Organometallic Oxides, Alkoxides, and Peroxides. Part IV.[1] Reaction of Phenylmercury(II) Alkoxides, Oxide, and Hydroxide with Organic Isocyanates

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Crystalline 1:1 adducts ($PhHgNR \cdot CO_2R^1$) are formed by reaction of phenylmercury(II) methoxide ($R^1 = Me$), t-butoxide ($R^1 = Bu^t$), or oxide ($R^1 = HgPh$) with equimolar quantities of alkyl or aryl isocyanates. Phenylmercury(II) hydroxide gives 1:1 adducts ($HNR \cdot CO_2HgPh$) with ethyl and t-butyl isocyanates but with methyl isocyanate a high melting, poorly soluble material of stoicheiometry [$PhHgOH,(PhHg)_2O.MeNCO$] is obtained. Aryl isocyanates and phenylmercury(II) hydroxide react with loss of carbon dioxide to yield NN'-diaryl-N-phenyl-mercurioureas ($PhHgNAr \cdot CO \cdot NHAr$) mixed with phenylmercury arylcarbamates ($HNAr \cdot CO_2HgPh$) and/or N-phenylmercurio-arylamines ($PhHgNHAr$). The latter compounds have been synthesised by azeotropic dehydration of arylamine–phenylmercury(II) hydroxide mixtures and characterised as adducts with phthalic anhydride.

THE varying reactivity of metal-to-hydrogen, -carbon, -nitrogen, -oxygen, and -sulphur bonds in organometallic reagents (M–X) towards substitution [equation (1)]

$$M{-}X + A{-}B \longrightarrow M{-}A + B{-}X \qquad (1)$$

$$M{-}X + A{=}B \rightleftharpoons M{-}A{-}B{-}X \qquad (2)$$

and addition–elimination [equation (2)] processes forms the basis of many new organic syntheses. These synthetic procedures usually involve suitable combinations of substitution, addition, and elimination, subtle

[1] Part III, A. J. Bloodworth, *J. Chem. Soc. (C)*, 1970, 2051.

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variations of which have been developed extensively with organotin reagents.[2] However, for many other metals even the basic reactions have received only scanty attention.

Thus reports of addition processes involving organo-mercury compounds are very limited with respect to both X and A=B. The insertion of sulphur dioxide into mercury–carbon bonds [*e.g.* equation (3)] has been studied in some detail,[3] but information about other additions is sparse. Sulphur trioxide adds across the mercury–carbon bond of diphenylmercury[4a] and di-methylmercury,[4b] and carbon dioxide is inserted into the mercury–oxygen bond of alkylmercury(II) oxides

respect to both M and X. Reactions with organo-metal–oxygen addenda are documented for derivatives of zinc,[8] aluminium,[9] germanium,[10] tin,[2] and lead.[11] The only similar report for mercury is a short communication [12] in which the adduct between phenylmercury(II) methoxide and phenyl isocyanate [equation (7)] is described.

$$\text{PhHgOMe} + \text{PhNCO} \longrightarrow \text{PhHgNPh·CO}_2\text{Me} \qquad (7)$$

With the identification of the separate compounds, phenylmercury(II) oxide and hydroxide,[13] and the development of simple methods for converting them into alkoxides,[1] three types of organomercury(II)–oxygen

TABLE 1

Phenylmercury(II) alkoxide–isocyanate adducts, $\text{PhHgNR·CO}_2\text{R}^1$

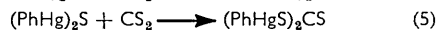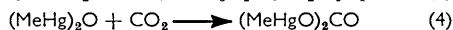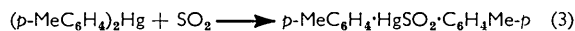|			Chemical shifts[a] (τ)			Found (Required) (%)		
R^1	R	M.p. (°C)	Ph	R^1	R	C	H	N
Me	Me	96—98	2·8[b]	6·45[b]	7·0[b]	29·35 (29·55)	2·85 (3·0)	3·95 (3·85)
Me	Ph	122—124[c]	2·7[b]	6·35[b]	2·7[b]	39·5 (39·3)	3·15 (3·05)	3·4 (3·3)
But	But	84—86	2·75	8·45	8·55	38·0 (40·05)	4·85 (5·1)	3·3 (3·1)
But	Ph	92—94	2·7	8·35	2·7	43·6 (43·45)	4·2 (4·05)	3·1 (3·0)
But	Np[d]	116—118	2·65	8·3br	2·65	48·3 (48·5)	4·1 (4·05)	2·85 (2·7)

[a] 60 MHz [1]H n.m.r. spectra of solutions (10—20%) in dichloromethane. [b] In carbon tetrachloride. [c] Lit.,[12] 127·5—128·5°. [d] Np = 1-naphthyl.

