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ORGANOMERCURY COMPOUNDS

XXVI*. THERMAL DECOMPOSITION OF MERCURIC 2,6-DISUBSTITUTED BENZOATES

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Summary

The main thermal decomposition path for mercuric 2,6-disubstituted benzoates, $(RCO_2)_2Hg$ ($R = 2,6\text{-}X_2C_6H_3$; X = F, Cl, Br, or Me), can be varied considerably. In boiling dimethyl sulphoxide, decarboxylation occurs giving the corresponding diarylmercurial (X = F or Cl) or $RHgO_2CR$ derivative (X = Me or Br). There is considerable competition from reaction of the mercuric salt with the solvent in the last three cases. With boiling pyridine as medium, the 2,6-difluorobenzoate yields a mixture of R_2Hg and $RHgO_2CR$ derivatives, but the 2,6-dichlorobenzoate only gives $(RCO_2)_2Hg(py)_2$. Thermal decomposition of the mercuric benzoates under vacuum yields the carboxylic acids and complex mercuration products, mainly based on 3-mercurated 2,6-disubstituted benzoates, with partial additional mercuration and/or decarboxylation. Pyrolysis of mercuric 2,6-dichlorobenzoate at atmospheric pressure results in both mercuration and decarboxylation, giving *m*-dichlorobenzene as the main volatile product and a complex mercurial with 1,3-dimercurated-2,6-dichlorobenzene repeating units and 2,6-dichlorophenyl terminal groups.

Introduction

There are two main paths for thermal decomposition of mercuric benzoates [2], viz mercuration (1)

$$n(C_6H_{5-m}X_mCO_2)_2Hg \rightarrow nC_6H_{5-m}X_mCO_2H + \left(HgC_6H_{4-m}X_mCO_2\right)_n \qquad (1)$$

or decarboxylation (*ipso* mercuration) (2).

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$$(C_6H_{5-m}X_mCO_2)_2Hg \rightarrow (C_6H_{5-m}X_m)_2Hg + 2CO_2 \quad (2)$$

Reaction (2) is an important synthetic route to diarylmercurials [2]. Whilst it is known in general terms that thermal decarboxylation is favoured by inductively electron withdrawing substituents [2,3], and mercuration by electron donating substituents [4-6], the scope and limitations of decarboxylation as a preparative method for diarylmercurials has not been established. In an attempt to define more clearly the factors controlling reactions (1) and (2), we are investigating the thermal decomposition of a range of partly substituted mercuric benzoates, and now report the decomposition of some mercuric 2,6-disubstituted benzoates under a variety of conditions.

Results and Discussion

(a) Preparation and characterization of the mercuric carboxylates

The mercuric benzoates $(2,6\text{-}X_2C_6H_3CO_2)_2Hg$ (X = F, Cl, Br, or Me) were prepared straightforwardly by reaction (3), and their properties and characterization are summarized in Table 1.

$$2\ 2,6\text{-}X_2C_6H_3CO_2H + (CH_3CO_2)_2Hg \rightarrow (2,6\text{-}X_2C_6H_3CO_2)_2Hg\downarrow + 2CH_3CO_2H \quad (3)$$

For X = Cl, Br, or Me, the relatively large separations between the $\nu(CO_2)$ frequencies (Table 1) (cf. 225 cm^{-1} for sodium 2,6-dichlorobenzoate) are consistent [7] with unidentate carboxylate coordination. Evidence of decarboxylation under electron impact was obtained for all compounds. However, it is not possible to extrapolate from mass spectrometric behaviour to thermal decarboxylation [8,9].

(b) Thermal decomposition of mercuric benzoates in boiling dimethyl sulphoxide

Details of several reactions are given in Table 2. Decarboxylation giving the diarylmercurial [reaction (4)] was observed when R = $2,6\text{-}F_2C_6H_3$ or

$$(RCO_2)_2Hg \rightarrow R_2Hg + 2CO_2 \quad (4)$$

$2,6\text{-}Cl_2C_6H_3$, whereas the organomercuric carboxylate [reaction (5)] was the sole organometallic product when R = $2,6\text{-}Br_2C_6H_3$ or $2,6\text{-}Me_2C_6H_3$. No mercurial was

$$(RCO_2)_2Hg \rightarrow RHgO_2CR + CO_2 \quad (5)$$

obtained on decomposition of mercuric benzoate. Mercuration [e.g. reaction (1), X = F, Cl, Br, Me, or H; m = 2] was not observed. However, there was considerable competition from reaction of the mercuric salt with the solvent [reaction (6)] in all cases except mercuric 2,6-difluorobenzoate, which decarboxylated more rapidly than the other carboxylates.

