The Reaction of Dibenzylmercury with Arenes and Cyclohexene on Molecular Sieves

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The thermal decomposition of dibenzylmercury in aromatic solvents in the pores of 13X molecular sieve gives benzylated aromatic substitution products, rather than the hydrogen-abstraction and radical combination products obtained in the absence of the zeolite. The intermediacy of an electrophilic benzyl 'cation' is postulated.

The decomposition of dibenzylmercurials in unreactive organic solvents has been studied extensively:[1–4] the decomposition normally follows equation (1). In the presence of compounds containing abstractable hydrogen such as substituted toluenes[1,5] or 9,10-dihydroanthracene,[6] some hydrogen transfer takes places according to equation (2), but reactions of type (2) are often not fast, and competing dimerization of benzyl radicals cuts down the amount of products from the solvent-based radicals S$^\bullet$.

$$\mathrm{ArCH_2{-}Hg{-}CH_2Ar} \longrightarrow \mathrm{ArCH_2^\bullet} + {}^\bullet\mathrm{Hg{-}CH_2Ar} \longrightarrow \mathrm{Hg} + {}^\bullet\mathrm{CH_2Ar} \qquad (1)$$

$$\mathrm{ArCH_2^\bullet} + \mathrm{H{-}S} \longrightarrow \mathrm{ArCH_3} + \mathrm{S^\bullet} \qquad (2)$$

This paper describes work carried out on the decomposition of solutions of dibenzylmercury in the pores of zeolites, especially 13X whose channels are large enough to accommodate the molecule. It was hoped that after decomposition of the mercurial, radicals which escaped from the solvent cage would diffuse more slowly because of the channel restrictions and give a greater probability of reaction with solvent molecules before dimerization.

Results and Discussion

Dibenzylmercury decomposes in solution in *p*-chlorotoluene to give bibenzyl, *p*-chlorobibenzyl, and *p,p'*-dichlorobibenzyl as products,[1] by reactions (1) and (2) followed by self- and cross-combination of benzyl and *p*-chlorobenzyl radicals. We confirmed this result, then carried out the decomposition within the pores of 13X zeolite, hoping as stated above for an increased yield of *p,p'*-dichlorobibenzyl. Somewhat to our surprise, g.l.c. showed that although a small quality of bibenzyl was present in the products, neither *p*-chloro- or *p,p'*-dichloro-bibenzyl was present, but two peaks were observed close to the expected position of *p*-chlorobibenzyl. These were assigned as 2-chloro-5-methyldiphenylmethane and 3-chloro-6-methyldiphenylmethane by analogy with the results of the reaction in benzene described below.

When dibenzylmercury was decomposed in benzene on 13X zeolite, a relatively small quantity of bibenzyl was formed; diphenylmethane was the major product. Again, in the absence of the molecular sieve, bibenzyl was the major product and no diphenylmethane was detected. Similar results were obtained with *p*-xylene (see Table 1).

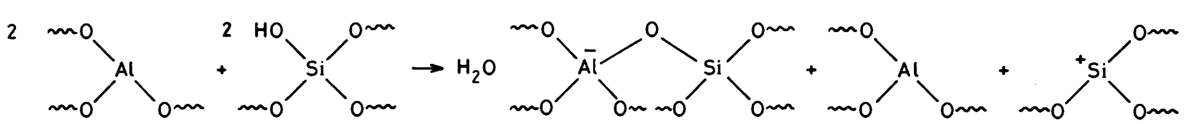

(4)

Table 1. Decomposition of dibenzylmercury in aromatic solvents (**I**) on molecular sieves

Solvent (**I**)		Mercurial concentration (mg g^{-1})	Molecular sieve	Products [mol/100 mol $(\mathrm{PhCH_2})_2\mathrm{Hg}$]			
X	Y			(**II**)	(**III**)	(**IV**)	(**V**)
CH_3	Cl	12	13X	2			38[a]
CH_3	Cl	12	13X[b]	18			38[a]
CH_3	Cl	12		74	17	3	
CH_3	CH_3	14	13X	2			35
CH_3	CH_3	21	13X[b]	1			51
H	H	20	13X	17			41
H	H	20	13X[b]	39			11
H	H	15	5A	12			53
H	H	20	5A[b]	35			21
H	H	20	4A	40			15
H	H	20		67			

[a] Approximately equal quantities of the two possible aromatic substitution products. [b] Molecular sieve used for a second time.