TABLE 2

Phenylmercury(II) oxide–isocyanate adducts, $\text{PhHgNR·CO}_2\text{HgPh}$

		Chemical shifts[a] (τ)		Found (Required) (%)			
R	M.p. (°C)	Ph	R	C	H	Hg	N
Me	88—90	2·8	6·9	26·55 (26·75)	2·2 (2·05)	63·7 (63·85)	2·35 (2·25)
Et	65—105	2·8	{6·4 (q, CH$_2$)[c] / 8·7 (t, CH$_3$)}	28·0 (28·05)	2·5 (2·35)	62·5 (62·45)	2·3 (2·2)
But	116—117	2·8[d]	8·25, 8·6[e]	30·2 (30·45)	3·05 (2·85)		2·05 (2·1)
Ph	105—120	2·85	2·85	33·05 (33·05)	2·3 (2·15)	58·05 (58·1)	2·15 (2·05)
Tol[f]	108—110	2·85	{2·85 (C$_6$H$_4$) / 7·65 (CH$_3$)}	33·8 (34·1)	2·65 (2·4)		1·9 (2·0)
Np[g]	130—132		h	37·1 (37·3)	2·45 (2·3)	54·0 (54·2)	2·0 (1·9)

[a] 60 MHz [1]H n.m.r. spectra of solutions (10—20%) in dichloromethane. [b] J([199]Hg, H$_{ortho}$) 168—174 Hz. [c] J 7 Hz. [d] Pattern more complex than for the other compounds; integration of this and the other two signals indicated an approximate ratio of 10 : 4 : 5. [e] Partially resolved doublet. [f] Tol = p-MeC$_6$H$_4$. [g] Np = 1-Naphthyl. [h] Insoluble.

[*e.g.* equation (4)].[5] Phenylmercury(II) sulphide and alkylmercury(II) alkoxides add to carbon disulphide [equations (5)[6] and (6)[7]].

$$(p\text{-MeC}_6\text{H}_4)_2\text{Hg} + \text{SO}_2 \longrightarrow p\text{-MeC}_6\text{H}_4\text{·HgSO}_2\text{·C}_6\text{H}_4\text{Me-}p \qquad (3)$$
$$(\text{MeHg})_2\text{O} + \text{CO}_2 \longrightarrow (\text{MeHgO})_2\text{CO} \qquad (4)$$
$$(\text{PhHg})_2\text{S} + \text{CS}_2 \longrightarrow (\text{PhHgS})_2\text{CS} \qquad (5)$$
$$(\text{PrHg})_2\text{O} + \text{EtOH} + \text{CS}_2 \longrightarrow \text{PrHgS·CS·OEt} \qquad (6)$$

Alkyl and aryl isocyanates are amongst the most re-active acceptors known and the most versatile with

addenda have become readily available. The reactions of these with representative isocyanates are now reported.

Phenylmercury(II) methoxide and t-butoxide com-bined with equimolar quantities of alkyl or aryl iso-cyanates at room temperature to afford the corre-sponding N-mercuriocarbamates, $\text{PhHgNR·CO}_2\text{R}^1$, characteristics of which are presented in Table 1. Although we have formulated the adducts in this way, we accept that the isomeric structure, RN:C(OR^1)OHgPh, cannot be ruled out, and this is discussed again later. In general the mercuriocarbamates, unlike the starting

[2] A. J. Bloodworth and A. G. Davies, *Chem. and Ind.*, 1972, 490.

[3] N. A. D. Carey and H. C. Clark, *Canad. J. Chem.*, 1968, 46, 649; G. B. Deacon and P. W. Felder, *Austral. J. Chem.*, 1969, 22, 549; P. J. Pollick, J. P. Bibler, and A. Wojcicki, *J. Organometallic Chem.*, 1969, 16, 201; W. Kitching, B. F. Hegarty, S. Winstein, and W. G. Young, *ibid.*, 20, 253.

[4] (a) R. Otto, *J. prakt. Chem.*, 1870, 1, 183; (b) K. A. R. Salib and J. B. Senior, *Chem. Comm.*, 1970, 1259.

[5] D. Grdenic and F. Zado, *J. Chem. Soc.*, 1962, 521.

[6] L. Pesci, *Gazzetta*, 1899, 29, 394.

[7] I. A. Koten and R. Adams, *J. Amer. Chem. Soc.*, 1924, 46, 2764.

[8] J. G. Noltes and J. Boersma, *J. Organometallic Chem.*, 1969, 16, 345.

[9] T. Hirabayashi, T. Sakakibara, and Y. Ishii, *J. Organo-metallic Chem.*, 1972, 35, 19.

[10] Y. Ishii, K. Itoh, A. Nakamura, and S. Sakai, *Chem. Comm.*, 1967, 224.

[11] A. G. Davies and R. J. Puddephat, *J. Chem. Soc.*, 1967, 2663.

[12] A. G. Davies and G. J. D. Peddle, *Chem. Comm.*, 1965, 96.

[13] Part II, A. J. Bloodworth, *J. Organometallic Chem.*, 1970, 23, 27.

alkoxides, are not particularly susceptible towards hydrolysis and they can be handled in air.

Phenylmercury(II) oxide also gave 1 : 1 adducts with both alkyl and aryl isocyanates (see Table 2). Two of the carbamates (R = Et or Ph) consistently melted over a wide temperature range but all their other characteristics were satisfactory. The adducts are hydrolytically stable, but preliminary experiments with 2 : 1 mixtures of methyl or ethyl isocyanate and oxide indicated that multiple additions can take place.

The ^{1}H n.m.r. spectrum of the oxide–t-butyl isocyanate adduct showed two (or perhaps three) t-butyl signals, the integral sum of which was in the correct ratio to the aromatic absorptions. A possible explanation for this is that the three isomeric structures available to the adduct [(Ia), (Ib), and (II)] are all present and any interconversion is slow on the n.m.r. time scale.
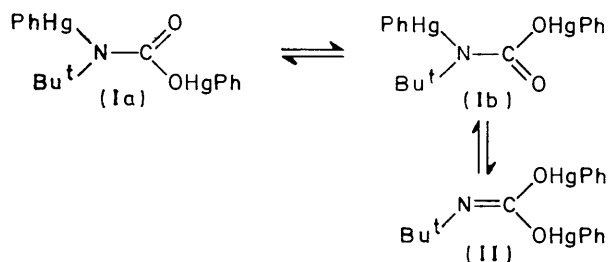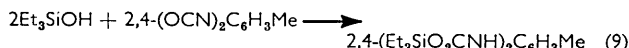

Structures (I) and (II) are related to those suggested earlier for alkoxide adducts, and the cis–trans-isomers of the former (Ia and b) may be distinct if there is hindered rotation due to partial multiplicity in the N–C bond of the type found in amides. It has been suggested [14] that the organotin group in analogous organotin carbamates could be mobile between O- and N-sites, and n.m.r. spectroscopic evidence has recently been presented [15] in support of a similar phenomenon in an organoaluminium carbamate. Thus the possibility of interconvertible isomers [cf. (I) and (II)] should be borne in mind when considering all the adducts described in this paper.

