NUCLEAR MAGNETIC RESONANCE AND ^{203}Hg EXCHANGE STUDIES OF ALLYLMERCURY SYSTEMS: A COMMENT ON ALLYLMERCURIC PERCHLORATE

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SUMMARY

Nuclear magnetic resonance data for allyl-, β-methallyl-, crotyl- and cinnamyl-mercuric halides and acetates are presented and the dramatic effect of added mercuric salts on some of these spectra is discussed. The exchange of mercury between allyl- and β-methallylmercuric halides (chloride or bromide) and the appropriate mercury-(II) halide, utilising ^{203}Hg as a tracer, is very rapid (statistical exchange in less than a minute at 20°) and appears to be one of the fastest organic–inorganic Hg^{II} exchanges reported. Mechanisms of the $S_E i'$ variety are suggested, and the significance of the exchange in relation to the effect of Hg^{II} halides on the PMR spectra of allylmercury systems is pointed out.

The preparation and some properties of a compound argued to be allyl-mercuric perchlorate are presented.

INTRODUCTION

In other connections[1,2] we have briefly commented on some aspects of the PMR spectra of certain allylmercury compounds, and in particular have drawn attention to the pronounced effect that mercuric halides have on the spectra of allyl-mercuric halides. The recent report of Ziegler and Roberts[3] concerning diallyl-mercury, prompted us to present our NMR data fully, as well as our studies of mercury exchange in these systems. While engaged in solvolytic studies[4,5] of allylmercury systems, a compound considered to be allylmercuric perchlorate was isolated, and our information on this compound is disclosed.

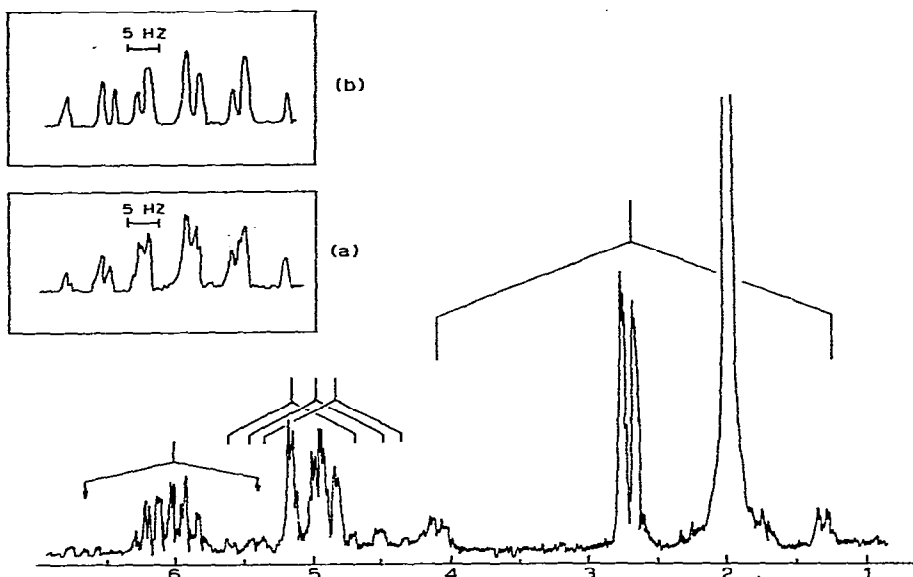* To whom inquiries should be directed.

** Deceased November 23rd, 1969.

Fig. 1. The 100 MHz spectrum of $CH_2=CH-CH_2HgOCOCH_3$ in $CDCl_3$. $^{199}Hg-^1H$ *spin coupling is* indicated, and discussed in the text. Insert (a) shows an expanded version of the $=CH-$ resonance (60 MHz) while insert (b) shows the calculated pattern employing the coupling constants listed in Table 2.

