diagnosis of $(CH_3)_2Sn(O_2CCBr_3)_2$ using various techniques especially the multinuclear NMR spectral studies, was also carried out keeping in view the wide application of diorganotin(IV) carboxylates as catalysts and stabilizers.[5]

## Experimental

Tribromoacetic acid (Fluka) was used as such. Dimethyltin(IV) oxide was prepared by literature methods.[6,7] The solvents were dried and distilled before use.

The IR spectra were recorded as Nujol/hexachlorobutadiene/$CCl_4$ smears between AgCl plates on a Perkin-Elmer 1430 IR spectrophotometer. $^1$H, $^{13}$C (proton decoupled), and $^{119}$Sn NMR spectra were taken on a JEOL-FX-90Q spectrometer using TMS ($Me_4Si$), TMS($Me_4Si$), and TMT ($Me_4Sn$), respectively, as external references. Mass spectra (EI) were obtained on a Vg Micromass 7070 F at 70 eV. Melting points are uncorrected. All manipulations were carried out in a dry box filled with nitrogen.

**Synthesis of Tribromoacetic Anhydride.** Tribromoacetic acid (9.45 g, 31.8 mmol) and phosphorus(V) oxide (14.5 g) were loaded into a 100 cm$^3$ Pyrex reactor in a dry box, and 60 cm$^3$ of $CCl_4$ was added to it. The reactor was then fitted with a reflux condenser and a drying tube. The contents were refluxed at 77 °C for 20 h. The reaction mixture was filtered under positive pressure of dry nitrogen, and the residual portion was repeatedly washed with $CCl_4$ (5×10 cm$^3$). Tribromoacetic anhydride (7.35 g, 12.8 mmol) was obtained as a white solid, mp 62—64 °C, yield: 80% after removing the solvent from the filtrate in vacuo. The product was checked for the absence of phosphorus and then recrystallized from $CCl_4$ as a shining white solid, mp 63—64 °C, yield: 72%. Found: C, 8.31; Br, 82.94%. Calcd for $C_4Br_6O_3$: C, 8.33; Br, 83.33%. IR[#]: 1855 sh, 1830 vs, 1778 m, 1265 vw, 1125 m, 1085 ms, 935 m, 780 m, 745 sh, 685 vw, 615 ms, 580 sh cm$^{-1}$.

**Preparation of Dimethyltin(IV) Tribromoacetate.** Tribromoacetic anhydride (1.18 g, 2 mmol) dissolved in 30 cm$^3$ of $CCl_4$ was added to 0.33 g (2 mmol) of dimethyltin(IV) oxide in a 100 cm$^3$ Pyrex reactor in a dry box. The contents were heated to reflux (80 °C) till a clear solution was obtained. The white solid separated out on cooling the solution to room temperature, was filtered under positive pressure of dry nitrogen and washed twice with $CCl_4$ (1 cm$^3$) and finally dried in vacuo. $(CH_3)_2Sn(O_2CCBr_3)_2$ (1.36 g, 1.8 mmol) was obtained as a white solid, mp 145—147 °C, yield: 90%. Found: C, 9.6; H, 0.83; Br, 64.1; Sn, 15.6%. Calcd for $C_6H_6Br_6O_4Sn$: C, 9.72; H, 0.81; Br, 64.8; Sn, 16.02%. IR: 1605 s, 1460 vw, 1360 ms, 1277 vw, 955 mw, 925 w, 805 mw, 760 ms, 720 sh, 515 vw, 460 m cm$^{-1}$. NMR ($CD_2Cl_2$) $^1$H, $\delta$=1.19 ($^2J(^{119}\text{Sn}, ^1\text{H})$ 83.5 Hz); $^{119}$Sn, $\delta$=−190.6; $^{13}$C ($C_6D_6$) $\delta$=4.6 ($^1J(^{119}\text{Sn}, ^{13}\text{C})$ 680 Hz).

## Results and Discussion

Reaction between tribromoacetic acid and phosphorus(V) oxide in $CCl_4$ at 77 °C results in the formation of tribromoacetic anhydride in good yield.

$$2CBr_3\,COOH \xrightarrow[20\text{ h, }77\,^\circ\text{C}]{P_4O_{10},\ CCl_4} (CBr_3CO)_2O$$

The progress of the reaction was monitored by $^1$H NMR and IR spectroscopy. The reaction was considered to be complete when the test solution did not show any peak relating to OH of the $CBr_3COOH$ in its IR and $^1$H NMR spectra (tribromoacetic acid has sufficient solubility in warm $CCl_4$ to check its IR and NMR). Attempts to purify tribromoacetic anhydride by distillation, even under reduced pressure (0.1 Torr, 1 Torr=133.322 Pa), resulted in its significant decomposition. Purification was rather achieved by recrystallizing the product from $CCl_4$.

Tribromoacetic anhydride is a shining white powder stable at room temperature for more than 20 days in a dry atmosphere. Nearly 5% decomposition of the product was observed in 40 days. The decomposition of $(CBr_3CO)_2O$ was taken into account by the formation of free $Br_2$ in the storage vessel. Tribromoacetic anhydride is soluble in common organic solvents giving colorless solutions. It is extremely moisture sensitive and reacts readily with water to give tribromoacetic acid. The IR spectrum of $(CBr_3CO)_2O$ free from $CBr_3COOH$ absorptions was obtained as a Nujol smear between AgCl optics. The anhydride is reactive towards KBr plates. Attempts to obtain IR spectra of neat anhydride led to the formation of some $CBr_3COOH$ due to its hydrolysis by atmospheric moisture. A parent or molecular peak was not observed in the EI mass spectra of $(CBr_3CO)_2O$. However, peaks relating to $CBr_3COO^+$, $CBr_3CO^+$, $CBr_3^+$, $CBr_2COOH^+$, $CBr_2CO^+$, $Br_2CH^+$, $Br_2C^+$, $Br_2^+$, $BrCO^+$, $BrCH^+$, $BrC^+$, $BrH^+$, $Br^+$ fragment ions were observed. The

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[#] s, strong; m, medium; w, weak; v, very; sh, shoulder.

above protonated fragment ions observed in the mass spectra are due to hydrolysis of $(CBr_3CO)_2O$ by traces of moisture either in the probe or during manipulations.