Three distinct types of behaviour were found when phenylmercury(II) hydroxide was treated with isocyanates. Ethyl and t-butyl isocyanates added to equimolar quantities of phenylmercury(II) hydroxide to yield mercury carbamates [equation (8); R = Et or

$$\text{PhHgOH} + \text{RNCO} \longrightarrow \text{RNH·CO}_2\text{HgPh} \qquad (8)$$
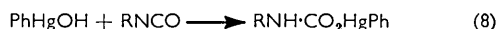
Bu^t]. We believe this formulation to be more likely than the alternative possibilities [PhHgNR·CO$_2$H and RN:C(OH)OHgPh]. The adduct is thus represented as the product of HO-addition rather than HgO-addition, but no mechanistic implications are intended since it seems probable that any mobility of the phenylmercury group will be matched by mobility of the proton. This behaviour parallels that of triethylsilanol with toluene

di-isocyanate [16] [equation (9)], but contrasts with that

$$2\text{Et}_3\text{SiOH} + 2,4\text{-(OCN)}_2\text{C}_6\text{H}_3\text{Me} \longrightarrow$$
$$2,4\text{-(Et}_3\text{SiO}_2\text{CNH)}_2\text{C}_6\text{H}_3\text{Me} \qquad (9)$$

of triethyltin hydroxide and phenyl isocyanate where dehydration to the oxide rather than formation of a tin carbamate takes place.[14]

Phenylmercury(II) hydroxide and methyl isocyanate afforded a sparingly soluble white solid (A) which melted at 169—170°, considerably higher than any of the mercury carbamates described here. A higher yield of the same material was obtained by use of only 0·5 mol. equiv. of methyl isocyanate, but elemental analysis suggested a stoicheiometry nearer to (PhHgOH)$_3$,-MeNCO. The correct stoicheiometry of compound (A) was (PhHg)$_2$O,PhHgOH,MeNCO, since an identical product was obtained by treating the oxide–isocyanate adduct with an equimolar amount of phenylmercury(II) hydroxide. We therefore suggest that the oxide–isocyanate adduct is an intermediate in the formation of compound (A) from the hydroxide–isocyanate mixture. Several pathways to the oxide–isocyanate adduct can be envisaged, but perhaps the most attractive is that of mercuration [equation (10)] of an hydroxide–isocyanate adduct of the type known to be formed with other alkyl isocyanates.

$$\text{MeNH·CO}_2\text{HgPh} + \text{PhHgOH} \longrightarrow$$
$$\text{PhHgNMe·CO}_2\text{HgPh} + \text{H}_2\text{O} \qquad (10)$$
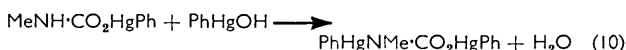
The high m.p., the low solubility, and the stoicheiometry of compound (A) suggested that it might be a salt, the most likely structures for which would be PhHgO$_2$C-$\overset{+}{\text{N}}$Me(HgPh)$_2$ $\bar{\text{O}}$H [related to the bisphenylmercurio-ammonium compounds (PhHg)$_2\overset{+}{\text{N}}$H$_2$ $\bar{\text{X}}$ [17]] or (PhHg)$_3\overset{+}{\text{O}}$ $\bar{\text{O}}_2$CNHMe [analogous to the trismethylmercurio-oxon-ium salts, (MeHg)$_3\overset{+}{\text{O}}$ $\bar{\text{X}}$ [5]]. However, a conductivity measurement on a 10^{-3}M-solution of (A) in nitromethane indicated that it is a non-electrolyte, and ruled out the presence of free ions. The foregoing formulations might still be tenable if the anions are co-ordinated to mercury atoms in the cations sufficiently strongly to provide tight ion pairs. Alternatively the non-ionic structure, PhHgNMeC(OHgPh)$_2$OH, arising from addition of phenylmercury(II) hydroxide across the carbonyl group of the carbamate, can be written. It is conceivable that such an 'orthocarbamate' could exist as the zwitterion, PhHg$\overset{+}{\text{N}}$HMeC(OHgPh)$_2\bar{\text{O}}$.

The third type of behaviour with phenylmercury(II) hydroxide was found in its reactions with aryl isocyanates; carbon dioxide was evolved upon mixing the reagents. The products isolated from reactions with phenyl and p-tolyl isocyanates were shown to be mixtures containing diaryl-N-phenylmercurioureas and unchanged phenylmercury(II) hydroxide together with

[14] A. J. Bloodworth and A. G. Davies, J. Chem. Soc., 1965, 6245.
[15] T. Hirabayashi, T. Sakakibara, and Y. Ishii, J. Organometallic Chem., 1971, 32, C5.

