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SYMMETRISATION OF ORGANOMERCURIC HALIDES ON ALUMINA, SILICA AND MAGNESIUM OXIDE

R. J. CROSS and C. M. JENKINS
Chemistry Department, The University, Glasgow, G12 8QQ, (Great Britain)
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SUMMARY

Organomercuric halides, RHgX, undergo symmetrisation to R_2Hg and HgX_2 on chromatography columns of active basic alumina or magnesium oxide. Acidic alumina is less effective, and no reaction is observed using silica. The efficiency of symmetrisation also depends on R and X and decreases along the series $X = I > Br > Cl$ and $R = aryl > alkyl$. A mechanism involving active participation of the column material as a nucleophile towards RHgX is indicated.

INTRODUCTION

Symmetrisation reactions of organomercuric halides [eqn. (1), left to right] have been widely investigated and numerous reactions involving many compounds have been reported[1]. Despite this, relatively few comparative studies on different symmetrising agents and the effects of different R and X groups have been made, and detailed mechanistic studies are rare. The reverse reaction is generally thermodynamically favoured[2], and one role at least of symmetrising reagents is to effectively remove the inorganic mercury salt (by complexation, precipitation, or reduction) thereby forcing the equilibrium to the right.

$$2\,RHgX \rightleftharpoons R_2Hg + HgX_2 \qquad (1)$$

An interesting, though little studied, method of symmetrisation is the use of chromatographic alumina. Thus $(o\text{-}C_6H_4I)HgI$[3] and $(C_5H_5)Fe(C_5H_4HgCl)$[4] have been converted in good yield to $(o\text{-}C_6H_4I)_2Hg$ and $[(C_5H_5)FeC_5H_4]_2Hg$, respectively, simply on passing the organomercuric halide down an alumina chromatography column. Also, alumina treated with sodium cyanide has been found to be an effective symmetrising agent for arylmercuric salts, though anion exchange was the only reported effect with alkylmercuric halides[5]. The cyanide ion itself is an efficient symmetrising agent[6].

The use of chromatographic materials in symmetrisation reactions is of great potential value, as the method inherently effects separation and purification of the products. We report here an investigation of the behaviour of some aryl- and alkylmercuric halides on alumina, silica, magnesium oxide and "treated alumina" columns.

EXPERIMENTAL

Aluminium oxide (activity grade 1: acid, neutral and basic) was obtained from M. Woelm (Germany); silica gel and magnesium oxide (chromatographic grade) carried out on columns 15 cm × 2 cm. Typical experiments are described below and from B.D.H. Except where mentioned otherwise, chromatography experiments were results are reported in Tables 1 and 2. Analytical thin-layer chromatography was carried out on silica gel (Merck, G.F.$_{254}$), eluting with 2/1 benzene/petroleum (60–80°) and using an ethanol solution of Michler's thioketone [4,4'-bis(dimethylamino)-thiobenzophenone] as developing reagent for the mercurials.

o-Tolylmercuric iodide on basic alumina

o-Tolylmercuric iodide (0.47 g) in dry THF (3 ml) was admitted to the top of a basic alumina column prepared in dry benzene. Elution with benzene afforded di-*o*-tolylmercury (0.23 g, m.p. 104–106° *ex* ethanol). Subsequent elution of the column with methanol afforded red mercuric iodide (0.24 g).

o-Tolylmercuric chloride on basic alumina

o-Tolylmercuric chloride (0.44 g) in THF (2 ml) was admitted to the top of a basic alumina column prepared in dry benzene. Elution with benzene, then 3/1 benzene/chloroform, produced di-*o*-tolylmercury (0.05 g). Elution by 1/1 benzene/chloroform gave a white solid (0.32 g) consisting mainly of *o*-tolylmercuric chloride and some di-*o*-tolylmercury (examined by TLC). Final elution with methanol produced mercuric chloride (0.05 g, identified by its m.p. and IR spectrum).

Ethylmercuric iodide on basic alumina

Ethylmercuric iodide (0.33 g) in THF (2 ml) was added to a basic alumina column and eluted with benzene as described above. Concentration of the first 50 ml of eluant to about 1 ml and ^{1}H NMR spectroscopic analysis showed the presence of a small amount of diethylmercury. Subsequent elution by chloroform, then methanol, gave, respectively, ethylmercuric iodide (0.27 g) and red mercuric iodide (0.03 g).

o-Tolylmercuric chloride on neutral alumina treated with potassium iodide

An aqueous solution of potassium iodide (16 ml of 1 *M*) was added to alumina (100 g) and the whole shaken thoroughly for 4 h. The resulting solid was then dried by heating at 150° under vacuum for several hours. A chromatography column of the usual size was then constructed from this material (40 g) in benzene. *o*-Tolylmercuric chloride (0.33 g) in THF (2 ml) was then admitted to this column and eluted with benzene to afford di-*o*-tolylmercury (0.18 g, m.p. 106–107° *ex* EtOH).

DISCUSSION

Results obtained from standard chromatographic materials under comparable conditions are listed in Table 1. Tolyl derivatives were used because of their relatively high solubility. When dissolved in THF, concentrated solutions were obtained and the compounds were introduced onto the columns in well-defined bands. Separate experiments showed that phenyl derivatives gave similar results to the tolyls, and there is no reason to believe that other aryls might behave differently.

