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THE PYROLYSIS OF PHENYLTIN BENZOATES AND RELATED SUBSTANCES

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SUMMARY

When diphenyltin dibenzoate is subjected to pyrolysis at 300°, almost exactly two moles of benzene (plus a small amount of biphenyl) are recovered and a non-volatile residue is left behind:

$$(C_6H_5)_2Sn(O_2CC_6H_5)_2 \rightarrow 2\,C_6H_6 + Sn(O_2CC_6H_4)_2$$

Chemical degradation of this residue shows that the benzene originated from the tin-bound phenyl groups, that the hydrogen is abstracted from the benzoic acid residue, and that new Sn–C bonds had formed between the metal and the benzoate group. There is no significant reduction of Sn^{IV}. When this pyrolysis is carried out in cumene, no interaction products of phenyl radicals and cumene are observed. It appears that this reaction is probably not of the classical homolytic type.

Triphenyltin benzoate, on pyrolysis at 350°, loses two phenyl groups almost exclusively as benzene. Diphenylantimony benzoate loses two phenyl groups as benzene (400°) and phenylmercury benzoate loses one phenyl group (as benzene), as well as a molecule of carbon dioxide (300°), leaving a residue of $(C_6H_4Hg)_n$. Neither diphenylarsenic benzoate nor triphenylsilyl benzoate decompose at 400°.

INTRODUCTION

During an examination of model compounds, which were representative of thermally stable metal-organic polymer systems, diphenyltin dibenzoate was prepared. It was noticed that on heating this compound to about 300°, benzene was formed and a residue remained which did not melt below 360°. The nature of this reaction has now been examined in order to discover what changes had taken place.

Organotin compounds are generally quite stable to heat. For example, tetraphenyltin decomposes only gradually at its boiling point (about 400°). This is due to the fairly high thermodynamic stability of the carbon–tin bond ($Sn–C_{arom}$, $\bar{D}=61$ kcal/mole[1]). Despite this, the mobility of organic groups bound to tin is impressive. Tetraphenyltin reacts with tin tetrachloride at about 200°[2] to form disproportionation products, $(C_6H_5)_nSnCl_{4-n}$. At its melting point (121°), bis(triphenyltin) oxide rearranges quantitatively to tetraphenyltin and poly[diphenyltin oxide][3], while the latter decomposes at 400°, to largely tetraphenyltin and a tin oxide[4]. Aromatic groups bound

to tin are readily moved from one tin atom to another with the eventual formation of the most stable species, *e.g.*, tetraphenyltin.

A brief survey of the literature discloses that only few alkyl or aryltin carboxylates decompose smoothly to yield recognizable products.

Triphenyltin cyanoacetate[5],

$$(C_6H_5)_3SnO_2CCH_2C{\equiv}N \xrightarrow{140°/vac.} (C_6H_5)_3SnCH_2C{\equiv}N + CO_2 \quad (1)$$
$$49\%$$

and bis(triphenyltin) acetylenedicarboxylate[6],

$$(C_6H_5)_3SnO_2C{-}C{\equiv}C{-}CO_2Sn(C_6H_5)_3 \xrightarrow[vac.]{185-200°}$$
$$(C_6H_5)_3Sn{-}C{\equiv}C{-}Sn(C_6H_5)_3 + 2\,CO_2 \quad (2)$$
$$93\%$$

lose carbon dioxide readily to form the more stable Sn–C bonded compounds illustrated above. Contrary to this, triethyltin trifluoroacetate appeared to be stable at its boiling point (218°)[7]. The decomposition of triphenyltin trichloroacetate in refluxing cyclooctene resulted in 13% of the phenyl groups appearing as benzene; phenylmercury trifluoroacetate under these reaction conditions yielded 59% benzene[8]. Similar silicon derivatives, triphenylsilyl cyanoacetate and the corresponding benzoate, appeared to be stable at 200°[9].