[16] V. V. Astakhin, I. P. Losev, and K. A. Andrianov, Doklady Akad. Nauk S.S.S.R., 1957, 113, 581 (Chem. Abs., 1957, 51, 14,582).
[17] G. B. Deacon and J. H. S. Green, J. Chem. Soc. (A), 1968, 1182.

phenylmercury arylcarbamates and/or N-phenylmercurio-arylamines. We believe that the mercury carbamates are once again formed but, unlike those derived from alkyl isocyanates, they readily lose carbon dioxide. Unimolecular decarboxylation will give the N-mercurioamines [equation (11a)], which can compete for isocyanate with the resultant formation of the N-mercurioureas [equation (11b)]. Bimolecular displacement of carbon dioxide from the mercury carbamate by isocyanate, the more powerful acceptor, can also be envisaged [equation (11c)].
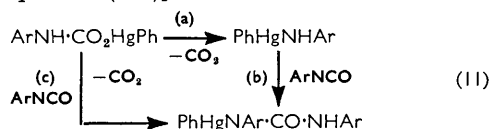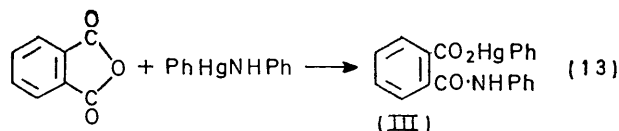
The composition of the mixtures was determined from their i.r. spectra and their behaviour when treated

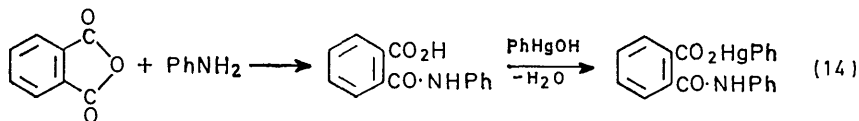$$PhHgOH + PhNH_2 \longrightarrow PhHgNHPh + H_2O \qquad (12)$$
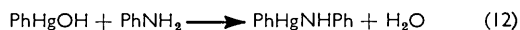
with phthalic anhydride in comparison with similar data obtained for authentic samples of the components.

This required the independent synthesis of the N-phenylmercurio-arylamines. Surprisingly little is

known about the N-organomercurio-amines in general. The only well-characterised examples are $MeHgN(CF_3)_2$,
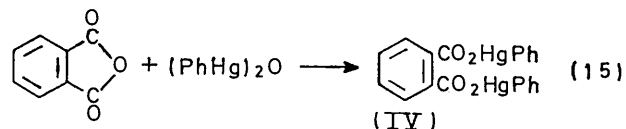
mercury(II) hydroxide in refluxing 95% ethanol [equation (12)]. Unfortunately the product was characterised only by m.p. and mercury analysis, and few experimental details were given.

We found that the mercuration of aniline was unsuccessful in boiling 95% ethanol, but that it proceeded rapidly and quantitatively in refluxing benzene with azeotropic removal of water. The product was identified as N-phenylmercurioaniline by C, H, and N analysis, from its i.r. spectrum, which showed many features similar to those of aniline, and from its ^1H n.m.r. spectrum, which was consistent with N-mercuration and ruled out the alternative possibility of C-mercuration in the aromatic ring, a process which occurs when aniline is treated with mercuric salts.[22] It was further characterised by conversion into NN'-diphenyl-N-phenylmercuriourea, which both confirmed that reaction (11b) can occur and provided an authentic sample of the N-mercuriourea, and by reaction with phthalic anhydride to give compound (III) [equation (13)]. For reference this derivative was also synthesised by mercuration of phthalanilic acid [equation (14)].

Compound (III) was obtained when the mixture derived from phenylmercury(II) hydroxide and phenyl isocyanate was treated with phthalic anhydride, but diphenylurea and compound (IV), identified by independent synthesis from phenylmercury(II) oxide and phthalic anhydride [equation (15)], were also formed. Corresponding results were obtained for the product derived from p-tolyl isocyanate.

A separate experiment showed that compound (IV)

which was prepared by disproportionation of a mixture of the symmetrical mercurials,[18] and $RHgN(SiMe_3)_2$ (R = Me or Et), which were obtained by refluxing the corresponding alkylmercury chlorides with the appropriate lithium amide in toluene.[19] Neither of these methods was readily applicable to the synthesis of N-phenylmercurio-arylamines (PhHgNHAr), but there was some evidence that these might be available by direct mercuration of the amine. Thus the products obtained by treating propylmercury(II) t-butoxide with diethylamine at 50—60° have been interpreted in terms of decomposition of $PrHgNEt_2$,[20] and $PhHgNH_2$ has been suggested as a possible intermediate in the reactions of phenylmercury(II) acetate with ammonia.[17] But most important was the report[21] that N-phenylmercurioaniline can be prepared by treating aniline with phenyl-

and diphenylurea are produced when a mixture of NN'-diphenyl-N-phenylmercuriourea and phenylmer-

cury(II) hydroxide is treated with phthalic anhydride; reactions (16) and (17) are probably involved.
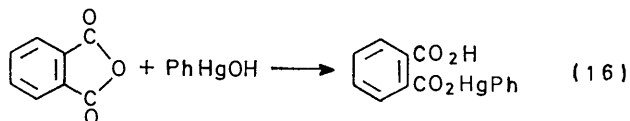
N-Phenylmercurioaniline absorbed carbon dioxide at room temperature to give a viscous oil, presumably the

[18] R. C. Dobbie and H. J. Emeléus, *J. Chem. Soc. (A)*, 1966, 367.

[19] J. Lorberth and F. Weller, *J. Organometallic Chem.*, 1971, **32**, 145.