(**I**), *p*-$\mathrm{XC_6H_4Y}$; (**II**), $\mathrm{PhCH_2CH_2Ph}$; (**III**), *p*-$\mathrm{YC_6H_4CH_2CH_2Ph}$; (**IV**), (*p*-$\mathrm{YC_6H_4CH_2})_2$; (**V**), $\mathrm{PhCH_2C_6H_3XY}$.

Since benzyl radicals do not react with simple benzenoid compounds to give appreciable quantities of aromatic substitution products under normal conditions,[4,7] it appears likely that free benzyl radicals are not involved in these reactions. A reaction at the surface of the zeolite seems likely.

The presence of electrophilic centres in zeolites is well established:[8] if residual water is present, dissociation of hydrated polyvalent cations gives rise to protons [reaction (3)] and, in more anhydrous conditions, reactions of type (4) have been postulated. These electrophilic centres are important in the high-temperature catalytic reactivity of zeolites, *e.g.* in cracking and isomerization reactions. Although mechanisms involving complexing of the zeolite with either the dibenzylmercury or the solvent are possible, the simplest explanation of our results would involve the attack by an electrophilic centre ($\mathrm{H^+}$ or $\geqslant\mathrm{Si^+}$) on a dibenzylmercury molecule as in (5) to give a 'benzyl cation' which would then undergo rapid reaction with the solvent to give the electrophilic aromatic substitution product observed, regenerating a cation which can initiate the

$$\mathrm{M(OH_2)}^{n+} \longrightarrow \mathrm{M(OH)}^{(n-1)+} + \mathrm{H^+} \qquad (3)$$

Table 2. Decomposition of dibenzylmercury in cyclohexene on molecular sieves

Mercurial concentration (mg g^{-1})	Molecular sieve	Products [mol/100 mol $(PhCH_2)_2Hg$] (II)	(VI)	(VII)	(VIII)
30	13X	Trace	41	Small	Small
20	13X[a]	Trace	49	Small	
30	13X	Trace	37	Small	
20	13X[a]	Trace	57	Small	
30	5A	15	Small	6	
30		31	13	24	

[a] Molecular sieve in use for the second time.

(II), $PhCH_2CH_2Ph$; (VI), 1-Benzylcyclohexene; (VII), 3-Benzylcyclohexene; (VIII), Benzylidenecyclohexane.

decomposition of a further dibenzylmercury molecule. The ions have been shown as 'free' in equations (5) and (6), but interactions with the surface will almost certainly be important.

$$X^+ + PhCH_2\text{-}Hg\text{-}CH_2Ph \longrightarrow PhCH_2X + Hg + PhCH_2^+ \quad (X = H^+ \text{ or } {\geqslant}Si^+) \qquad (5)$$

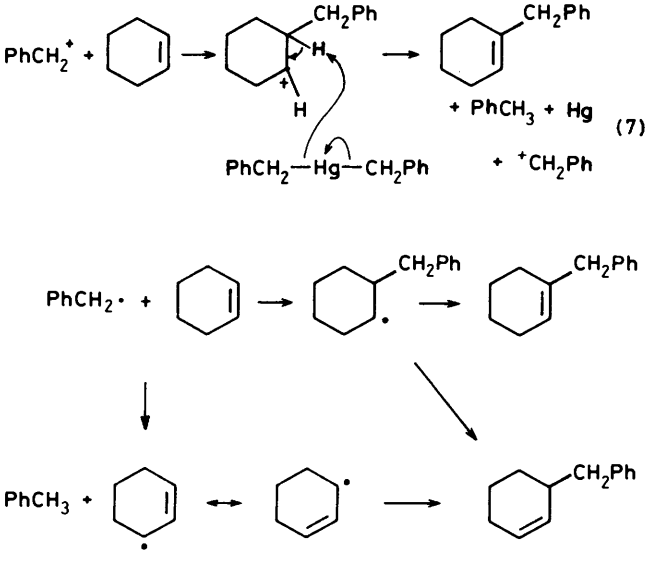
$$PhCH_2^+ + ArH \longrightarrow PhCH_2Ar + H^+ \qquad (6)$$