TABLE 1

PROPERTIES OF MERCURIC 2,6-DISUBSTITUTED BENZOATES

$(RCO_2)_2Hg$ R	m.p.[a] (°C)	Found (Calc.) C(%)	 H(%)	$\nu(CO_2)$[b] (cm^{-1})	^1H n.m.r.[c] H3,5 δ	 H4	Mass spectra[d] M^+	 $RHgO_2CR^+$ m/e	 R_2Hg^+
$2,6-F_2C_6H_3$	192	32.5	1.2	e	7.0 - 7.7[f]		516	472	428
	277-280	(32.7)	(1.2)	1345					
$2,6-Cl_2C_6H_3$	216	29.2	1.2	1626	7.50	7.40	580	536	492
	265	(29.0)	(1.0)	1325	$^3J(H,H)$ 8.0Hz				
$2,6-Br_2C_6H_3$	218	22.6	1.1	1617	7.67	7.23			672
		(22.2)	(0.8)	1321	$^3J(H,H)$ 7.5Hz				
$2,6-Me_2C_6H_3$	165	43.0	3.9	1623	7.03[g]	7.13[g]	500	456	412
	280	(43.3)	(3.6)	1340	$^3J(H,H)$ 8.0Hz				

[a] With effervescence. Where two values are given, the compound melted at the lower value, and then solidified and remelted on further heating. [b] All absorptions s or vs and often broad. [c] AB_2 pattern except for R = $2,6-F_2C_6H_3$ (complex multiplet). [d] Most intense peak of a cluster with the correct isotope pattern for the assignment given. [e] Bands at 1621s, 1599s, 1582s, and 1553s are attributable to $\nu_{as}(CO_2)$ and/or $\nu(CC)$. [f] ^{19}F n.m.r. 118.6,s ppm upfield of internal $CFCl_3$. [g] Together with 2.31,s,CH_3; intensity ratio H3,4,5:CH_3 = 1:2.

TABLE 2

THERMAL DECOMPOSITION OF MERCURIC BENZOATES IN REFLUXING DIMETHYL SULPHOXIDE

$(RCO_2)_2Hg$ R	g	Me_2SO (ml)	Reaction Time (h)	Products CO_2 (%)	 Mercurial	 Yield (%)
$2,6-F_2C_6H_3$	2.08	15	2	75	R_2Hg	40[a]
$2,6-Cl_2C_6H_3$	1.07	10	1.3	32	R_2Hg	*ca.* 2[b]
$2,6-Cl_2C_6H_3$	1.18	10	9	37	R_2Hg	13[b]
$2,6-Me_2C_6H_3$	0.53	6	0.8	43	$RHgO_2CR$[c]	8
$2,6-Br_2C_6H_3$	0.46	5	9	48	$RHgO_2CR$[c]	<2
C_6H_5	1.01	10	2.5	12	RCO_2H[d]	49

[a] After recrystallization from ethanol (yield 63%), and benzene/petrol (b.p. 60-110°C). [b] After recrystallization from benzene/petrol (b.p. 90-110°C). [c] Identified by ^1H n.m.r. spectroscopy. [d] No mercurial obtained.

$$2n(CH_3)_2SO + n(RCO_2)_2Hg \rightarrow 2nRCO_2H + nHgS + n(CH_3)_2S + 2(CH_2O)_n \qquad (6)$$

The low yield of mercurials by comparison with carbon dioxide when R = 2,6-$Br_2C_6H_3$ or 2,6-$Me_2C_6H_3$ (Table 2) indicates that other decarboxylation products must be formed. Mercury metal was obtained in both reactions and tetramethylbiphenyl when R = 2,6-$Me_2C_6H_3$. Their formation can be explained by the radical decarboxylation path (7) - (10).

$$(RCO_2)_2Hg \rightarrow RCO_2^{\cdot} + RCO_2Hg^{\cdot} \qquad (7)$$

$$RCO_2Hg^{\cdot} \rightarrow Hg + RCO_2^{\cdot} \qquad (8)$$

$$RCO_2^{\cdot} \rightarrow R^{\cdot} + CO_2 \qquad (9)$$

$$R^{\cdot} + (RCO_2)_2Hg \rightarrow RCO_2Hg^{\cdot} + R_2 + CO_2 \qquad (10)$$

A similar path has been proposed to explain the formation of unsymmetrical biphenyls on pyrolysis of diphenyllead bis(polyfluorobenzoates) [10]. It is also possible that aromatic carboxylic acids formed by (6) slowly decarboxylate under the conditions used.

The position of mercury in the bis(2,6-dihalogenophenyl)mercurials (Table 2) can be unambiguously established from their n.m.r. and infrared spectra. Thus, the single fluorine resonance of the difluoro compound is indicative of symmetrical substitution, the chemical shift is as expected (cf. (m-$HC_6F_4)_2Hg$ [11] and 3,5-$H_2C_6F_3HgCl$ [12]) for fluorine *ortho* to mercury and hydrogen, and the mercury-fluorine coupling constant is in good agreement with ^3J(Hg, F) of bis(pentafluorophenyl)mercury [11,13]. The ^1H n.m.r. spectrum of bis(2,6-dichlorophenyl)-mercury shows a characteristic AB_2 pattern, the magnitude of J(H, H) indicating three adjacent hydrogen atoms. However, the corresponding spectrum of (2,6-$F_2C_6H_3)_2Hg$ is too complex for simple analysis. Intense infrared absorptions of (2,6-$X_2C_6H_3)_2Hg$ compounds at 785 (X = F) and 772 (X = Cl) cm^{-1} [γ(CH)] and weaker features at 699 (X = F) and 693 (X = Cl) cm^{-1} are consistent [14] with three adjacent hydrogen atoms.