[20] S. F. Zhil'tsov and V. M. Kashin, *J. Gen. Chem. (U.S.S.R.)*, 1971, **41**, 2121.

[21] M. A. Smalt, C. W. Kreke, and E. S. Cook, *J. Biol. Chem.*, 1957, **224**, 999.

[22] F. C. Whitmore, ' Organic Compounds of Mercury,' Chem. Catalog Comp., New York, 1921, ch. 10; L. G. Makarova and A. N. Nesmeyanov, ' The Organic Compounds of Mercury,' North-Holland, Amsterdam, 1967, pp. 98, 484.

phenylmercury(II) phenylcarbamate [reverse of equation (11a)]. Furthermore this product reacted with phthalic anhydride to afford a quantitative yield of the derivative (III) [equation (18)]. These results suggest that the N-mercuriourea is formed from isocyanate and hydroxide by the bimolecular process [equation (11c)] and that the mercury carbamate, rather than the N-mercurio-amine, is the precursor of compound (III), unless the heat generated during the formation of the mercury carbamate is sufficient to induce its decarboxylation [equation (11a)].

light petroleum (b.p. 60—80°) (see Table 1). The common features of the i.r. spectra (mulls) were strong, broad absorptions at 1640—1670 cm^{-1} ($v_{C=O}$) and the bands generally associated with the phenyl group of phenyl-mercury(II) compounds.[1]

Reaction of Phenylmercury(II) *Oxide with Isocyanates.*—The isocyanate (1·0 mol. equiv.) in dichloromethane (ca. 5 ml.) was added with swirling to a slurry of the oxide (ca. 5 mmol) in dichloromethane (ca. 7 ml). A clear solution was rapidly formed and its i.r. spectrum confirmed that all the isocyanate had been consumed. Evacuation at 0·01 mmHg yielded analytically pure phenylmercury N-phenylmercurio-

$$
\text{[structure]} \begin{array}{l} CO_2H \\ CO_2HgPh \end{array} + PhHgNPh \cdot CONHPh \longrightarrow \text{[structure]} \begin{array}{l} CO_2HgPh \\ CO_2HgPh \end{array} + (PhNH)_2CO \qquad (17)
$$

$$
\text{[phthalic anhydride structure]} + PhHgO_2CNHPh \longrightarrow \text{[structure]} \begin{array}{l} CO_2HgPh \\ CO \cdot NHPh \end{array} + CO_2 \qquad (18)
$$

The intrinsic interest in the N-mercurio-amines and their potential value in synthesis as sources of nucleophilic amide encouraged us to investigate the generality of the simple route to them provided by mercuration of amines with phenylmercury(II) hydroxide. Preliminary results indicate that whereas diphenylamine is N-mercurated smoothly in refluxing benzene [equation

$$
PhHgOH + Ph_2NH \longrightarrow PhHgNPh_2 + H_2O \qquad (19)
$$
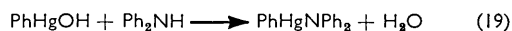
(19)], the reaction fails with dibenzylamine and even with N-methyl- and N-ethyl-aniline under these conditions.

EXPERIMENTAL

Phenylmercury(II) hydroxide, oxide, and alkoxides were prepared as previously described.[1,14] Commercial organic isocyanates were redistilled, and dichloromethane was distilled from phosphorus pentoxide. All manipulations of alkoxides and isocyanates were carried out in a dry-box. Aniline was redistilled at reduced pressure under a stream of nitrogen; p-toluidine and diphenylamine were recrystallised from ether–light petroleum. Phthalic anhydride was recrystallised from boiling chloroform to remove any phthalic acid.

N.m.r. spectra were recorded on a Perkin-Elmer R12 spectrometer. I.r. spectra were recorded for Nujol mulls and solutions (15—20%) in dichloromethane with Perkin-Elmer 457 or Unicam SP 1000 instruments, with potassium bromide optics. The conductivity measurement was made at 27° with a Philips conductivity measuring bridge (PR 9500) and immersion cell (PR 9510).

Reaction of Phenylmercury(II) *Alkoxides with Isocyanates.*—The isocyanate (0·9—1·0 mol. equiv.) was added neat by microsyringe or, preferably, as a solution in dichloromethane (5 ml) to the alkoxide (ca. 5 mmol) dissolved in dichloromethane (10 ml); the latter solution was either prepared individually or was an aliquot portion of a stock solution. The crude N-phenylmercuriocarbamate (88—100%) was isolated by evacuation of the resultant solution at 0·01 mmHg and was recrystallised from dichloromethane–

carbamate (95—99%) (see Table 2). The only variation was that the 1-naphthyl isocyanate derivative crystallised out (97·5%) from the initially clear solution without removal of the solvent; in contrast to the other adducts it was slightly coloured. The i.r. spectra of both solutions and mulls were characterised by very broad absorptions in the 1510—1590 cm^{-1} region.