Two features reflect trends previously noted for other symmetrising agents[7]. These are that arylmercuric halides appear more amenable to symmetrisation than their equivalent alkyls, and that ease of symmetrisation decreases in the order I > Br > Cl. In addition, the acidity of the chromatographic medium exerts a critical effect. Thus basic alumina is more efficient than neutral and acidic alumina. Magnesium oxide appears to be marginally better than even basic alumina, whereas silica shows no activity at all. In those cases where incomplete symmetrisation is indicated in Table 1, significant improvements can be obtained either by using a longer column, allowing a larger contact time with the chromatographic material, or increasing the activity of the column material by prolonged drying (conversely, deactivation by adding water can drastically reduce the column's efficiency).

TABLE 1

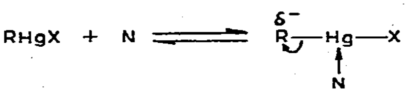
SYMMETRISATION OF RHgX ON STANDARD CHROMATOGRAPHIC MATERIALS

Organomercuric halide	*Column material*	*Yields of symmetrised products (%)*
o-TolHgI	Basic alumina	100
o-TolHgBr	Basic alumina	40
o-TolHgCl	Basic alumina	25
o-TolHgBr	Neutral alumina	30
o-TolHgBr	Acidic alumina	20
o-TolHgI	Silica gel	0
o-TolHgI	Magnesium oxide	100
o-TolHgCl	Magnesium oxide	30
EtHgI	Basic alumina	17
EtHgI	Magnesium oxide	12

Two mechanisms can plausibly be discussed to rationalise the experimental observations. These are (a) spontaneous symmetrisation of the organomercuric halide in solution, followed by chromatographic separation of the products, and (b) a mechanism involving active participation of the chromatographic medium in the symmetrisation step.

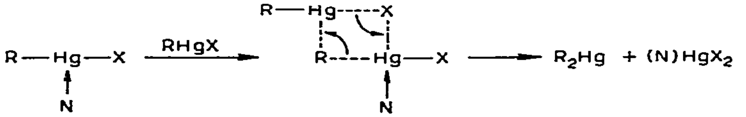
Mechanism (a), which is attractive in its simplicity, is at first sight supported by the observations that mercuric halides are much more strongly retained on the column materials than RHgX or R_2Hg, and that the order of decreasing ease of symmetrisation I > Br > Cl follows a corresponding reduction in the equilibrium constants for eqn. (1)[2]. We feel this mechanism must be rejected, however, since the mercuric halides are strongly adsorbed on all the alumina samples tested, irrespective of their symmetrising ability. Thus whilst strong absorption of HgX_2 is obviously a necessary feature to allow separation of the products, an active role [mechanism (b)] is indicated for the column material.

We propose that the column material assists in the symmetrisation of RHgX by acting as a nucleophilic catalyst. Coordination of the nucleophilic material (N) to mercury would lead to increased electron density on the R group [eqn. (2)] which would enhance its ability as an electrophilic substrate to the second RHgX molecule.



(2)

Such a mechanism has been proposed by Jensen[8] to account for the symmetrisation of organomercuric halides by ammonia, and has recently been discussed in detail by Reutov *et al.* . Attack of the second molecule leads to an intermediate complex which may decompose via a four-centre transition state [eqn. (3)] to give the observed products.



(3)

Alumina is known to have surface oxide sites[10] which would be capable of acting as the nucleophilic centres. The reactivity difference of basic, neutral and acidic material can be explained by a progressive decrease in availability of these sites until finally, on deactivation by the addition of water, all the oxide sites are blocked and no reaction occurs. The high reactivity of the magnesium oxide can be accounted for by its basic nature[10,11]. As well as basic oxide sites, it has surface hydroxy groups which behave as OH^- ions. Silica on the other hand has surface hydroxy groups which are acidic in character[10], and this, presumably, accounts for the inactivity of this material.

TABLE 2

SYMMETRISATION OF RHgX ON TREATED COLUMNS

Organomercuric halide	*Column material*	*Products*	*Yield (%)*
o-TolHgBr	Basic alumina + NaOH	$(o\text{-Tol})_2Hg$	95
o-TolHgCl	Neutral alumina + KI	$(o\text{-Tol})_2Hg$	90
MeHgBr	Neutral alumina + KI	MeHgI	70
		MeHgBr	20

A few experiments were performed using columns treated with known symmetrising agents, after the manner of Rausch and co-workers[5]. Results are shown in Table 2. Doping alumina with sodium hydroxide or potassium iodide leads to improved yields of di-*o*-tolylmercury from *o*-TolHgCl or *o*-TolHgBr (though recovery of the mercuric halide is sacrificed). The reported results for sodium cyanide on alumina are similar[5]. These reactions are probably promoted by the nucleophilic action of OH^-, I^- or CN^-. Alkylmercuric halides were not symmetrised on any of these columns, but underwent anion-exchange reactions.

In conclusion, it seems that for arylmercuric halides at least, conditions can be found which will promote complete symmetrisation by chromatographic methods. The convenience of the method is, however, seriously reduced by the limited solubility of most of the compounds in question. The ratio of sample to column size can be very small, requiring long experiment times. We therefore believe that, unless direct recovery of the mercuric halide in necessary, conventional symmetrisation methods[6,12] are more useful.

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