2,6-Dimethylphenylmercuric 2,6-dimethylbenzoate (Table 2) was identified by an intense parent ion in the mass spectrum, and by two sets of aromatic resonances, one attributable to 2,6-dimethylbenzoate, and two methyl resonances, one with satellites, in the ^1H n.m.r. spectrum (Experimental Section). The mercury-methyl coupling constant is similar to J(Hg, o-CH_3) of mesitylmercuric acetate and o-tolylmercuric acetate [15]. Identification of 2,6-dibromophenylmercuric 2,6-dibromobenzoate (Table 2) is more tentative. The ^1H n.m.r. spectrum of the reaction products showed an AB_2 multiplet indicative of 2,6-dibromobenzoato-mercury groups overlapping a weaker AB_2 multiplet plausibly attributable to 2,6-dibromophenylmercury groups. Accordingly, a mixture of the $RHgO_2CR$ (R =

$2,6\text{-}Br_2C_6H_3$) derivative and unreacted mercuric carboxylate was probably obtained. Mass spectrometry was uninformative. The highest cluster corresponded to the fully decarboxylated species $(C_6H_3Br_2)_2Hg^+$, as observed for $(2,6\text{-}Br_2C_6H_3CO_2)_2Hg$ (Table 1).

(c) Thermal decomposition of mercuric benzoates in boiling pyridine

Decarboxylation of mercuric 2,6-difluorobenzoate proceeded less readily in boiling pyridine (Table 3) than in dimethyl sulphoxide (Table 2), and a mixture of unreacted mercuric carboxylate, bis(2,6-difluorophenyl)mercury [from reaction (4), R = $2,6\text{-}F_2C_6H_3$], and 2,6-difluorophenylmercuric 2,6-difluorobenzoate [from reaction (5), R = $2,6\text{-}F_2C_6H_3$] was obtained. A key factor in identification of the last compound was the mercury-fluorine coupling constant (Experimental Section), which was similar to $^3J(Hg, F)$ of pentafluorophenylmercuric acetate [13] and was significantly larger than $^3J(Hg, F)$ of bis(2,6-difluorophenyl)mercury. The ratio $^3J(Hg, F)_{RHgO_2CR} : {}^3J(Hg, F)_{R_2Hg}$ is 1.3 : 1 for both R = C_6F_5 [13] and R = $2,6\text{-}F_2C_6H_3$. When the decomposition was carried out in the presence of a free radical scavenger, *p*-dinitrobenzene [16], the yield of carbon dioxide (56%) was essentially unchanged.

Although an earlier preliminary study (1971) indicated that mercuric 2,6-dichlorobenzoate slowly decarboxylated in boiling pyridine, no significant decarboxylation of this compound was observed in the present study (e.g. Table 3), despite the use of several different samples of pyridine of varying purity and dryness. Invariably, the product was bis(2,6-dichlorobenzoato)di(pyridine)-mercury(II), which showed infrared absorption bands attributable [17] to *coordinated* pyridine at 1011, 693, 630, and 414 cm^{-1}. The $\nu(CO_2)$ absorptions (1594, coincident with $\nu(CC)$, and 1370 cm^{-1}) have a separation similar to that of sodium 2,6-dichlorobenzoate [section (a)], consistent [7] with bidentate or

TABLE 3

BEHAVIOUR OF MERCURIC BENZOATES IN REFLUXING PYRIDINE

$(RCO_2)_2Hg$ R	g	Pyridine (ml)	Reaction Time (h)	Yields of Products CO_2 (%)	R_2Hg (%)	$RHgO_2CR$ (%)	$(RCO_2)_2Hg$[a] (%)
$2,6\text{-}F_2C_6H_3$	0.57	6	2	51	26	19	26
$2,6\text{-}F_2C_6H_3$	0.52	5[b]	2	4	0	*ca.*3	*ca.*97
$2,6\text{-}Cl_2C_6H_3$	0.51	5	3	0	0	0	59
$2,6\text{-}Cl_2C_6H_3$	1.00	10	20[c]	*d*	0	8	*d*

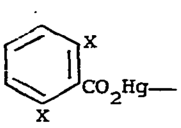
[a] Isolated as $(RCO_2)_2Hg(py)_2$ when R = $2,6\text{-}Cl_2C_6H_3$. [b] In boiling xylene.
[c] At 140°C in a sealed Carius tube. [d] Not examined.

bridging bidentate carboxylate coordination. The most likely structure is polymeric with bridging benzoate groups, *trans* pyridine ligands, and six coordinate mercury, similar to that of dichlorobis(pyridine)mercury(II) [18]. Slight decarboxylation giving 2,6-dichlorophenylmercuric 2,6-dichlorobenzoate [reaction (5), R = 2,6-$Cl_2C_6H_3$] was observed on heating mercuric 2,6-dichlorobenzoate in pyridine under more agressive conditions (Table 3). The presence of 2,6-dichlorophenylmercury groups in the reaction product was established by formation of 1,2,3-trichlorobenzene on treatment of the product with chlorine.