Reaction of Phenylmercury(II) *Hydroxide with Isocyanates.*—(a) *Ethyl and t-butyl isocyanates.* A solution of ethyl isocyanate (0·509 g, 7·15 mmol) in dichloromethane (5 ml) was added with swirling to a slurry of phenylmercury(II) hydroxide (2·089 g, 7·1 mmol) in dichloromethane (7 ml). An exothermic reaction took place and a clear solution was obtained which was unchanged overnight. A sample was removed to record the ^{1}H n.m.r. spectrum and the remainder was evacuated at 0·01 mmHg to give white crystalline *phenylmercury*(II) *ethylcarbamate* (2·224 g, 86%), m.p. 65—70°; τ (16% in CH$_2$Cl$_2$) 2·8 (Ph), 6·8 (poorly resolved q, HN·CH$_2$), and 8·8 (t, *J* 7 Hz, HN·CH$_2$·CH$_3$); $v_{max.}$ (mull) 3340 (NH), 1645m, 1545s,br (CO), 1290s, 690s, and 670s cm^{-1} (Found: C, 29·2; H, 3·15; N, 3·95. C$_9$H$_{11}$HgNO$_2$ requires C, 29·55; H, 3·0; N, 3·85%); or *phenylmercury*(II) *t-butylcarbamate*, m.p. 135—137°; τ (16% in CH$_2$Cl$_2$) 2·85 (Ph) and 8·6 (Bu^t); $v_{max.}$ (mull) 3330m, 3250w (NH), 1640m, 1560s (CO), 720s, and 690m cm^{-1} (Found: C, 34·1; H, 4·05; N, 3·65. C$_{11}$H$_{15}$HgNO$_2$ requires C, 33·55; H, 3·8; N, 3·55%).

(b) *Methyl isocyanate.* (i) *With 1 mol. equiv. of isocyanate.* Methyl isocyanate (0·404 g, 7·1 mmol) in dichloromethane (5 ml) was added with swirling to a slurry of phenylmercury(II) hydroxide (2·083 g, 7·05 mmol) in dichloromethane (7 ml). Heat was evolved and a clear solution was obtained from which crystals began to separate within 15 min. The mixture was left overnight and a clear solution was then decanted from a mass of crystals, which was washed with a little dichloromethane and dried *in vacuo* (1·688 g, 68% of material taken), m.p. 169—170°; $v_{max.}$ (mull) 3180m, 1500s, 1270s, 1000s, 725s, 695s, 545m, 465m, and 450m cm^{-1} [Found: C, 25·65; H, 2·1; N, 1·5. Calc. for HNMe·CO$_2$HgPh (C$_8$H$_9$HgNO$_2$): C, 27·3; H, 2·55; N, 4·0. Calc. for C$_{20}$H$_{19}$Hg$_3$NO$_3$ (PhHgOH,PhHgOHgPh,-MeNCO): C, 26·0; H, 2·05; N, 1·5%].

A second crop of crystals (0·09 g, 3·5%), m.p. 160—162°, was obtained. The ^{1}H n.m.r. spectrum of the soluble fraction showed signals at τ 2·8 (Ph) and 7·15 (small) and 7·25 (Me) with relative intensities of 5 : 8·9. Since equimolar amounts of methyl- and phenyl-containing species were taken initially this suggests that the insoluble fraction contains methyl and phenyl in the ratio 1 : 3. The solvent was removed under reduced pressure and the solid thus obtained (0·56 g, 23%) was dried by washing with ether; m.p. 138—140°; the i.r. spectrum (mull) showed all the bands present in that of the first crop of crystals and additional absorptions at ν_{max} 3330s, 1600s,br, and 510m cm^{-1}.

(ii) *With 0·5 mol. equiv. of isocyanate.* A similar experiment with methyl isocyanate (3·7 mmol) and phenylmercury(II) hydroxide (6·9 mmol) afforded insoluble crystals of the same material (84%), m.p. 168—170°. This material was hydrolysed by boiling water and turned grey on prolonged exposure to light.

(iii) *Establishment of stoicheiometry of crystals, m.p.* 169—170°, *by independent synthesis.* A solution of phenylmercury(II) N-methyl-N-phenylmercuriocarbamate (4·97 mmol) in dichloromethane (12 ml), prepared as already described, was added with swirling to a slurry of phenylmercury(II) hydroxide (1·46 g, 4·95 mmol) in dichloromethane (5 ml). A clear solution was quickly formed and white crystals began to separate 5 min later. After 3·5 h the mixture was filtered and the residue washed with dichloromethane (5 ml) and dried under suction, then *in vacuo* (3·840 g, 84%). It was identical (m.p., mixed m.p., and i.r. spectrum) with the insoluble material obtained from hydroxide and isocyanate as just described. The measured resistance of a solution of the solid (0·09323 g) in nitromethane (100 ml) was 3 × 10^5 ohm; the cell constant was 1·47; hence the molar conductance was 2·3 cm^2 ohm^{-1} mol^{-1} (Found: C, 26·15; H, 2·10; N, 1·6%).

N.B. A clear solution was similarly obtained by treating phenylmercury(II) hydroxide with an equimolar quantity of phenylmercury(II) N-ethyl-N-phenylmercuriocarbamate in dichloromethane; however no precipitation occurred overnight. The product was very soluble in dichloromethane, showed a complex melting pattern and had no i.r. bands at 3180 or 545 cm^{-1}.

(c) *Phenyl and* p-*tolyl isocyanates.* Phenyl isocyanate (0·830 g, 6·95 mmol) in dichloromethane (5 ml) was added with swirling to a slurry of phenylmercury(II) hydroxide (1·981 g, 6·7 mmol) in dichloromethane (7 ml). Strong effervescence occurred and a clear solution was formed. The bulk of the solvent was removed at the water pump, light petroleum (b.p. 40—60°) was added and the mixture was taken to dryness at 0·1 mmHg to leave a pale yellow solid (2·604 g), m.p. 70—100° (decomp.), ν_{max} (mull) 3400, 1615, 1595, 1570, 1510, 1340, 1300, 1230, 1020, 995, 750, 725, 690, 500, and 450 cm^{-1}. This infrared spectrum was consistent with the presence of PhHgNPh·CONHPh and PhHgO$_2$CNHPh (see later).

