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REACTIONS BETWEEN MERCURY AND SOME ARYLMETAL COMPOUNDS

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SUMMARY

A series of phenylmetal compounds, selected for their differing structures, have been allowed to react with a labelled mercury surface. Where the structure approximates to linear or planar, substitution of the metal has been shown to occur. The reactions may be explained in terms of an S_Ei transition state similar to that previously postulated for mercury/diphenylmercury exchange reactions.

INTRODUCTION

The exchange between metallic mercury and a series of substituted diphenylmercury compounds at the mercury surface has been extensively kinetically investigated, and an S_Ei mechanism proposed[1-3].

$$Hg^*(m) + HgPh_2 \rightarrow Hg(m) + Hg^*Ph_2$$

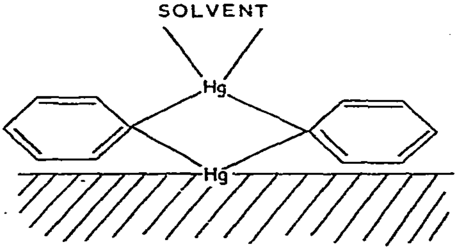

Fig. 1. S_Ei transition state for mercury exchange.

An investigation into the effect of solvent on this reaction[4] has shown the importance of the structure of the aryl compounds and the transition state with regard to the rate of reaction. As the coordinating power of the solvent increases, the rate decreases, due presumably to the change in hybridisation of the mercury from approximately linear (sp) to angular (approaching sp^3) in the aryl molecule, and the consequent difficulty of aryl adsorption as a prerequisite to exchange.

A number of other phenylmetal compounds exist in a variety of structures about the metal–carbon bonds ranging from linear to tetrahedral, and it seemed a

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logical extension to these exchange reactions to expect that substitution reactions would occur with mercury in sterically favourable cases. Using a radioactive label, ^{203}Hg, and the experimental technique previously described[2,3], a survey of substitutions of mercury into a series of arylmetal compounds has been carried out according to the general equation:

$$\tfrac{n}{2}\mathrm{Hg^{*}(metal)} + \mathrm{MPh}_n \rightarrow \tfrac{n}{2}\mathrm{Hg^{*}Ph_2} + \mathrm{M(amalgam)}$$

The series of arylmetal compounds was chosen on the basis of structural differences, and ease of preparation.

EXPERIMENTAL

Materials

Mercury (1 kg) was cleaned with dilute nitric acid, while under agitation from a stream of air. Samples for each reaction were washed free of acid with distilled water. The bulk was labelled by addition of 1 mCi ^{203}Hg as 1 g of mercury metal (Radiochemical Centre, Amersham, England).

Benzene (May & Baker) was dried with fused calcium chloride and sodium wire and fractionally distilled. Pyridine (B.D.H.Analar) was dried with potassium hydroxide and fractionally distilled.

Diphenylmercury (J. Sas and Co.) was recrystallised twice from benzene with decolourising charcoal, and again recrystallised from benzene. It was dried at 60° for 15 min and then over silica gel and fused calcium chloride at 2 mm of mercury for 24 h before use.

Diphenylcadmium was prepared from cadmium bromide and bromobenzene via the Grignard synthesis and recrystallised from benzene. All stages of the synthesis were carried out under nitrogen.

Diphenylzinc was prepared from zinc chloride via the Grignard sysnthesis, precipitated with dioxane, and recrystallised from benzene. The preparation was carried out under nitrogen.

Diphenylmagnesium etherate was prepared from phenylmagnesium bromide by precipitation with dioxane and ether. Dioxane was subsequently removed by heating, and the product recrystallised from an ether/benzene mixture. All operations were carried out under nitrogen.

Tetraphenyltin and tetraphenyllead were recrystallised twice from chloroform and air dried.

Triphenylbismuth was recrystallised from absolute alcohol and air dried.

Diphenylthallium bromide was prepared from thallic chloride via the Grignard synthesis, and was recrystallised from pyridine.

All compounds conformed to the reported melting points and physical properties.

RESULTS

In each case the reaction was carried out by stirring excess metallic mercury (75.0) with the aryl in solution in benzene (20 ml) at 55.0±0.1°, under nitrogen where necessary to prevent decomposition. Due to solubility problems in benzene, pyridine was used as a solvent in the case of diphenylthallium bromide. The concentration used was also regulated by the solubility in each case. The final concentration selected was 0.1 mole·l^{-1}, or as near to this as solubility allowed. The time of reaction was chosen so as to ensure that no significant decomposition occurred during reaction. Samples (4 ml) were removed from the mixture, centrifuged, and the clear liquid counted using a NaI (Tl) scintillation counter as previously described[2,3]. The specific activity was used to calculate the extent of the reaction assuming that it proceeded only in the manner described by the equations above, as has been suggested by the work of Hilpert and Grüttner[5]. The results are shown in Table 1 expressed as a percentage of the maximum theoretical substitution. The error due to sampling and counting was approximately 5% of the measured exchange.