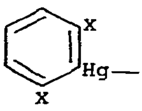
(d) Thermal decomposition of mercuric benzoates under vacuum

When the mercuric 2,6-disubstituted benzoates were heated under vacuum, the corresponding carboxylic acids were formed, hence mercuration occurred [reaction (1), n = 2, X = F, Cl, Br, or Me]. In two cases, traces of the corresponding diarylmercurial were also detected, indicative of slight decarboxylation [reaction (4), R = 2,6-$X_2C_6H_3$, X = F or Cl]. Besides these volatile products, an involatile residue containing the bulk of the mercury was obtained in all reactions.

The ^{19}F n.m.r. spectrum of the residue from decomposition of mercuric 2,6-difluorobenzoate (Experimental Section) was very complex precluding clear identification of satellites from mercury-fluorine coupling. However, use of substituent chemical shifts derived from bis(2,6-difluorophenyl)mercury, 2,6-difluorophenylmercuric 2,6-difluorobenzoate, and reported polyfluorophenylmercurials [12] enabled the groups A - D (X = F) to be identified in the involatile product. It was also possible to distinguish between 2,6-difluorophenylmercury groups (B; X = F) attached to carboxyl groups and ones attached to aromatic carbon atoms (Experimental Section). Observation of several resonances attributable to fluorine *ortho* to two mercury substituents (e.g. in D; X = F) can be attributed to small differences between fluorine chemical shifts when both



A



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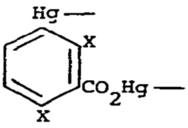

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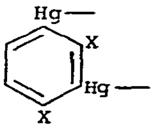

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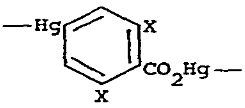

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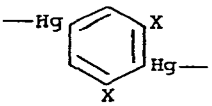

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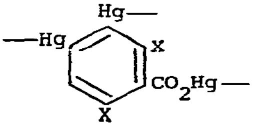

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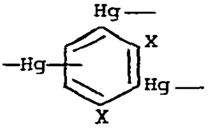


H

mercury atoms of D are attached to carboxyl groups, when one is attached to carboxyl and one to an aromatic carbon, and when both are attached to aromatic carbon atoms. In addition to A - D, the groups E - H (X = F) may be present, related species being obtained on pyrolysis of mercuric 2,6-dichlorobenzoate (below). Groups E - G differ from A - C respectively only in attachment of a further mercury *meta* to both fluorines, and this would only have a minor effect on the fluorine chemical shifts. The presence of H (either possibility) would assist in explaining the complexity of the lower field resonances. Thus, the reaction product contains the bridging groups C and D (and possibly E - H) and the terminal groups A and B.

Cleavage of the involatile residue from thermal decomposition of mercuric 2,6-dichlorobenzoate with chlorine gave a mixture of polychlorobenzoic acids and polychlorobenzenes (Table 4), indicative of the presence of the groups A - H (X = Cl) in the pyrolysis residue. The relationship between specific groups and the cleavage products is given in Table 4. Appropriate blank experiments established that chlorination (chlorodeprotonation) of possible cleavage products did not occur under the chlorodemercuration conditions. The predominant species formed was the 3-mercurated 2,6-dichlorobenzoate group C (X = Cl), and this is consistent with the electronic effects of chlorine and carboxyl [19,20]. 2,6-Dichlorobenzoate groups (Table 4) were presumably present as terminal groups for the units C - H (X = Cl) rather than unreacted mercuric 2,6-dichlorobenzoate, since heating was continued until evolution of 2,6-dichlorobenzoic acid ceased. Some variations in the pyrolysis conditions were examined (see Experimental), but gave a qualitatively similar distribution of products to that in Table 4.

TABLE 4

POLYCHLOROBENZENES FROM CHLORODEMERCURATION OF THE INVOLATILE RESIDUE FROM DECOMPOSITION OF MERCURIC 2,6-DICHLOROBENZOATE (i) UNDER VACUUM[a] AND (ii) UNDER NITROGEN AT ATMOSPHERIC PRESSURE[b]

Polychlorobenzoic acid	%[c] (i)	%[c] (ii)	Source[d]	Polychlorobenzene	%[c] (i)	%[c] (ii)	Source[d]
2,6-$Cl_2C_6H_3CO_2H$	26	0	A	1,2,3-$Cl_3C_6H_3$	8	26	B
2,3,6-$Cl_3C_6H_2CO_2H$	27	1	C	1,2,3,4-$Cl_4C_6H_2$	19	56	D
2,4,6-$Cl_3C_6H_2CO_2H$	2	0	E	1,2,3,5-$Cl_4C_6H_2$	3	5	F
2,3,4,6-$Cl_4C_6HCO_2H$	3	0	G	C_6HCl_5	12	12	H

[a] At 220°C for 3 h. [b] At 230-240°C for 1.5 h. [c] Relative amounts of the polychlorobenzenes. [d] Aromatic group from which the chlorocarbon is derived, X = Cl for A - H.

