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EXCHANGE REACTIONS OF ORGANOMERCURY COMPOUNDS[a]

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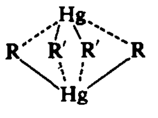
Abstract—Spectroscopic studies (PMR and UV) have been carried out on mixtures of symmetrical organomercury compounds at room temperature in DMSO, pyridine, and ethanol as solvents. It has been shown that for a range of diarylmercurials, Ar_2Hg, and di-(acetaldehyde)mercury, $Hg(CH_2CHO)_2$, an exchange reaction occurs with the formation in solution of the unsymmetrical compound $ArHgCH_2CHO$. Facile exchange also occurs between pairs of diarylmercurials. A mechanism involving a four centre transition state is proposed. Simple dialkylmercurials do not undergo this exchange under mild conditions.

The exchange or redistribution reactions of organometallic compounds have been known for many years, and the mechanisms of many of these processes have been examined in some detail.[1] Organomercury compounds, because of their stability and relative ease of preparation, have received particular attention, and the exchanges which occur between organomercury compounds and organomercury salts or inorganic mercury salts have been established as electrophilic substitutions.[2] However, the mechanism of the isotopic exchange reaction between pairs of symmetrical organomercury compounds, usually represented by equation 1 has remained in doubt.

$$R_2Hg + R'_2Hg^* \rightleftharpoons R'_2Hg + R_2Hg^* \qquad (1)$$

This process is usually referred to as the four-alkyl or four-aryl exchange reaction.

Comparatively little work has been undertaken in this type of system; the chemical similarity of the reactants frequently makes their separation and quantitative estimation difficult. However, Reutov[3] has observed a facile exchange under mild conditions between di-(acetaldehyde)-mercury and a number of diarylmercury compounds, and recently Pollard has reported a similar exchange between diphenylmercury and di-(*p*-chlorophenyl)mercury. Since unsymmetrically disubstituted mercurials (of type RHgR') were not observed, it was concluded that the exchange takes place by way of a 6-centre transition state (1)[3-5] in which the two metal atoms become equivalent. A 4-centre transition state (2) would require the formation of unsymmetrical species as an intermediate. 6-Centre transition states have also been postulated for exchanges between organomercury and organothallium compounds.[6]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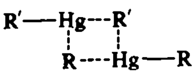
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In contrast to the above reports, unsymmetrical intermediates have been detected in the products from other exchange reactions. For example, dibenzylmercury and diphenyl mercury are reported to give on fusion together phenylmercury benzyl as well as other products,[7] and an unsymmetrical intermediate is formed when a mixture of dimethylmercury and deuterated dimethylmercury is heated to 65° for 78 h.[8] Although these intermediates were detected only for reactions carried out at higher temperatures it was felt that they cast some doubt on the interpretation of the results obtained under mild conditions. It was decided, therefore, to perform experiments specifically designed to detect the presence of unsymmetrical compounds in solution at or near room temperature. Two series of experiments were carried out. In the first series the proton magnetic resonance spectra of solutions (in DMSO and pyridine) of pairs of symmetrical mercurials which had been shown to undergo radioisotopic exchange were examined. In the second series the UV spectra of solutions of mixtures of mercurials (in EtOH) were examined.

RESULTS AND DISCUSSION

(a) *PMR studies.* In these investigations di-(acetaldehyde)-mercury was commonly used as one of the reactants, partly because of the previous studies using this compound, and also because the proton signals are particularly convenient structural indicators. The spectrum consists of an aldehyde triplet at $\delta = 9{\cdot}53$ ppm,‡ and

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‡Chemical shifts are given in parts per million downfield from internal tetramethylsilane.

a methylene doublet at $\delta = 2{\cdot}44$ ppm (Fig. 1b). An interesting and useful feature is the symmetrically disposed satellite doublet signals, $^2J(HgCH) = 196$ Hz, on each side of the methylene doublet; these satellites are caused by the presence of 16·9 per cent of the spin-$\frac{1}{2}$ isotope ^{199}Hg. When a second organomercury compound was added to a solution of di-(acetaldehyde)mercury in deuterated DMSO, spectral changes occurred which showed the presence of a third substance in solution shortly after mixing. This is illustrated (Fig. 1a) for the reaction between di-(acetaldehyde)mercury and diphenylmercury. It can be seen that additional triplet and doublet signals appear, close to the original signals, and the new doublet is surrounded by satellite signals with a reduced coupling constant, $^2J(HgCH) = 161$ Hz. These changes indicate that the new substance is an organomercury compound, and are consistent with the structure $C_6H_5HgCH_2CHO$.