RESULTS

Diphenyltin dibenzoate is prepared most conveniently and in probably the highest state of purity (as judged by the m.p.) from the dihalide and dry sodium benzoate in an inert solvent. The alternate route (free acid, triethylamine, diphenyltin dihalide) seems to yield a less pure product. Triphenyltin benzoate is made simply from bis(triphenyltin) oxide and benzoic anhydride by heating in an inert solvent. Polydiphenyltin oxide, on heating with benzoic anhydride, does not lead to diphenyltin dibenzoate. The reaction of stoichiometric quantities of benzoic acid and tetraphenyltin in boiling xylene, which could be expected to yield the respective diphenyltin dibenzoate[10], instead gave rise to a mixture of tin tetrabenzoate and unreacted tetraphenyltin.

Triphenyltin benzoate as well as the diphenyltin dibenzoate were found to be monomeric in dilute freezing benzene. These compounds also have the typical "carboxylate" infrared absorptions (ν_{sym} 1335 s and ν_{asym} 1620 s cm^{-1}, nujol mull or KBr) indicative of the bidentate $-CO_2^-$ group[11]. The IR spectra of the triphenylsilyl benzoate and the diphenylarsenic benzoate have the typical carbonyl (monodentate $-C\overset{O}{\underset{O}{<}}$) absorptions at 1700 and 1280 cm^{-1} while the phenyltin, -antimony, and -mercury benzoates all have the carboxylate (bidentate $-C\overset{O}{\underset{O}{<}}$) absorptions at 1550 and 1300 cm^{-1}.

The thermal decomposition of diphenyltin dibenzoate results in a nearly theoretical weight loss (at 300°). Duplicate experiments yielded the data shown in Table 1.

TABLE 1

Exp.	Weight loss (% of theory[a])	Distillate			C_6H_5Br
		Yield (% of theory[a])	Composition (wt.%)		
			C_6H_6	$(C_6H_5)_2$	
A	96.8	82.7	90.4	9.6	
B	91.3	92.4	97.3	2.7	6.5[b]

[a] For loss of 2 mole C_6H_6/mole Sn. [b] % of theoretical phenyl groups found as C_6H_5Br on bromination of residue.

The residue was a hard, light tan, brittle solid, infusible below 360°, soluble only in pyridine. This substance analyzed quite accurately for $(C_6H_4CO_2)_2Sn$ in which the tin is in the form of Sn^{IV}. When this pyrolysis residue was dissolved in cold pyridine and treated with a slight excess of bromine at 90° (a technique which quantitatively cleaves all Sn–C bonds, but does not brominate bromobenzene or benzoic acid), then an additional 6.5% (experiment B) of the total tin-bound phenyl groups was recovered as bromobenzene (no dibromobenzenes were in evidence). Ninety-seven percent of the total tin-bound phenyl groups in experiment B were accounted for. The removal of pyridine and excess bromine, acid hydrolysis of the residue and conversion of the organic fraction to the methyl ester yielded a tan solid whose C/Br ratio was 8.0/0.9 (theory 8/1 for $BrC_6H_4COOCH_3$). The IR spectrum of this ester mixture showed that it consisted principally of the *o*-bromobenzoic acid methyl ester with no more than 10% of the *para* and *meta* isomers present.

When another portion of the total pyrolysis residue was hydrolyzed with boiling aqueous acid (cleaving the Sn–C and Sn–O bonds) and the resulting organic fraction was isolated, it was found that its neutralization equivalent was 123 (calcd. 121 for benzoic acid). This indicates that each phenyl group has one carboxyl residue attached to it. The IR spectrum of this substance shows a predominant amount of

TABLE 2

RESULTS OF PYROLYSIS OF PHENYLMETAL BENZOATES

Compounds	Pyrolysis conditions (°C/h)	Products			
		Distillate		Residue	
		Yield[a]	Composition	Yield[a]	Analysis
$C_6H_5HgO_2CC_6H_5$	300/1	97.4	99% $C_6H_6+CO_2$	98.4	"HgC_6H_4"
$(C_6H_5)_2SbO_2CC_6H_5$	400/1	93.8	98.6% C_6H_6 +1.1% $(C_6H_5)_2$	95.2	"$C_6H_3CO_2Sb$"
$(C_6H_5)_2AsO_2CC_6H_5$	400/1	[b]			
$(C_6H_5)_3SiO_2CC_6H_5$	400/1	[b]			

[a] Wt.% of theory. [b] No reaction.