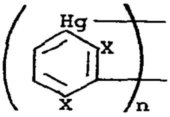
The residue from decomposition of mercuric 2,6-dibromobenzoate was not as extensively investigated. The infrared spectrum showed carboxyl groups to be present, and the ^{1}H n.m.r. spectrum revealed both AB_2 and AB patterns, indicative of 2,6-dibromobenzoate and 3-mercurated 2,6-dibromobenzoate (C, X = Br) groups respectively. Thus, the two major units in the involatile decomposition product were similar to those obtained from mercuric 2,6-dichlorobenzoate.

The formation of the groups C (X = F, Cl, or Br) and E (X = Cl) can be explained by reaction (1) (n = 2) or reaction (11) (R = $2,6\text{-}X_2C_6H_3$).

$$2(\mathrm{RCO_2})_2\mathrm{Hg} \rightarrow 3\text{- or } 4\text{-}(\mathrm{RCO_2Hg})\text{-}2,6\text{-}\mathrm{X_2C_6H_2CO_2HgO_2CR} + \mathrm{RCO_2H} \qquad (11)$$

Groups D (X = F or Cl) and F (X = Cl) can be derived from C and E respectively by decarboxylation. The alternative route to D and F, viz. hemidecarboxylation (5) followed by mercuration, e.g. (12) (R = $2,6\text{-}X_2C_6H_3$) (similar to the thermal decomposition of $\mathrm{PhHgO_2CPh}$ [21]), can be ruled out because it does not explain the formation of carboxylic acids in good yield and because substantial yields of *m*-dihalogenobenzenes were not obtained. Groups G and H (X = Cl) are considered to be derived from further mercuration of C or E and D or F respectively.

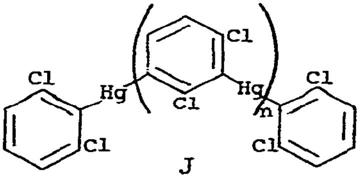
$$n\,\mathrm{RHgO_2CR} \rightarrow n\,\mathrm{CO_2} + n\,m\text{-}\mathrm{X_2C_6H_4} + \qquad (12)$$



I

(e) *Thermal decomposition at atmospheric pressure*

Pyrolysis of mercuric 2,6-dichlorobenzoate at 230-240°C under an atmosphere of nitrogen gave *m*-dichlorobenzene as the main volatile product (cf. $2,6\text{-}Cl_2C_6H_3CO_2H$ under vacuum), together with much smaller amounts of 2,6-dichlorobenzoic acid and bis(2,6-dichlorophenyl)mercury. Chlorodemercuration of the residue established that decarboxylation was essentially complete, that groups D (most common), B, F, and H were present (Table 4), and that the main products can be represented by J. The formation of J can be explained by the reaction sequence, hemidecarboxylation giving 2,6-dichlorophenylmercuric 2,6-dichlorobenzoate [reaction (5), R = $2,6\text{-}Cl_2C_6H_3$], mercuration and decarboxylation (12) giving I (X = Cl), and attachment of terminal 2,6-dichlorophenylmercury groups (13).



J

$$\mathrm{I}\ (\mathrm{X = Cl}) + \mathrm{R_2Hg}\ (\mathrm{R} = 2,6\text{-}\mathrm{Cl_2C_6H_3}) \longrightarrow \mathrm{J} \qquad (13)$$

(f) Conclusions and mechanistic comments

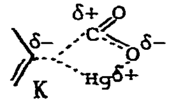
It has been shown that the main reaction path on thermal decomposition of mercuric 2,6-disubstituted benzoates varies with the reaction conditions. In polar organic solvents, decarboxylation giving diarylmercurials (4) or arylmercuric carboxylates (5) predominates. Under vacuum, mercuration (1) predominates and may be followed by decarboxylation and/or further mercuration. At atmospheric pressure decarboxylation and mercuration both occur and the reaction sequence, (5), (12), and (13), differs from that under vacuum. These results suggest that thermal decomposition reactions of mercuric carboxylates have greater scope in organometallic synthesis than has been realised hitherto.