A precedent for this type of reaction is the reaction of dibenzylmercury with trifluoroacetic acid[9] to give mercury and toluene among the products.

In support of the 'surface electrophilic centre' mechanism, the decomposition of dibenzylmercury in octane is faster in the presence of molecular sieve: at 140 °C after 30 min, appreciable decomposition to metallic mercury was observed in the presence, but not in the absence, of 13X molecular sieve. Additionally, if the zeolite is re-used for a second experiment, there is a tendency towards the formation of less aromatic substitution products but more bibenzyl (see Table 1), supporting the view that active sites, important in promoting substitution reactions, are deactivated at least partially during reaction. With the deactivation of the electrophilic centres, the normal radical decomposition takes place with the eventual formation of bibenzyl.

A few experiments were carried out with 5A and 4A molecular sieves. In spite of the smaller pore sizes (which should not accommodate the mercurial[10]) the effectiveness of 5A zeolite in promoting diphenylmethane formation in experiments involving dibenzylmercury in benzene was somewhat greater than that of 13X zeolite, indicating that reactions on the outside surfaces are equally as effective as reactions within the cavities, but with 4A zeolite, the major product was bibenzyl, with relatively little diphenylmethane, a result intermediate between the solution and the 5A–13X values.

We have also carried out reactions of dibenzylmercury with cyclohexene in the presence and absence of molecular sieve. In the presence of 13X sieve, 1-benzylcyclohexene was the almost exclusive product (see Table 2), which would be accounted for by sequence (7). In the absence of sieve, bibenzyl, 3-benzylcyclohexene, and 1-benzylcyclohexene are formed in substantial amounts, with the 3-isomer predominating over the 1-isomer. Here allylic abstraction of hydrogen by the benzyl radical may compete with addition of the benzyl radical to the C=C bond (Scheme).



Scheme.

In the presence of 5A sieve, the overall yield was lower. About half the quantity of bibenzyl was formed (compared with the experiment in the absence of zeolite) and 3-benzylcyclohexene predominated over the 1-isomer.

Experimental

Solvents were dried and distilled before use; the purity was >99%. Molecular sieves (13X, 5A, and 4A) were dried at 100 °C and 0.01 mmHg for 2 h. For ampoule experiments, a solution of the dibenzylmercury in the appropriate solvent was introduced into a Pyrex ampoule, sufficient molecular sieve was added to absorb all the solution, and the ampoules were degassed by three freeze–thaw cycles before being sealed under vacuum. After an appropriate thermal decomposition time in a thermostatted oil-bath or air-oven (2 days at 126 °C for experiments in cyclohexene, 2 days at 140 °C for the other solvents), the ampoules were opened and the contents extracted with ether before g.l.c. analysis (5% PEGA or SE 30 on 100—120 mesh Chromosorb G support) using dodecane or octadecane as internal standards. Dibenzylmercury,[11] 1-benzylcyclohexene,[12] 3-benzylcyclohexene,[13] benzylidenecyclohexane,[14] *p*-chlorobibenzyl[15] (*via* the Grignard reagent) and *p,p'*-dichlorobibenzyl[16] (by-product from *p*-chlorobibenzyl preparation, fractionated) were prepared by standard methods and had physical constants in accord with reported data.

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