A similar reaction occurred with p-tolyl isocyanate to give a pale yellow solid, m.p. 50—100° (decomp.).

Reaction of Phenylmercury(II) *Hydroxide with Amines.*— (a) *Aniline.* A stirred mixture of aniline (2·211 g, 23·8 mmol) and phenylmercury(II) hydroxide (3·347 g, 11·4 mmol) in benzene (60 ml) was heated under reflux in a flask fitted with a Dean–Stark trap. After 10 min, a clear yellow solution was obtained from which benzene (55 ml) was removed by distilling into the trap. The remaining

benzene and the excess of aniline were removed at 45° (bath) and 0·05 mmHg to leave N-*phenylmercurioaniline* (3·97 g, 95%). The pale yellow solid was powdered under light petroleum (b.p. 40—60°) and dried *in vacuo*; m.p. 68—75°, τ (19·4% in CDCl$_3$) 2·78 [s, PhHg; J (^{199}Hg,H$_{ortho}$) 156 Hz] overlapping with *ca.* 6 peaks split into two groups (PhNH) and 6·35br (s, NH); integration 9 : 1 (calc. for PhHgNHPh: 10 : 1). The compound reacted slowly with deuteriochloroform; ν_{max} (mulls in Nujol and hexachlorobutadiene) 3340m, 3065w, 2990w, 1595s, 1570m, 1485s, 1435m, 1350m, 1280s,br, 1180m, 1075m, 1025m, 995m, 985m, 870w, 835m, 750s, 730s, 690s, 495w, and 450w cm^{-1} (Found: C, 38·85; H, 3·15; N, 3·35. C$_{12}$H$_{11}$HgN requires C, 38·95; H, 3·0; N, 3·8%).

(b) p-*Toluidine.* The reaction was carried out as in (a) but with equimolar amounts of amine and hydroxide. A viscous brown oil was obtained which did not solidify even at $-25°$; ν_{max} (film) 3400m, 3080s, 1625s, 1520s, 1440m, 1355m, 1300s, 1185m, 1115m, 1045w, 850m, 825s, 760m, 740s, and 700s cm^{-1}.

(c) *Diphenylamine* (with M. KNIGHT). The reaction was carried out as in (a) but with equimolar amounts of amine and hydroxide. A pale yellow solid was obtained (78%), m.p. 166—176°, which was washed with cold ether to leach out unchanged diphenylamine and leave N-*phenylmercuriodiphenylamine*, m.p. 174—176°; ν_{max} (mull in hexachlorobutadiene) 3050m, 1485s, 1440m, 1330m, 1300s, 1215s, 1025m, 905m, 890m, 880m, 745s, 725s, and 695s cm^{-1} (Found: C, 47·0; H, 3·4. C$_{18}$H$_{15}$HgN requires C, 48·5; H, 3·4%).

Reactions of N-*Phenylmercurioaniline.*—(a) *With phthalic anhydride.* A mixture of phenylmercury(II) hydroxide (1·295 g, 4·4 mmol) and aniline (0·421 g, 4·5 mmol) was azeotropically dehydrated in benzene as described earlier. The benzene was removed under reduced pressure and dichloromethane (12 ml) added. Phthalic anhydride (0·648 g, 4·4 mmol) in dichloromethane (7 ml) was added to the resultant solution and the mixture was left overnight. The solution was concentrated to half volume, light petroleum (10 ml) was added and the solution was then taken to dryness at 0·05 mmHg to give a white solid (2·23 g, 98%), identified (m.p., i.r. spectrum) as *phenylmercury*(II) 2-*phenylcarbamoylbenzoate* (III). This was synthesised independently as follows.

A solution of aniline (2·727 g, 29·4 mmol) in dichloromethane (10 ml) was added to a stirred solution/suspension of phthalic anhydride (4·346 g, 29·4 mmol) in dichloromethane (20 ml). 2-Phenylcarbamoylbenzoic acid (6·90 g, 97%) was filtered off, washed with dichloromethane (20 ml), and dried under suction; m.p. 163—166°, resolidified and melted again at 192—195° (lit.,[23] m.p. 170° with dehydration to N-phenylphthalimide, m.p. 210°). This acid (1·563 g, 6·5 mmol) was added to a stirred suspension of phenylmercury(II) hydroxide (1·913 g, 6·5 mmol) in dichloromethane (25 ml); a clear solution was formed immediately. Magnesium sulphate (dried) was added and the mixture was stirred for 45 min then filtered. The filtrate was concentrated to half volume, light petroleum (15 ml) was added, and the solvent was slowly removed at a water pump; white solid (III) was formed which was dried at 0·02 mmHg (3·28 g, 97%), m.p. (slow heating) 174—175° (decomp.) (the melting pattern was dependent upon the rate of heating), ν_{max} (mull) 3330m, 1670s, 1610s, 1550m,

[23] Heilbron's ' Dictionary of Organic Compounds,' 4th edn., Eyre and Spottiswoode, London, 1965, p. 2740.

1460s, 1350s, 755m, 730m, and 695m cm^{-1} (Found: C, 46·2; H, 3·15; N, 2·6. $C_{20}H_{15}HgNO_3$ requires C, 46·35; H, 2·9; N, 2·7%).