Since mercuric 2,6-difluorobenzoate decarboxylates in pyridine [section *(c)*], but not in the higher boiling but less polar xylene (Table 3), polar solvents clearly aid decarboxylation. This suggests a polar rather than a free radical mechanism. Further confirmation is provided by the failure of the radical inhibitor, *p*-dinitrobenzene, to suppress decarboxylation in pyridine [section *(c)*]. On the other hand it is possible that $RHgO_2CR$ (R = $2,6\text{-}Me_2C_6H_3$ or $2,6\text{-}Br_2C_6H_3$) derivatives (Table 2) are formed by the radical decarboxylation sequence (7) - (9), (14), since other possible radical decarboxylation products

$$R^{\bullet} + (RCO_2)_2Hg \rightarrow RHgO_2CR + RCO_2^{\bullet} \qquad (14)$$

are obtained [section *(b)*]. However, the absence of phenylmercuric benzoate on decomposition of mercuric benzoate is inconsistent with radical formation of organomercuric carboxylates, because all substituents reduce the reactivity of mercuric benzoate in radical decarboxylation [22].

The ease of formation of mercurials from $(2,6\text{-}X_2C_6H_3CO_2)_2Hg$ derivatives [reactions (4) and (5)] in pyridine and dimethyl sulphoxide falls in the sequence X = F > Cl ≈ Me > Br > H. This is clearly inconsistent with classical electrophilic aromatic substitution, and with steric assistance of decarboxylation in the case of the halogeno compounds. The observations can be explained by electrophilic attack on an essentially sp^2 hybridized carbon atom (hence minimising resonance effects of ring substituents), which either develops carbanionic character, e.g. K (stabilised by X = F > Cl > Br > H) or carbonium ion character (stabilised by X = Me > H) depending on whether C-C bond breaking occurs ahead of or behind Hg-C bond formation. Similar substituent dependent mechanisms have been proposed for sulphur dioxide insertion into aryl-tin bonds [23] and for decarboxylation in molten mercuric trifluoroacetate [24]. Polar solvents not only stabilise the polar transition state, but also decrease the electrophilicity of mercury and hence competition from mercuration.



K

Although decarboxylation proceeds more readily in dimethyl sulphoxide than pyridine [sections *(b)* and *(c)*] owing to the combination of high polarity and higher boiling point, the preparative advantages are limited by the side reaction (6). Investigation of other polar high boiling solvents may reveal one with greater synthetic utility.

Experimental

1. *General*

Microanalyses were by the Australian Microanalytical Service, Melbourne. Infrared spectra of compounds as Nujol and hexachlorobutadiene mulls were recorded with a Perkin-Elmer 521 spectrophotometer. Silver chloride plates were used for examination of carboxylate complexes, to prevent the possibility of group exchange [7]. Mass spectra were recorded with a VG Micromass 7070F spectrometer. For compounds containing Hg and Br or Cl, each listed m/e value is the most intense peak of a cluster with the correct isotope pattern. N.m.r. spectra were obtained with a Bruker WH-90 spectrophotometer, and $(CD_3)_2SO$ was used as solvent unless indicated otherwise. ^1H and ^{19}F chemical shifts are in p.p.m. downfield from internal tetramethylsilane and upfield of internal trichlorofluoromethane respectively. G.l.c. was carried out with a Hewlett-Packard 5750 chromatograph, fitted with a 6' x $\frac{1}{8}$" column packed with 10% SE 30 on acid-washed DCMS Chromosorb W80/100.

2. *Reagents and solvents*

2,6-Difluorobenzoic acid was from Bristol Organics, 2,6-dichlorobenzoic acid from Fluka, 2,6-dimethylbenzoic acid from Ega, and the preparation of 2,6-dibromobenzoic acid has been given [24]. Trichlorobenzenes, 1,2,3,4-tetrachlorobenzene, and pentachlorobenzene were from Aldrich, 1,2,3,5-tetrachlorobenzene was from Fine Chemicals of Australia, 2,3,6-trichlorobenzoic acid from Amchem, and 2,3,4,6-tetrachlorobenzoic was provided by M. O'Donoghue (Chem. Dept., Monash). 2,4,6-Trichlorobenzoic acid.— Butylithium (15% in hexane, 15 ml) was slowly added to a stirred solution of 1,3,5-trichlorobenzene (5.1 g) in dry tetrahydrofuran (30 ml) at -78°C under nitrogen. Carbonation (-78°C, 1 h; -78°C - ambient, 0.5 h), hydrolysis, evaporation to low volume, acidification, ether extraction, and purification by dissolution in aqueous Na_2CO_3 and precipitation with HCl gave the *acid* (yield, 51%), m.p. 161-162°C, lit. [25], m.p. 164°C (Found: C, 37.1; H, 1.5. $C_7H_3Cl_3O_2$ calcd.: C, 37.3; H, 1.3%). ^1H n.m.r. spectrum [$(CD_3)_2CO$] 7.61,s, H3,5; 11.4,s(br) (exchangeable), O*H*. G.l.c. of the methyl ester showed a single peak.

Solvents for thermal decomposition reactions: Dimethyl sulphoxide was dried over potassium hydroxide and then calcium hydride, from which it was distilled under nitrogen onto molecular sieves (Grade 4A). Pyridine was dried over potassium hydroxide, and was distilled under nitrogen onto molecular sieves. Xylene was dried over sodium.