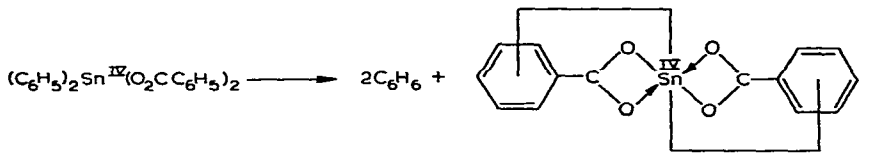
monosubstituted phenyl plus a few other bands (one at 747 cm^{-1}) which may be due to disubstituted phenyl groups.

When diphenyltin dibenzoate was pyrolyzed at 300° in cumene, no 2,2-diphenylpropane or 2,3-diphenyl-2,3-dimethylbutane could be found in the product. Phenyl benzoate was found in the product (13.4 wt.%), the remainder was benzene (79.5%), biphenyl (5.2%) and a little benzoic acid (2.9%).

Tin tetrabenzoate does not decompose at 300° (1 h); at 350° triphenyltin benzoate loses two of its three phenyl groups almost exclusively as benzene. The results of the pyrolysis of the other benzoates are listed in Table 2.

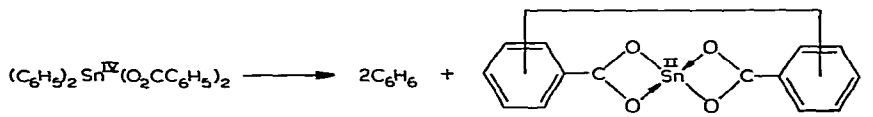
DISCUSSION

Stoichiometry required that the expulsion of two benzene molecules and the concurrent formation of two new Sn–C bonds, during the pyrolysis of diphenyltin dibenzoate, result in no valence change of the tin atom:



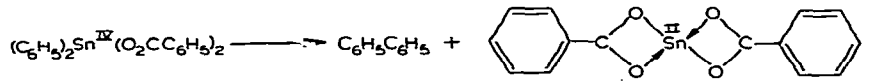
(3)

On the other hand, for the formation of each new C–C bond between benzoic acid residues and the loss of two benzene molecules:



(4)

the valence of the tin atom is reduced from IV to II. A similar valence reduction must be observed when one biphenyl molecule is expelled during the decomposition of one diphenyltin dibenzoate molecule:

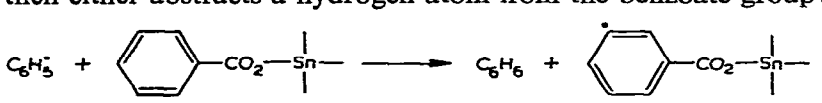


(5)

The experimental results show clearly that two of the three processes must have taken place but that the first was by far the predominant one (90–95% total yield of C_6H_6). No valence change of the tin in the gross pyrolysis product could be observed, yet biphenyl certainly and possibly a little diphenyldicarboxylic acid were present. These contradictory facts point to experimental inaccuracies which could not be resolved despite careful attempts to do so. The nature of the products of this pyrolysis reaction point to a homolytic decomposition of the phenyl–tin bond to yield a phenyl radical:

$$(C_6H_5)_2Sn(O_2CC_6H_5)_2 \rightarrow C_6H_5^{\bullet} + C_6H_5Sn^{III}(O_2CC_6H_5)_2 \quad (6)$$

which then either abstracts a hydrogen atom from the benzoate group:

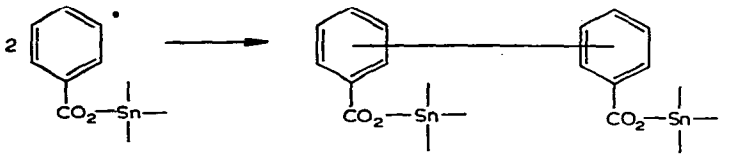


(7)

or dimerizes:

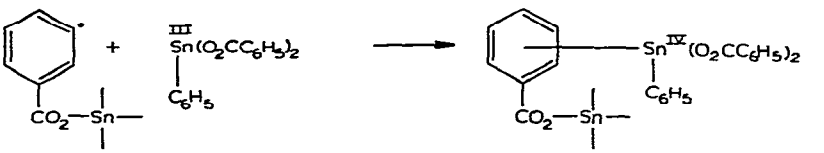
$$2\,C_6H_5^{\bullet} \rightarrow C_6H_5{-}C_6H_5 \qquad (8)$$

The resulting benzoic acid radical has the choice of dimerizing with its own kind:



(9)

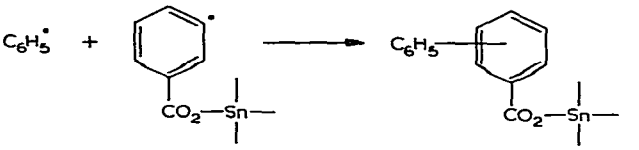
or of forming a tin–carbon bond (the predominant reaction):



(10)

This mechanism would seem to account fairly well for most of the experimental observations and is in accord with the behavior of phenyl radicals in general[12]. Several other observations are in varience with this scheme.

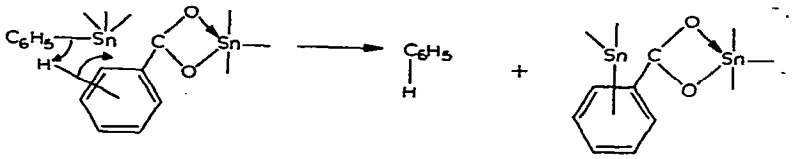
When this pyrolysis was carried out in cumene—a fairly good radical scavenger—then none of the expected phenyl radical–cumene interaction products [*e.g.* $(C_6H_5)_2C(CH_3)_2$ or $C_6H_5{-}C(CH_3)_2{-}C(CH_3)_2{-}C_6H_5$] were found despite a careful search. Further, no substantial evidence was found that the phenyl radical had dimerized with the hypothetical benzoic acid radical:



(11)

to form phenyl substituted benzoic acid residues.

This is fairly strong evidence against a radical mechanism. As an alternate path, one could suggest a concerted H-abstraction by a pseudo phenyl anion (due to the strong polarizability of the Sn–C bond it would be expected that such a shift would proceed with the phenyl group retaining its pair of bonding electrons) and a simultaneous tin–carbon bond formation:

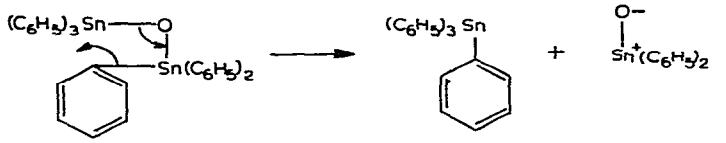


(12)

This would account for the predominant formation of benzene, the formation of the carbon–tin bonds and a maintenance of the Sn^{IV} valence, but not for the formation of biphenyl. This dichotomy suggests that two mechanisms are operating simultaneously: a concerted formation of benzene and new tin–carbon bonds (>95%)

and a homolytic cleavage of the tin–phenyl bond and the formation of biphenyl (~5%). The absence of reaction products with cumene may be due to the relatively small fraction of the total reaction which is of homolytic nature and the consequent small concentrations of interaction products which proved undetectable by the vapor phase chromatographic methods used.

The concerted migration of phenyl groups, probably with their bonding electrons, is not particularly novel in heavy metal or tin-organometallic chemistry. The quantitative rearrangement of bis(triphenyltin) oxide to tetraphenyltin and poly-[diphenyltin oxide][3] can be visualized as proceeding through such a mechanism:



(13)

while the migration of a phenyl group from tin to mercury in an aqueous caustic medium[13],

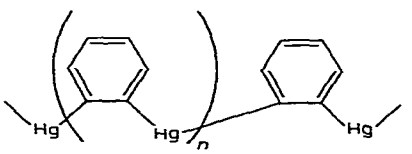
$$C_6H_5SnO_2H + H_2O + HgO \xrightarrow{OH^-} (C_6H_5)_2Hg + SnO_2 \quad (14)$$

may well involve such a mechanism. Numerous reactions of this type exist in the main group heavy metal organometallic chemistry.