Similarly *phenylmercury*(II) 2-p-*tolylcarbamoylbenzoate* was prepared both by treating the oil derived from *p*-toluidine and phenylmercury(II) hydroxide (see before) with phthalic anhydride, and by treating 2-*p*-tolylcarbamoylbenzoic acid (from *p*-toludine and phthalic anhydride) with phenylmercury(II) hydroxide; m.p. (fast heating) 107—110° (decomp.), resolidified and melted again at 180—182°. The i.r. spectrum in the range 1300—3500 cm^{-1} closely resembled that of the *N*-phenyl compound (Found: C, 47·2; H, 3·5; N, 2·5. $C_{21}H_{17}HgNO_3$ requires C, 47·4; H, 3·2; N, 2·65%).

(b) *With phenyl isocyanate then phthalic anhydride.* Phenyl isocyanate (0·31 ml, 2·85 mmol) was added by micro-syringe to a solution of *N*-phenylmercurioaniline (1·053 g, 2·84 mmol) in dichloromethane (10 ml). After the solution had cooled, light petroleum (b.p. 60—80°; 10 ml) was added and the solvent was removed *in vacuo* to leave a foam. This was broken up to give a pale yellow powder which was dried at 0·05 mmHg (1·34 g, 97%), m.p. range beginning at 45°, $v_{max.}$ (mull in hexachlorobutadiene) 3320m, 3070w, 1655m, 1600s, 1560s, 1495s, 1445s, 1350s, 1320s, 1235s, 1025w, 750s, 725s, and 695s cm^{-1}. The material became sticky upon exposure to the air and when some of it was redissolved in dichloromethane a small residue of *NN'*-diphenylurea was obtained. It therefore appears that *NN'*-diphenyl-*N*-phenylmercuriourea is hydrolysed slowly by atmospheric moisture; this probably accounts for the analysis (Found: C, 46·05; H, 3·5; N, 5·0. Calc. for $C_{19}H_{16}HgN_2O$: C, 46·7; H, 3·3; N, 5·75%).

A solution of the partially hydrolysed material (*i.e.* PhHgNPh·CO·NHPh + PhHgOH; 1·17 g) in dichloromethane (10 ml) was treated with phthalic anhydride (0·354 g) in dichloromethane (10 ml). After 2 h a precipitate of *NN'*-diphenylurea (m.p., i.r. spectrum; 0·227 g) was filtered off. Concentration of the filtrate afforded a second fraction which was shown (i.r. spectrum) to be a mixture of diphenylurea and bis[phenylmercury(II)] phthalate (IV) (see later). Unchanged phthalic anhydride was present in the final filtrate.

(c) *With carbon dioxide then phthalic anhydride.* Carbon dioxide was bubbled through a stirred solution of *N*-phenylmercurioaniline (0·920 g, 2·48 mmol) in dichloromethane (20 ml) for 20 min. The solution was concen-trated at the water pump to half volume, light petroleum (b.p. 60—80°; 10 ml) was added and then all solvent was removed under reduced pressure to give a viscous oil, $v_{max.}$ (film) 3380w, 3060m, 1620m, 1600s, 1500s,br, 1435m, 1325sh; 1305s,br, 1200w,br, 1025m, 995w, 835w,br, 750m, 725s, and 695s cm^{-1}.

The oil was redissolved in dichloromethane (7 ml) and treated with phthalic anhydride (0·355 g, 2·4 mmol) in dichloromethane (7 ml). The solvent was removed under reduced pressure to give compound (III) (i.r. spectrum).

Treatment of the Product from Phenylmercury(II) *Hydroxide and* p-*Tolyl Isocyanate with Phthalic Anhydride.*—Phthalic anhydride (0·391 g, 2·64 mmol) in dichloromethane (5 ml) was added to the *p*-MeC$_6$H$_4$·NCO–PhHgOH product (1·009 g) in dichloromethane (5 ml). Filtration next day afforded *NN'*-di-*p*-tolylurea (m.p., i.r. spectrum; 0·102 g) and a filtrate from which was obtained a solid (1·28 g). Recrystallisation of this from dichloromethane–light petroleum at −5° gave a first fraction of bis[phenylmercury(II)] phthalate (m.p., i.r. spectrum; 0·203 g). The i.r. spectrum of the remaining material was consistent with it being a mixture of phenylmercury(II) 2-*p*-tolylcarbamoylbenzoate and unchanged phthalic anhydride.

Similar treatment of the PhNCO–PhHgOH product (4·27 mmol) afforded a precipitate of diphenylurea (0·071 g) and a filtrate containing compounds (III) and (IV) and unchanged phthalic anhydride (i.r. spectrum).

Synthesis of Bis[phenylmercury(II)*] Phthalate* (IV).—Phthalic anhydride (0·520 g, 3·51 mmol) in dichloromethane (10 ml) was added with swirling to a slurry of phenyl-mercury(II) oxide (2·022 g, 3·52 mmol) in dichloromethane (10 ml). A clear solution was obtained from which a white solid began to separate a few seconds later. After 5 min, the mother solution was decanted off and the residue dried at 0·05 mmHg to give bis[phenylmercury(II)] phthalate (2·34 g, 92%), m.p. 208—209° (decomp.), $v_{max.}$ (mull) 1620s, 1585s, 1570m,sh, 1550w,sh, 1475m,sh, 1460s, 1425w, 1380s,sh, 1350vs, 1145m, 1075m, 1020m, 995w, 865w, 840w, 800w, 745m, 730s, 710m, 695m, and 660w cm^{-1} (Found: C, 33·0; H, 2·0. $C_{20}H_{14}Hg_2O_4$ requires C, 33·4; H, 1·95%).

This compound was previously prepared from phenyl-mercury(II) hydroxide and phthalic acid (m.p. 214°).[24]

[24] P. Pfeiffer and H. Jäger, *Chem. Ber.*, 1947, **80**, 1.