3. *Preparations of mercuric benzoates*

Mercuric 2,6-disubstituted benzoates (Table 1) were precipitated as white powders in 75-85% yield on mixing solutions of the stoichiometric amounts of the carboxylic acid and mercuric acetate in warm (*ca.* 50°C) aqueous ethanol (*ca.* 10:1, v/v), containing a few drops of acetic acid for the latter, and cooling to 0°C. Details of their characterization are in Table 1. Mercuric benzoate was obtained in a similar manner, m.p. 166-167°C, lit. [26], m.p. 165°C.

4. *Thermal decomposition reactions in dimethyl sulphoxide*

The mercuric benzoate in dimethyl sulphoxide was refluxed under nitrogen (purified by BASF catalyst R3/11 and molecular sieves), which was then passed through aqueous barium hydroxide. Liberated carbon dioxide was precipitated as barium carbonate, which was determined gravimetrically. Details of reactions are given in Table 2. Except in the decomposition of mercuric 2,6-difluorobenzoate, mercuric sulphide and mercury (identified qualitatively) were precipitated, and a sublimate of paraformaldehyde collected in the condenser (infrared identification [27]) (Found: C, 38.5; H, 6.9; O, 54.7. CH_2O calcd.: C, 40.0; H, 6.7; O, 53.3%). The reaction mixture was filtered, and the organometallic product was precipitated by addition of water to the filtrate.

Bis(2,6-difluorophenyl)mercury. (nc) Recrystallized from ethanol, m.p. 145°C (Found: C, 33.7; H, 1.5; Hg, 46.9. $C_{12}H_6F_4Hg$ calcd.: C, 33.8; H, 1.4; Hg, 47.0%). Mass spectrum: 428(M^+), 315($C_6H_3F_2Hg^+$). ^1H n.m.r. spectrum: 6.8-7.6,m, H3,4,5. ^{19}F n.m.r. spectrum: 91.1,m, with satellites J(Hg, F) 430 Hz, F2,6. ν(CC): 1604s, 1576s, 1445s.

Bis(2,6-dichlorophenyl)mercury. (nc) Recrystallized from benzene/petrol (b.p. 90-110°C), m.p. 228°C (Found: C, 29.4; H, 1.4; Cl, 28.6; Hg, 40.5. $C_{12}H_6Cl_4Hg$ calcd.: C, 29.3; H, 1.2; Cl, 28.8; Hg, 40.7%). Mass spectrum: 492(M^+), 347($C_6H_3Cl_2Hg^+$). ^1H n.m.r. spectrum: AB_2 pattern, 7.29, H4; 7.50, H3,5; ^3J(H,H) 8.0 Hz. ν(CC): 1568m, 1552vs, 1415s. With reaction times < 9 h, purification of the diarylmercurial was very difficult.

2,6-*Dimethylphenylmercuric* 2,6-*dimethylbenzoate.* (nc) The compound remained after washing the water-insoluble product with petrol, m.p. 150-152°C. Mass spectrum: 456(M^+), 412($C_{16}H_{18}Hg^+$), 307($C_8H_9Hg^+$). ^1H n.m.r. spectrum: 2.37,s, 6H, CH_3 of RCO_2 (R = 2,6-$Me_2C_6H_3$), 2.56,s with satellites J(Hg, H) 22 Hz, 6H, CH_3 of RHg; 7.0,m, *ca.* 3H, H3,4,5 of RCO_2; 7.1,m, *ca.* 3H, H3,4,5 of RHg. Evaporation of the petrol washings gave a mixture of an unidentified dimethylphenylcarbonyl compound [ν(CO) = 1725 cm^{-1}] and tetramethylbiphenyl. Mass spectrum: 210(M^+), 162($C_{13}H_6^+$), 133($C_8H_9CO^+$), 105($C_8H_9^+$).

2,6-*Dibromophenylmercuric* 2,6-*dibromobenzoate* was obtained mixed with unreacted mercuric 2,6-dibromobenzoate. ^1H n.m.r. spectrum: Two overlapping AB_2 patterns, 7.24 and 7.72, H4 and H3,5 respectively of RCO_2 (R = 2,6-$Br_2C_6H_3$),

^3J(H, H) 7.5 Hz; 7.36 and 8.05, H4 and H3,5 respectively of RHg, ^3J(H, H) 7.0 Hz. RHg:RCO_2 = 1:11. Ether extraction of the aqueous dimethyl sulphoxide gave a yellow oil containing 2,6-dibromobenzoic acid (i.r. identification).

5. *Thermal decomposition reactions in pyridine*

The reactions in boiling pyridine were carried out in a similar manner to those of section *4*, and the crude products were isolated by evaporation to dryness under vacuum. Details are given in Table 3.

Mercuric 2,6-*difluorobenzoate*. Extraction of the products with benzene left a residue of the reactant (^{19}F n.m.r. identification). The solid obtained on evaporation of the benzene was extracted with cold ether, which was evaporated giving a mixture of bis(2,6-difluorophenyl)mercury (^{19}F n.m.r. identification) and 2,6-difluorophenylmercuric 2,6-difluorobenzoate. ^{19}F n.m.r. spectrum: 88.7,m with satellites J(Hg, F) 565 Hz, 2F, F2,6 of RHg (R = 2,6-$F_2C_6H_3$); 111.6,m, 2F, F2,6 of RCO_2. The ether-insoluble residue was a mixture of the latter compound and mercuric 2,6-difluorobenzoate.

