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Symmetrization of Organomercury(II) Chlorides using Basic Alumina

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The symmetrization reaction of organomercury(II) chlorides (RHgCl) to R_2Hg and $HgCl_2$ in toluene solution under identical conditions using a basic alumina column has been studied in order to compare the effect of the nature of the R groups on the extent of symmetrization. The efficiency of symmetrization depends markedly on the electron-withdrawing nature of R, varying from 90–94% for R = trichlorovinyl or phenyl to 11% for R = 2,6-dimethylphenyl. © 1998 John Wiley & Sons, Ltd.

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INTRODUCTION

Different forms of mercury from a variety of sources enter the environment and are converted to methylmercury by micro-organisms, with sediments being major sites of methylation,[1–8] although abiotic methylation via transalkylation reactions may also contribute to its formation.[9–11] Methylmercury(II) is extremely toxic to living organisms because of its high affinity for thiols and, due to its lipophilic nature, bioaccumulation in the food chain occurs, making it especially dangerous to higher organisms.[12]

Organomercurials of the types R_2Hg and RHgX are extremely important reagents in organic synthesis and as organic transfer reagents in organometallic chemistry.[13,14] The interconversion of RHgX into R_2Hg and HgX_2, which are formed simultaneously (Eqn[1]) is a process known as symmetrization. This process has been widely investigated and often used for the preparation of organomercurials of the R_2Hg type.[15] It can be effected by reducing agents or by strong complexing agents such as cyanide, iodide or tertiary phosphine which force the equilibrium to the right by removing the mercury(II) salt by complexation, precipitation or reduction.

$$2RHgX \rightleftharpoons R_2Hg + HgX_2 \qquad [1]$$

Studies have been carried out on the kinetics, stereochemistry and mechanisms of the symmetrization and desymmetrization of organomercury derivatives.[15] Two mechanisms have been considered for the little-studied symmetrization route using alumina or magnesium oxide columns on the basis of studies with *o*-tolyl and ethylmercury halides.[16] These were: (a) spontaneous symmetrization of the organomercury halide solution followed by chromatographic separation of the products; and (b) a mechanism involving the chromatographic medium as an active participant in the symmetrization step. Mechanism (a) could be used to interpret the results, as it has been observed that the mercury(II) halides are much more strongly retained on the column materials than RHgX and R_2Hg, and that the order of decreasing ease of symmetrization is $I > Br > Cl$, following the decreasing order of equilibrium constant for Eqn [1]. However, it was felt that this mechanism did not satisfactorily explain the fact that the acidity of the column exerts a critical effect, with basic alumina being more efficient than neutral or acidic alumina and with magnesium oxide being slightly better than basic alumina, while silica shows no activity. Thus it was proposed[16] that (b) should be the accepted mechanism, where the column medium (D, Scheme 1) plays an active role by acting as a nucleophilic catalyst with its basic sites coordinating to mercury, resulting in an increase in electron density of the R group, hence increasing its nucleophilicity to a second RHgX molecule and leading to a four-centre transition state which then decomposes to give the symmetrized product. The

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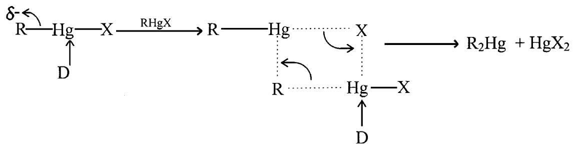


Scheme 1

HgX_2 molecules are more strongly held on the column as they are better Lewis acids than R_2Hg, thus allowing separation of the two products.[16]

In order to provide further substance for this mechanism and to examine the versatility of this reaction we now report the symmetrization of a greater range of organomercury halides on basic alumina columns.

EXPERIMENTAL

Syntheses

***p*-Tolymercury(II) chloride (1)**
This was prepared by diazotization of *p*-toluidine followed by the addition of mercury(II) chloride and decomposition of the double diazonium salt with copper powder as previously described.[15] Recrystallization from aqueous ethanol yielded silver flakes, m.p. 236–238 °C; lit.m.p.[15,] 238–239 °C.

Di(*p*-toly)mercury(II) (2)
Symmetrization of **1** with potassium iodide in acetone gave **2**, which was isolated as colourless crystals, m.p.239–240 °C; lit.m.p.,[17] 238 °C.

Bis(trichlorovinyl)mercury(II) (3)
Shaking of an aqueous solution of mercury(II) cyanide and potassium hydroxide with trichloroethene yielded silver flakes of **3** after recrystallization from hexane: m.p. 72–73 °C; lit.m.p.,[18] 72–73 °C.

Trichlorovinylmercury(II) chloride (4)
Compound **4** was prepared in good yield by cleavage of $(C_2Cl_3)_2Hg$ with $HgCl_2$ in equimolar quantities in methanol, yielding white crystals: m.p. 105–107 °C; lit.m.p.,[18] 109 °C.

2-Furylmercury(II) chloride (5)
The mercuration of furan in ethanol with mercury(II) chloride in aqueous sodium acetate solution yielded colourless crystals of **5**, m.p. 150–151 °C; lit.m.p.,[19] 151 °C.

Di(2-furyl)mercury(II) (6)
Colourless crystals of **6** were obtained by symmetrization of 2-furylmercury(II) chloride with sodium thiosulphate solution m.p. 114 °C; lit.m.p.,[19] 114 °C.

2-Thienylmercury(II) chloride (7)
Mercuration of thiophene with mercury(II) chloride/sodium acetate in ethanol, yielded colourless crystals of **7**, m.p. 182–184 °C; lit.m.p.[15] 183 °C.