The reaction between dimethyltin(IV) oxide and tribromoacetic anhydride in $CCl_4$ at 80 °C produces dimethyltin(IV) tribromoacetate in good yield:

$$(CH_3)_2SnO + (CBr_3CO)_2O \xrightarrow[80\,^{\circ}C]{CCl_4,\ 6\ h} (CH_3)_2Sn(O_2CCBr_3)_2$$

The reaction was complete in nearly 6 h, when a clear solution was obtained (dimethyltin(IV) oxide is completely insoluble in $CCl_4$ by itself). That the product is soluble in hot $CCl_4$ but separates out on cooling the solution to room temperature, serves the purpose of recrystallization. So this reaction provides a facile synthesis of $(CH_3)_2Sn(O_2CCBr_3)_2$ in one pot. The yield was not quantitative as some of the product remained in solution even at room temperature.

The preparation of $(CH_3)_2Sn(O_2CCBr_3)_2$ by the above route is not unprecedented. Dialkyltin(IV) acetates have been prepared by reacting dialkyltin(IV) oxide with acetic anhydride.8)

Dimethyltin(IV) tribromoacetate, a white solid is extremely moisture sensitive and soluble in common organic solvents. It has, however, very low solubility in $CCl_4$ at ambient temperature.

A comparison of IR frequencies of $(CH_3)_2Sn(O_2CCBr_3)_2$ (see experimental section) with that of sodium tribromoacetate9) revealed the covalently bonded tribromoacetato ligands in the former. The magnitude of $\Delta\nu$ ($\nu_{as}CO_2-\nu_sCO_2$) in $(CH_3)_2Sn(O_2CCBr_3)_2$ of the order of 245 $cm^{-1}$ ($\nu_{as}CO_2-\nu_sCO_2=1605-1360=245\ cm^{-1}$) is less than that in $NaO_2CCBr_3$ ($1664-1355=309\ cm^{-1}$) and is thus indicative of bidentate tribromoacetato ligand. The magnitude of $\Delta\nu$ has been used in deciding the bonding modes of a carboxylato group. Generally, the magnitude of $\Delta\nu$ in a given carboxylate complex greater or lesser than that of sodium carboxylate reveals the unidentate or bidentate carboxylato ligand.10,11) The splitting of $\nu_sCO_2$ mode i.e. an additional weak band at 1460 $cm^{-1}$, may be attributed to the unsymmetrical bidentate tribromoacetato ligand.

The excellent agreement12) of the NMR prediction and X-ray structure determination for $(CH_3)_2Sn(O_2CCH_3)_2$ has reinforced the power of the NMR structure correlations developed previously13—15) for the structural analysis of methyltin(IV) compounds in solution and in solid state. It has been shown that the magnitude of tin-hydrogen $J$ coupling, $|^2J(^{119}Sn, {}^1H)|$ ($|^2J|$), is related to the $H_3C$-Sn-$CH_3$ angle according to the quadratic expression:14)

$$\theta=(0.0161)(|^2J|)^2-1.32(|^2J|)+133.4$$

and the magnitude of tin-carbon $J$ coupling, $^1J(^{119}Sn, {}^{13}C)$ ($|^1J|$), is linearly related to the $H_3C$-Sn-$CH_3$ angle by the following equation:14)

$$|^1J|=11.4(\theta)-875$$

Where $\theta$ is the $H_3C$-Sn-$CH_3$ angle in deg and $|^1J|$ and $|^2J|$ are in Hz.

These relationships provide a simple method for estimating $H_3C$-Sn-$CH_3$ angles of methyltin(IV) solids from coupling constant values.

The $^1J$ and $^2J$ values for $(CH_3)_2Sn(O_2CCBr_3)_2$ are found to be 680 and 83.5 Hz, respectively. $H_3C$-Sn-$CH_3$ angle calculated for $(CH_3)_2Sn(O_2CCBr_3)_2$ from $^1J$ and $^2J$ values by using the above expressions, comes out to be 136.4° and 135.4°, respectively. These findings are in excellent agreement with that calculated (135°) for $(CH_3)_2Sn(O_2CCH_3)_2$ from $^1J(^{119}Sn, {}^{13}C)$ both in solution and solid state and from $^2J(^{119}Sn, {}^1H)$ values.12,14) $H_3C$-Sn-$CH_3$ angle in $(CH_3)_2Sn(O_2CCH_3)_2$ has been found to be 135.9° by X-ray structural studies.12) So distorted octahedral geometry may be anticipated around tin in $(CH_3)_2Sn(O_2CCBr_3)_2$ similar to that in $(CH_3)_2Sn(O_2CCH_3)_2$ on the basis of $H_3C$-Sn-$CH_3$ angle. The $^{119}Sn$ chemical shift of the order of −190.6 ppm relative to TMT also supports the six coordination12,15—17) around tin in $(CH_3)_2Sn(O_2CCBr_3)_2$.

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