Phenylmercury benzoate also lost benzene and carbon dioxide in almost theoretical quantity:

$$C_6H_5HgO_2CC_6H_5 \rightarrow C_6H_6 + CO_2 + \text{“}C_6H_4Hg\text{”} \quad (15)$$

When this “C_6H_4Hg” residue was reacted with bromine in pyridine (25°), a clear solution resulted quickly. Vapor phase chromatography showed little bromobenzene (0.9%), 85.1% dibromobenzene (55.9% *ortho*, 7.8% *meta*, 21.4% *para*), 9.8% tri-, and 0.9% tetrabromobenzenes (all area %). No brominated biphenyls appeared to be present. The high *ortho* content of the dibromobenzene was surprising. Evidently, the “C_6H_4Hg” structure must be in large part:



(16)

This structure is similar to the known $(C_6H_4Hg)_6$ hexamer, m.p. 326° (decompn.)[14,15].

Diphenylantimony benzoate also decomposed to benzene and a nonvolatile residue (no carbon dioxide in evidence) while the arsenic compound and triphenylsilyl benzoate did not decompose at 400°. The latter compound did seem to decompose at about 525°.

EXPERIMENTAL

These tin benzoates are quite readily hydrolyzed. Therefore, precautions must be taken to exclude moisture. The preparative work and reagent transfers were carried out in a nitrogen filled drybox.

Preparation of diphenyltin dibenzoate

A benzene (75 ml) solution of benzoic acid (0.0462 mole) and triethylamine (0.0462 mole) was added to a benzene (50 ml) solution of diphenyltin dibromide (0.0231 mole). The resulting slurry was filtered after 30 min of stirring. The dry filter cake weighed 8.4 g, 100% of theory for triethylamine hydrobromide. The clear filtrate was evaporated until a mush remained and then enough benzene was added to yield a clear solution at 60°. Cooling, filtering and drying yielded 9.65 g (81%) of diphenyltin dibenzoate, m.p. 116–117°. (Found: C, 60.46; H, 4.08; Sn, 23.7. $C_{26}H_{20}O_4Sn$ calcd.: C, 60.59; H, 3.88; Sn, 23.10%.) Alternate method (usually gives a better product).

Dry sodium benzoate (0.10 mole) was treated with a benzene (300 ml) solution of diphenyltin dibromide (0.0462 mole) at reflux overnight. Filtration and recrystallization as above gave 9.5 g diphenyltin dibenzoate, 80% yield, m.p. 119–121°. (Found: C, 59.83; H, 3.83; Sn, 23.1; mol.wt. cryoscopic in benzene under N_2, 489. $C_{26}H_{20}O_4Sn$ calcd.: C, 60.59; H, 3.88; Sn 23.10%; mol.wt., 515.)

Preparation of triphenyltin benzoate

A hexane (100 ml) solution of bis(triphenyltin) oxide (0.01398 mole) and benzoic anhydride (0.01398 mole, benzoic acid free) was refluxed for 16 h. The clear solution was allowed to cool and the resulting crystals filtered to give 10.5 g. (80% yield) of triphenyltin benzoate, m.p. 82–84°, (lit.[16] 82.5–84.0°). (Found: C, 64.29; H, 4.60; Sn, 25.5; mol.wt. cryoscopic in benzene under N_2, 483. $C_{25}H_{20}O_2Sn$ calcd.: C, 63.68; H, 4.24; Sn, 25.3%; mol.wt., 471.)

Reaction of benzoic acid with tetraphenyltin

Benzoic acid (0.236 mole) and tetraphenyltin (0.117 mole) were refluxed in xylene (250 ml) for 20 h. Then 50 ml of distillate was removed and examined by GLC. It contained 0.247 mole of benzene (1.05 mole C_6H_6/mole benzoic acid). All volatiles were removed from the reaction mass and the resulting solids were refluxed for two h with aqueous caustic (300 ml water plus 20 g NaOH). The remaining solids were filtered off, washed until neutral with water and air dried to give 24.2 g of tetraphenyltin (0.0567 mole, 48.5% of charge), identical with authentic material by mixed m.p. and IR spectrum. The aqueous liquors were acidified (hot) and the copious precipitate filtered, washed with water and dried to give 8.35 g of white, infusible solids. (Found: Sn, 65.8%. SnO_2 calcd.: Sn, 78.8%.)