Di(2-thienyl)mercury(II) (8)
This compound was obtained by symmetrization of 2-thienylmercury(II) chloride with sodium iodide in acetone solution: m.p. 199 °C; lit.m.p.,[15] 198–199 °C.

Phenylmercury(II) chloride (9) and diphenylmercury(II) (10)
These were both commercially available and were purified by recrystallization from chloroform.

Bis(2,6-dimethylphenyl)mercury(II) (11)
Reaction of the corresponding Grignard reagent with mercury(II) chloride afforded **11** as colourless plates, m.p. 178–179 °C; lit.m.p.,[17] 180–181 °C.

2,6-Dimethylphenylmercury(II) chloride (12)
Equimolar quantities of **11** and mercury(II) chloride in ethanol yielded colourless plates, m.p. 216–218 °C; lit.m.p.,[17] 215–216 °C.

Symmetrization

The symmetrization reaction was carried out on a basic aluminium oxide (grade H) column, (15 cm × 2 cm) which had been activated by heating at 90 °C for 3 h. The organomercury compounds were identified by their melting points and by thin-layer chromatography on silica gel plates, eluting with a 2:1 mixture of benzene/petroleum ether (60–80 °C). The compounds were visualized by spraying successively with a solution of copper(II) sulphate (20% in 1 M HCl) and an aqueous solution of 5% KI/20% Na_2SO_3.[20] Identification of the mercury(II) halide was carried out by TLC on silica gel by elution with a 7:3 mixture of carbon tetrachloride/acetone and visualized as described above.

Table 1 Percentage yields of symmetrized products[a]

	yield (%)	
R	R_2Hg	$HgCl_2$
p-Tolyl	23	21
2,6-Dimethylphenyl	11	11
Phenyl	94	93
2-Furyl	88	84
2-Thienyl	77	79
Trichlorovinyl	92	90

[a] The relative amounts of symmetrized products formed did not alter significantly within small variations in loadings on the column.

Procedure

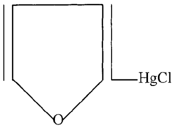
The organomercury(II) halide (0.45 g), dissolved in the minimum volume of tetrahydrofuran, was admitted to the top of the column, prepared in toluene, an hour before elution. The column was capped to prevent solvent evaporation and the temperature was maintained at 21 ± 1 °C. Elution with toluene, followed by evaporation under reduced pressure, afforded the organomercurial. Subsequent elution with toluene/chloroform (1:1) produced mainly the organomercury(II) halide. Final elution with methanol produced mercury(II) chloride, which was identified by TLC and its melting point.

RESULTS AND DISCUSSION

Table 1 shows the results found for the symmetrization reaction shown in Eqn [2] using a basic alumina column under identical conditions in toluene solution in each case.

$$2RHgCl \rightleftharpoons R_2Hg + HgCl_2 \qquad [2]$$

If the mechanism (b) described in the Introduction is generally applicable, then the reaction is clearly dependent on the ability of the R group to act as an electron acceptor, thus enhancing the compound’s ability to act as an electrophilic substrate. Thus compounds which exhibit good electron acceptor character would be expected to symmetrize readily. The arylmercury(II) halides show a decrease in the amount of symmetrization in the order phenyl > *p*-tolyl > 2,6-dimethylphenyl, demonstrating the effect of the addition of electron-releasing methyl groups to the phenyl ring system. The presence of a phenyl group attached to mercury would be expected to promote good symmetrization because of its ability to delocalize the increased electron density around the ring system; indeed, phenylmercury(II) chloride undergoes 94% symmetrization under the conditions used. With the successive addition of methyl groups as in *p*-tolylmercury(II) chloride (**1**) and 2,6-dimethylphenylmercury(II) chloride (**12**), there is a decrease in symmetrization due to the decreased ability of the phenyl ring to delocalize the increased electron density. The symmetrization behaviour of **1** (22%) is similar to that found earlier[16] for *o*-tolylmercury chloride (25%).



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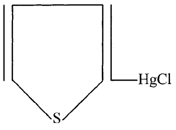

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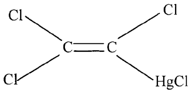

(4)

This explanation can also be seen to apply to the results obtained from the symmetrization of compounds which are structurally different. Thus the two heterocyclic organomercurials, 2-furylmercury(II) chloride (**5**) and 2-thienylmercury(II) chloride (**7**) do not symmetrize to the same extent as phenylmercury(II) chloride (**9**). This is as expected in the light of resonance stabilization, as the phenyl group would be able to delocalize the electron density more effectively then the heterocylic groups. Because of the greater electronegativity of oxygen compared with sulphur, the furylmercurial symmetrizes more readily than its sulphur analogue. A similar argument may be employed to explain why trichlorovinylmercury(II) chloride (**4**) readily undergoes a high degree of symmetrization similar to that of **9**. The increased electron density in the symmetrization process can be accommodated by the inductive effect of the sp^2-hybridized carbon atoms, which are electron withdrawing and hence help to enhance the ability of mercury to act as an electrophilic substrate to the second RHgCl molecule. Additionally the presence of the highly electronegative chlorine atoms enhances the ability of the R group to accommodate the increased electron density.

Thus this process provides a relatively cheap (the alumina can be recycled) non-chemical method, which is easy to operate, for the symmetrization of some organomercury halides and adds support to the symmetrization mechanism proposed by Cross and Jenkins.[16]

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