TABLE 1

SUBSTITUTION REACTIONS OF VARIOUS PHENYLMETAL COMPOUNDS

Compound	Time (h)	Exchange (%)	Concn. (mole·l^{-1})	Pauling electronegativity (X)	Bond dissociation energy (kcal·mole^{-1})	Structure
Diphenylmercury	3.0	77	0.100	1.9	29.2	*sp*
Diphenylthallium bromide	3.0	89[a]	0.023	1.9		*sp*[b]
Diphenylcadmium	5.0	53.4	0.050	1.7	33.3	*sp*
Diphenylmagnesium etherate	2.0	2.5	0.070	1.2		*sp*[c]
	7.0	3.9	0.070			
Diphenylzinc	4.5	1.6	0.090	1.6	42.0	*sp*
	6.0	1.7	0.090			
Triphenylbismuth	2.3	6.8	0.050	1.9	34.1	sp^2
	5.0	20.6	0.050			
Tetraphenyltin	6.0	0.0	0.025	1.8	52.1	sp^3
	72.0	0.0	0.025			
Tetraphenyllead	5.0	0.0	0.025	1.8	36.5	sp^3

[a] In pyridine. [b] As Tl$^+$. [c] Unsolvated.

DISCUSSION

Two factors were expected to determine the rates of reaction of this series. The first being the structure of the aryl and the second the strength of the metal–carbon bond. The electronegativity of the metal and the mean bond dissociation energy are measures of this latter quantity. Values for the Pauling electronegativities[6], and the metal–carbon dissociation energies[7] as found in the methyl compounds in kcal·mole^{-1} are given in Table 1. A set of values for the aryl compounds is not available.

By analogy with our work on solvent effects on the exchange reactions of diphenylmercury compounds[4], the phenyl rings need to be coplanar for adsorption on the surface to occur prior to reaction. Diphenylcadmium has the same structure and similar electronegativity and bond dissociation energy to diphenylmercury and the large percentage of reaction was to be expected. Diphenylthallium bromide is an interesting case, as in the ionised state $(TlPh_2)^+$ is isoelectronic with $HgPh_2$, and it gives similar results to the mercury compound. A quantitative comparison is not directly possible, as some solvent effects might be expected from the pyridine[4]. The lack of significant reaction for diphenylzinc must be associated with its high bond dissociation energy and low electronegativity, but such a low figure is somewhat surprising in view of its structure. Diphenylmagnesium etherate presumably fails to react to a significant extent due to the modification of its structure from *sp* to sp^3 by the coordinated ether molecules. Triphenylbismuth seems to give some degree of reaction due to its planar structure, and low bond dissociation energy and electronegativity, but the amount is surprisingly high. The structure of tetraphenyllead would be expected to prevent adsorption, and thus reaction, and in the case of tetraphenyltin the high bond dissociation energy is also against reaction occurring.

The reactivity of this series thus agrees well with the mechanism put forward for the diphenylmercury exchanges[2,3], and the reactions appear to occur by an S_Ei mechanism with a transition state similar to that quoted earlier in this article.

A detailed kinetic comparison has not been carried out using this stirring technique due to the behaviour of the mercury. In the original investigation of mercury exchanges[2,3] carried out with diphenylmercury it was found to break into droplets of predictable size, thus given a reproducible surface area for reaction. This is vital for quantitative work as even on a simple Collision Theory basis, the specific rate constant must be of the form $k = P \cdot \bar{n} \cdot C \cdot \exp(-E_a/RT)$. When $\bar{n}$ represents the number of particles per second striking unit surface area, C is the area of the phase boundary, and the other symbols have their usual significance. With the aryls used in this investigation C was visibly not constant; for instance with the two tetraphenyls, the mercury remained in one large globule, whilst with triphenylbismuth it was broken up to such an extent that by the end of the run it was almost colloidal. For the mercury exchange reactions it has been possible to develop a still surface exchange technique[4]. A similar procedure may be possible for a number of these substitution reactions. However it was found for the mercury exchanges that impurities in both the mercury and the aryl solution had gross effects on the surface, and thus the apparent exchange rate. As several of the above aryls are extremely unstable, practical difficulties may well limit further investigation and any evaluation of activation parameters for comparison with the mercury exchange reactions. Work is proceeding with the thallium compounds, as their stability is good, and they occupy a unique position in being isoelectronic in the ionised state with the corresponding thoroughly investigated mercury compounds.

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