Pyrolysis of diphenyltin dibenzoate

Diphenyltin dibenzoate (9.55 g, 0.01855 mole) was heated in a glass tube, which was connected to a dry ice trap, at 300° (Wood's metal bath) for 1 h. After 5 min heating, a considerable amount of volatiles appeared. At the end of the heating period, a slight vacuum was applied to the system. On cooling, 6.45 g of a brittle, tan residue remained (6.66 g theory). (Found; C, 47.73; H, 2.61; all Sn as Sn^{IV}*. $C_{14}H_8O_4Sn$ calcd.: C, 46.79; H, 2.23%.)

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* The sample was dissolved in conc. sulfuric acid, with nitrogen flushing. Deaerated water and conc. hydrochloric acid were then added in excess. Iodometric titration followed. The sample titre was same as blank titre. This method was employed with a known Sn^{II} compound (stannous octoate) with excellent recovery of all tin [27.0% Sn^{II} found *vs.* 27.4% Sn^{II} calcd.].

The trap contents (2.23 g) consisted of 97.2% benzene and 2.8% biphenyl (by GLC). A small amount of solid sublimate in the tube-trap connection (0.55 g) was shown to contain 30.0% biphenyl. The rest seemed to be sublimed diphenyltin dibenzoate. The total distillate, therefore, contained 0.0308 mole of C_6H_5, 83% of theoretical phenyl radicals.

A similar pyrolysis reaction resulted in a recovery of 92.4% of the phenyl groups as 97.3 mole % benzene and 2.7 mole % biphenyl.

Work-up of pyrolyzate solids with Br_2/pyridine

Bromine (0.0515 g-atom) was added slowly to a slurry of the pyrolyzate residue (4.75 g) in pyridine (24.6 g) at 25°. The reaction was initially exothermic and stirring was continued for 18 h. Then the liquid was heated to 90° for 20 min. GLC of the liquors showed these to contain 1.10 wt.% C_6H_5Br. This indicates that $24.6 \times 0.0110/157 = 0.00172$ mole of bromobenzene had been formed [6.5 mole % of available C_6H_5–Sn groups of $(C_6H_5)_2Sn(O_2CC_6H_5)_2$].

The pyridine solution was added to aqueous caustic (10 g NaOH in 75 ml H_2O, 3.0 g Na_2SO_3) and this evaporated to dryness. The solids were refluxed with aq. ethanolic HCl for 24 h and the organic fraction isolated by extraction with ether. The acids were then esterified with methanolic trimethyl orthoformate. This yielded a colorless solid (on removal of volatiles). (Found: C, 42.54; H, 2.67; Br, 31.79; O, 13.56. Ratio C/Br is 8.0/0.90. $C_8H_7BrO_2$ calcd.: C, 44.64; H, 3.26; Br, 37.20; O, 14.90%.)

The IR spectra of this ester mixture, as well as the free acids, showed that they consisted largely of the *o*-bromobenzoic acid (methyl ester). Very little of the *meta* and *para* isomers was present (< 10% total). Unfortunately, this mixture could not be resolved by gas chromatography (even using a 300 ft. capillary column).