Mercuric 2,6-*dichlorobenzoate*. The product had an infrared spectrum identical with that of bis(2,6-dichlorobenzoato)bis(pyridine)mercury(II) (nc), isolated by cooling a solution of mercuric 2,6-dichlorobenzoate in warm pyridine, m.p. 165–166°C (Found: C, 39.1; H, 2.4; N, 4.2. $C_{24}H_{16}Cl_4HgO_4N_2$ calcd.: C, 39.0; H, 2.2; N, 4.2%).

The attempted decomposition of mercuric 2,6-dichlorobenzoate in pyridine at 140°C (Table 3) was carried out in a sealed Carius tube. After reaction, the pyridine was removed under vacuum and the residue, which was insoluble in benzene, was cleaved with chlorine in dimethylformamide [method; section *7*] giving 1,2,3-trichlorobenzene (8%, i.r. identification).

6. *Attempted thermal decomposition in xylene*

The reaction was carried out as in section *4*. Details are in Table 3. The products were identified by ^{19}F n.m.r. spectroscopy.

7. *Thermal decomposition of mercuric benzoates under vacuum*

The carboxylate $(2,6\text{-}X_2C_6H_3CO_2)_2Hg$ (X = F, Cl, Br, or Me) was heated in a sublimator under vacuum (10^{-2}–10^{-3} mm) at the lowest temperature giving a significant sublimate. Heating was continued until sublimation ceased. A sublimate of 2,6-$X_2C_6H_3CO_2H$ was obtained in each case and contained a little (2,6-$X_2C_6H_3)_2Hg$ for X = F or Cl (i.r. and m.s. identification). Reaction conditions and characterization of the involatile residues are given below.

Mercuric 2,6-*difluorobenzoate* (0.72 g, 170°C, 3h): ^{19}F n.m.r. spectrum of the involatile residue: 67–71, complex m, F *ortho* to two Hg atoms in structure <u>D</u> (X = F); 88.9,m, F2,6 of <u>B</u> attached to carboxyl; 90.2,m, F2 of <u>C</u>; 91.1,m, F2,6 of B attached to an aromatic carbon; 111.8,m,F2,6 of A; 113.4,m,F6 of C. Part of the features at 88-92 ppm is also attributable to F *ortho* to mercury and hydrogen in D.

Mercuric 2,6-*dichlorobenzoate* (*ca.*0.5 g, at 210°C, 10 h; 220°C, 3 h; or 230°C, 2 h). Chlorine was bubbled through a suspension of the involatile residue in dimethylformamide (4 ml) at 0°C. After 5 min, the solid had dissolved and the solution was acidified (HCl). Ether extraction gave a partly crystalline oil, which was separated by extraction with Na_2CO_3 (10%) into a mixture of polychlorobenzoic acids and a mixture of polychlorobenzenes (Table 4) which were separately analysed by g.l.c., the former after conversion into methyl esters by reaction with diazomethane in ether.

Mercuric 2,6-*dibromobenzoate*. (0.11 g, 180-200°C, 5 h). ^1H n.m.r. spectrum of the involatile solid: Overlapping AB_2 and AB patterns, 7.22 and 7.67, H4 and H3,5 respectively of A (X = Br), $^3J(H, H)$ 7.5 Hz; 7.43 and 7.60, H4 and H5 respectively of C, $^3J(H, H)$ 7.5 Hz. $\nu(CO_2)$, 1638 and 1307 cm^{-1}.

Mercuric 2,6-*dimethylbenzoate* (0.54 g, 180°C, 3 h). $\nu(CO_2)$ of the involatile residue, 1600 and 1310 cm^{-1}.

8. *Decomposition of mercuric* 2,6-*dichlorobenzoate at atmospheric pressure*

The carboxylate (1.00 g) was heated at 230-240°C for 1.5 h under nitrogen in a small distillation apparatus. *m*-Dichlorobenzene (0.11 g) containing a little 2,6-dichlorobenzoic acid distilled off (i.r. and m.s. identification), and bis(2,6-dichlorophenyl)mercury (0.02 g) (i.r. identification) was obtained as sublimate. *Pyrolysis residue* (0.63 g). Mass spectrum: 838($C_{18}H_8Cl_6Hg_2^+$), 492($C_{12}H_6Cl_4Hg^+$), 347($C_6H_3Cl_2Hg^+$). I.r. absorption: No $\nu(CO_2)$ bands; 773vs [γ(CH)]. The residue was firstly heated at 220°C under vacuum for 2 h removing bis(2,6-dichlorophenyl)mercury (0.08 g), and the involatile solid was cleaved with chlorine (method: section 7) giving (g.l.c. analysis) a mixture of polychlorobenzenes (Table 4).

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