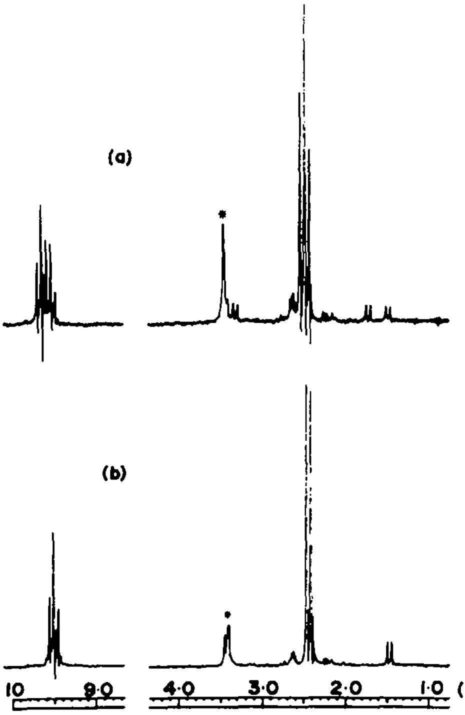

Fig 1. The PMR spectra in DMSO-d_6 as solvent of (a) an equimolar mixture of di-(acetaldehyde) mercury and diphenylmercury, and (b) a solution of di-(acetaldehyde) mercury alone.
*Signal partly obscured by impurity signal (water in solvent).

Additional experiments were carried out using other aromatic mercurials in place of diphenylmercury, and using pyridine, instead of DMSO, as solvent. For many of these systems the spectral evidence indicated that the unsymmetrical species of type $ArHgCH_2CHO$ is formed in the exchange reaction. When pyridine was used as solvent, no splitting of the methylene signal occurred, but the appearance of new satellite signals with a smaller value of $^2J(HgCH)$ proved that the unsymmetrical species is still formed. The changes in the value of the coupling constant are consistent with the general observation that the coupling constant increases as the group attached to mercury becomes more strongly electron withdrawing.[9]

The results of the above series of experiments and the PMR parameters of the intermediates are shown in Table 1. It is interesting to note that for those systems where reaction occurs, the exchange takes place rapidly under these mild experimental conditions. Certain other systems were examined, including the reaction of diphenylmercury with dibenzylmercury, and di-(2-phenylethyl)-mercury, in pyridine. There was no evidence of exchange reactions occurring until these solutions had been maintained at 80° for about 100 h.

(b) *UV studies*. The PMR technique is limited to those systems where the two reactants give signals in different regions of the spectrum. Possible reactions between closely related pairs of diarylmercury compounds could not be studied by this method. However, it was found that exchanges between such compounds could sometimes be monitored using UV spectroscopic techniques. For example, at spectroscopic dilution in ethanol distinct

Table 1. PMR parameters for the methylene group of the unsymmetrical organomercury compounds $ArHgCH_2CHO$ formed as intermediates in the exchange of $(OHC{\cdot}CH_2)_2Hg$ with Ar_2Hg

	Pyridine Solvent		DMSO Solvent	
Ar Group	Mercury-proton coupling constant ^2J	Chemical shift (δ) of CH_2 group	Mercury-proton coupling constant ^2J	Chemical shift (δ) of CH_2 group
$OHC{\cdot}CH_2$-	196	2·44	197	2·37
C_6H_5	158	2·44	161	2·41
p-$CH_3OC_6H_4$	158	2·44	157	2·35
p-$(CH_3)_2NC_6H_4$	154	2·44	154	2·38
p-$CH_3NHC_6H_4$	153	2·44	154	2·37
p-Bromophenyl	166	2·44	167	2·37
p-Ethylphenyl	154	2·44	156	2·37
p-Aminophenyl		No intermediate observed		

changes in the UV spectra of a mixture of ditolylmercury and di-(p-dimethylaminophenyl)mercury were observed; λ_{max} decreased from 234 and 282 nm to 224 and 280 nm, and the optical density at $\lambda = 234$ decreased by 11 per cent over a period of several hours (Fig. 2). The UV data for three reactions systems is shown in Table 2.

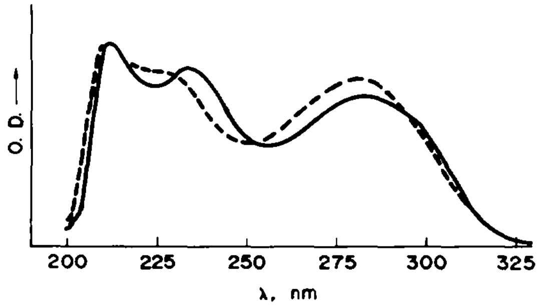

Fig. 2. UV absorbance of an ethanolic solution of an equimolar mixture of di-p-tolylmercury and bis-p-dimethylaminophenylmercury at time zero (——) and after 24 hr (-----) at room temp.