Acidic hydrolysis of diphenyltin dibenzoate pyrolysis residue

Some of the decomposition residue (3.60 g) was refluxed with aqueous, ethanolic hydrogen chloride for 7 days. The ethanol was distilled off and the residual liquors were extracted twice with benzene. This procedure was repeated with addition of some conc. sulfuric acid. The benzene liquors were carefully evaporated to dryness yielding 1.83 g of a colorless crystalline solid m.p. 102–112° (benzoic acid m.p. 121°). Crystallization from aqueous methanol yielded pure benzoic acid, m.p. 119–120°. (Found: C, 68.49; H, 4.38; O, 25.72; mol.wt. 1% in THF, vapor phase osmometer, 37°, 153, 154; neutr. equiv., 122, 124. $C_7H_6O_2$ calcd.: C, 68.86; H, 4.92; O, 26.22%; mol.wt., 122; neutr. equiv., 122.) This (1.83 g) represents a 76.4% yield of impure benzoic acid. Further hydrolysis did not result in a recovery of more benzene solubles. The IR spectrum of this uncrystallized, benzene soluble fraction was virtually superimposable with that of authentic benzoic acid but had a few additional bands (one at 747 cm^{-1}) which could be due to a biphenyldicarboxylic acid.

The aqueous liquors on neutralization and filtration yielded 1.45 g of a white solid; 1.51 g calcd. for SnO_2. (Found: C, 0.69; H, 1.07; ash, 87.0. SnO_2 calcd.: ash, 100.0%.)

Pyrolysis of diphenyltin dibenzoate in cumene

A solution of diphenyltin dibenzoate (0.00583 mole) in cumene (9.70 g) was

heated at 300° for 1 h in a sealed glass tube. On cooling, the liquid composition (exclusive of cumene) was shown to be: benzene, 79.5; biphenyl, 5.2; phenylbenzoate, 13.4; benzoic acid, 2.9 (all wt.%). No 2,2-diphenylpropane or 2,3-diphenyl-2,3-dimethylbutane could be found (used known standards).

Pyrolysis of triphenyltin benzoate

Triphenyltin benzoate (0.0440 mole) was heated at 350° for 2 h (15 min of heating at 300° yielded no decomposition products). The weight loss was 6.8 g (99.2% of theory for loss of 2 C_6H_6) which was recovered as a liquid containing 97.5 wt.% benzene and 0.2% biphenyl (and small amounts of other volatiles), 0.0872 mole "phenyl", 99.2% of theory. The brittle, tan residue weighed 14.2 g (13.89 g theory). (Found: C, 51.36; H, 2.83. $C_{13}H_8O_2Sn$ calcd.: C, 49.51; H, 2.54%.)

Pyrolysis of tin tetrabenzoate

The tin tetrabenzoate was prepared by refluxing tetraphenyltin (0.0586 mole) with dry benzoic acid (0.2344 mole) in xylene (250 ml). The benzene and xylene were distilled off to a pot temperature of 240° and the reaction mixture finally heated at 100°/0.1 mm for 1 h to give 34.0 g of residue (35.3 g theory). (Found: Sn, 19.0. $C_{28}H_{20}O_8Sn$ calcd.: Sn, 19.8%.)

This tin tetrabenzoate (15.0 g) was heated at 300° for 1 h. No volatiles collected in the dry ice trap but a small amount of sublimate appeared on the flask neck (1.5 g, m.p. 115–122°, probably benzoic acid). The flask residue, was a black, hard solid (13.3 g). (Found: Sn, 24.9%.) The IR spectrum showed the presence of carboxylate absorptions and monosubstituted phenyl groups and was essentially the same as the starting material.

Pyrolysis of phenylmercury benzoate

Phenylmercury benzoate (0.134 mole; Metal Salts Inc., recrystallized twice from benzene/heptane, m.p. 97–99°; decompn. 220–240° in capillary; lit.[17] m.p. 97–98°) in a flask with dry ice trap attached was placed into the 300° metal bath. The substance started to decompose almost at once, giving rise to a condensate and a non-condensable gas. After 1 h at 300°, the flask was removed and cooled. The white residue weighed 36.5 g (37.1 g theory for C_6H_4Hg) and did not melt below 400°. (Found: C, 21.20; H, 1.01; Hg, 72.5. C_6H_4Hg calcd.: C, 26.10; H, 1.45; Hg, 72.45%.)

TABLE 3

CHROMATOGRAPHIC DATA ON "C_6H_4Hg"–BROMINE REACTION PRODUCTS

Compound	Retention time (min) (OV-1, 175°)	Area (%)	Retention time (min) (Capillary column)	Area (%)
C_6H_5Br	0.9 (shoulder)	4.2		
o-$Br_2C_6H_4$	2.0–4.0 (unresolved)	85.1	12.1	55.9
m-$Br_2C_6H_4$			9.65	7.8
p-$Br_2C_6H_4$			10.2	21.4
$Br_3C_6H_3$	5.7 and 6.6	9.8		
$Br_4C_6H_2$	14.9	0.9		

The IR spectrum showed the absence of carboxyl group absorptions. The trap contents weighed 11.0 g (after a trap to trap distillation at 35°/vac.); 10.5 g theory for 0.134 mole benzene. GLC showed this liquid to be exclusively benzene. About 2.60 g of a colorless solid were recovered from the reaction flask top and trap connection.

Five grams of the pyrolyzate residue (18 mmole "C_6H_4Hg") were slowly added to bromine (0.075 g-atom) in pyridine (50 ml). The solid dissolved readily at r.t. within one h. After standing for one week, the gross liquid was analyzed for the various polybromobenzenes. Separation was carried out, first, on a 2 m OV-1 column at 175°. The isomeric dibromobenzenes were assayed on a Perkin–Elmer capillary instrument (150 m carbowax coated column, 140°, 20 psi He, 100/1 splitter ratio). Pure dibromobenzenes were used as standards. No brominated biphenyls appeared to be present.

Preparation of diphenylantimony benzoate

A slurry of diphenylantimony chloride (0.0965 mole) and dry sodium benzoate (0.0965 mole) was stirred at 25° in acetonitrile (200 ml) overnight. The solids were filtered off and the benzoate crystallized from about 100 ml of the solution, giving 7.30 g of needles (19.1% yield), m.p. 121–122.5°. (Found: C, 57.31; H, 3.98. $C_{19}H_{15}O_2Sb$ calcd.: C, 57.58; H, 3.79%.) The IR spectrum of this substance had the carboxylate doublet at 1335 cm^{-1} and 1610 cm^{-1}.

Pyrolysis of diphenylantimony benzoate

Diphenylantimony benzoate (0.0175 mole) was pyrolyzed at 400° for 1 h. The residue was a black, brittle solid, 4.25 g (4.21 g theory for $C_6H_3CO_2Sb$). (Found: C, 34.38; H, 1.37. $C_6H_3CO_2Sb$ calcd.: C, 35.00; H, 1.25%.)

The condensate trap (2.70 g; 2.73 g theory for 0.0370 mole benzene) contained 98.6 wt.% benzene and no more than 1.1% biphenyl in addition to a few other impurities.

Preparation of diphenylarsenic benzoate

A heptane (400 ml) solution of bis(diphenylarsenic) oxide (0.0191 mole) and benzoic anhydride (0.0191 mole) was refluxed for 24 h. The solvent was distilled off and the residue crystallized from hot benzene/cyclohexane giving 7.0 g of crystals (92% yield), m.p. 68–69°. (Found: C, 65.18; H, 4.41; As, 21.01. $C_{19}H_{15}AsO_2$ calcd.: C, 65.14; H, 4.29; As, 21.43%.)

The IR spectrum of this substance had a single, intense carbonyl absorption at 1695 cm^{-1}.

Attempted pyrolysis of diphenylarsenic benzoate

Diphenylarsenic benzoate was heated at 400° for 1 h. There appeared to be no weight loss or condensate in the trap.

Preparation of triphenylsilyl benzoate

An ether (300 ml) slurry of triphenylchlorosilane (0.0340 mole) and sodium benzoate (0.19 mole) was stirred for 48 h. This was then filtered, the ether distilled off, and the residue crystallized twice from hot cyclohexane to give 7.0 g (54% yield), m.p. 126–130°; lit.[18] m.p. 127–129°. (Found: C, 79.10; H, 5.39; Si, 7.57. $C_{25}H_{20}O_2Si$

calcd.: C, 78.95; H, 5.26; Si, 7.37%.)

The IR spectrum had an intense carbonyl absorption at 1700 cm^{-1}. This compound underwent no pyrolytic decomposition at 400° (1 h). At 525° there appeared to be decomposition to benzene, biphenyl and a residue which analyzed as $C_{12}H_9SiO_{1.4}$.

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