(c) *Conclusions*. The UV and PMR data described above shows that in solution at room temperature a facile reaction frequently occurs between pairs of diarylmercurials, or between diarylmercurials and di-(acetaldehyde)mercury, and the reaction is accompanied by the formation of a third species. The PMR spectra of the reactions involving di-(acetaldehyde)mercury show that this third species is the unsymmetrical mercury compound Ar–Hg–CH$_2$CHO, and it seems likely that the changes in the UV spectra of pairs of diarylmercurials result from the presence of a similar species. The exchange reaction should, therefore, be represented, not by Eq. (1), but by Eq. (2). Such a process clearly cannot proceed via the 6-centre transition state (1). Naturally, the results obtained do not prove definitely that the alternative 4-centre process occurs. Free radical mechanisms are observed for some reactions of organometallic compounds,[10] although this seems unlikely under the particular experimental conditions used in the present work. To eliminate this possibility, however, we demonstrated that under the reaction conditions diarylmercurials do not polymerize methylmethacrylate, and the exchange process is unaffected by the presence of free radical inhibitors or the use of degassed solvents. The most likely mechanism, therefore, is a bimolecular process involving the formation of unsymmetrical intermediates by way of the 4-centre transition state (2).

$$R_2Hg^* + R'_2Hg \rightleftharpoons RHgR' + RHg^*R' \rightleftharpoons R_2Hg + R'_2Hg^* \quad (2)$$

The 4-centre mechanism implies that the intermediates are not very stable in solution, i.e. they readily disproportionate. We attempted to prepare compounds PhHgAr (Ar = p-chlorophenyl and p-dimethylaminophenyl) by reacting phenylboronic acid with the appropriate arylmercuric halide, but were unable to isolate pure products. This is in agreement with Kharasch's reports[11] that such compounds are indeed unstable. We found, however, that mixed aryl-alkyl mercurials (Ar–Hg–R) can be prepared, and are stable over long periods. This is consistent with our observations that diphenylmercury and diethylmercury do not undergo facile exchange on mixing.

It is unfortunate that the experimental techniques used are limited in their application. Certain systems, for example diphenylmercury and di-(p-chlorophenyl)-mercury, could not be examined because of the great similarity of the UV and PMR spectra of the starting materials.

EXPERIMENTAL

(a) *Materials*. All the materials used in the investigations were prepared by standard methods. The di-(acetaldehyde)mercury was prepared from n-butyl vinyl ether, and had m.p. 94–95° (lit. value 93–95°). The diarylmercurials were generally prepared from the corresponding amines by the diazo method,[12] although some were prepared by direct mercuration of the aromatic substrate to give the arylmercuric acetate, which was subsequently symmetrised[12] to give the diaryl compound.

(b) *PMR experiments*. Equimolar (0·5 M) solns of both mercurials in pyridine or DMSO as solvent were mixed, and the resulting soln placed in an NMR tube. The spectra were then measured at known time intervals. For those systems described in Table 1, the intermediate was detected within 15 min.

The PMR spectra were recorded using Varian A60A and HA100 spectrometers.

(c) *UV experiments*. In the initial experiments, solns of two mercurials in abs EtOH were mixed, and this mixture monitored by UV spectroscopy. For certain pairs of reactants (Table 2) the spectrum of the mixture changed with time, although no changes occurred over the same period of time for solns of the single mercurials, i.e. the changes in the spectrum of the mixture is associated with interaction between the two organomercury compounds. Further experiments were then carried out as described below; the reaction between di-p-tolylmercury and bis-dimethylaminophenylmercury will be used as an example. Four optically matched cells were placed in the spectrometer in the following manner. Two cells were placed in the reference beam of the instrument; one contained an ethanolic solution of di-p-tolylmercury ($2{\cdot}58 \times 10^{-5}$ M), and the second contained a solution

Table 2. Values of λ_{max} for the UV absorption spectra of mixtures of pairs of diarylmercurials in ethanol at 25°

Reaction mixtures	$(C_6H_5)_2Hg$ + $(p\text{-}Me_2N\cdot C_6H_4)_2Hg$	$(p\text{-}ClC_6H_4)_2Hg$ + $(p\text{-}Me_2N\cdot C_6H_4)_2Hg$	$(p\text{-}MeC_6H_4)_2Hg$ + $(p\text{-}Me_2NC_6H_4)_2Hg$
Initial λ_{max} (nm)	221 and 283	234 and 284·5	234 and 282
Final λ_{max} (nm)	218 and 280·5	229 and 280·5	224 and 280

of bis-*p*-dimethylaminophenylmercury ($2{\cdot}86 \times 10^{-5}$ M). The two remaining cells were placed in the sample beam of the spectrometer, *each* containing an ethanolic soln of a mixture of di-*p*-tolylmercury ($1{\cdot}29 \times 10^{-5}$ M) and bis-*p*-dimethylaminophenylmercury ($1{\cdot}43 \times 10^{-5}$ M). In this way, the spectrum of the mixture could be compared directly with an "ideal" mixture of the separate, unreacting, components of the reaction. The differences observed indicated the formation of a new species in soln on mixing (Table 2 and Fig. 2). The maximum change in the spectrum was observed after 24 h at room temp.

The UV spectra were recorded using a Unicam SP800 spectrophotometer.

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