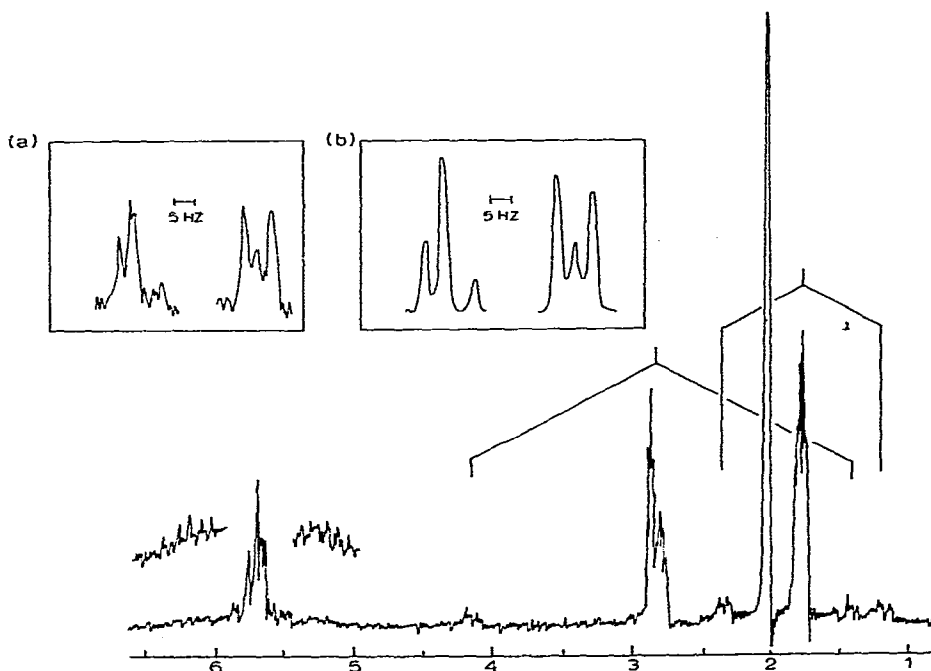Fig. 2. The 100 MHz spectrum of *trans*-$CH_3-CH=CH-CH_2HgOCOCH_3$ in $CDCl_3$ and $^{199}Hg-^1H$ coupling is indicated. Insert (a) shows the actual (60 MHz) resonance pattern of the vinyl and methylene protons of $C_6H_5-CH=CH-CH_2HgOCOCH_3$, while insert (b) shows the calculated patterns, using the coupling constants in Table 2.

RESULTS AND DISCUSSION

(a). NMR studies of allylmercury systems

Allylmercuric acetates

Because of their ready solubility in a wide range of solvents and the lack of averaging exchange processes, facilitating the acquisition of well resolved spectra, we commence with a discussion of the spectra of the acetates. This information is a useful starting point for the halides, whose spectral behaviour is less straight forward.

The spectra of crotyl and allylmercuric acetates are shown in Fig. 1, 2 and ^{199}Hg–^{1}H coupling is clearly visible, as it is in the spectra of cinnamyl and β-methallylmercuric acetates. The resonance positions are those expected for σ-allyl compounds, and compare in these respects with the spectra of other σ-allyl compounds, such as allyl chloride or acetate. The chemical shift data for the above compounds are located in Table 1.

TABLE 1

CHEMICAL SHIFT VALUES^a (PPM) FOR ALLYLIC MERCURIC ACETATES, RHgOAc

Structure 1: 4.83/4.85 H, H 6.07/~6.0^b; C=C; 5.0/5.07 H, CH$_2$ 2.52/2.72; 1.92/1.98 AcOHg

Structure 2: 4.57^c/4.74^c H, CH$_3$ 1.75/1.81; C=C; H, CH$_2$ 2.45/2.73; 1.85/2.00 AcOHg

Structure 3: 1.60/1.56 CH$_3$, H 5.50/5.47; C=C; 5.50^c/5.47^c H, CH$_2$ ~2.5^d/2.56; 1.87/1.98 AcOHg

Structure 4: 7.22$_e$ C$_6$H$_5$, H 6.37^c/6.23; C=C; 6.37^c/6.33 H, CH$_2$ ~2.6/2.72; 1.82/1.96 AcOHg

^{a} First value: DMSO-d_6; second value: CHCl$_3$. ^{b} Highly split. ^{c} Center of multiplet. ^{b} Solvent interferes. ^{e} Phenyl pattern obscured by solvent (spectrum in DMSO-d_6).
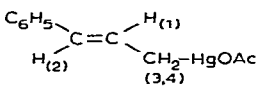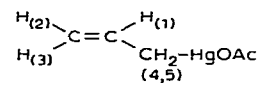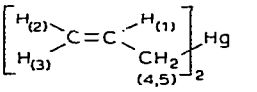
Because of the non-first order nature of the spectra and since some unexpected features as regards resonance patterns appeared in the cinnamyl case, some calculated spectra were obtained, to clarify these features and provide magnitudes of coupling constants in these systems. An IBM 7090 computer was used employing a program obtained from the Mellon Institute and described by Bothner–By*. The predicted spectra were plotted and compared with the experimental spectrum. The input data was refined until the calculated and actual spectra agreed. In Fig. 1, 2 are the actual and computed resonances for the β-proton (=CH–) of allylmercuric acetate and the comparison for the vinyl and methylene resonances of cinnamylmercuric acetate. The coupling constants used in the calculated spectra are shown in Table 2.

Although nicely reproducing the experimental spectra, these coupling con-

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* This program uses as input data the number of proton spins, the chemical shifts and spin coupling constants for each proton and a line width at half-height for the resonances. The program computes all the line positions and intensities in the desired frequency range and also a table of intensities for each step. This makes the shape of the computed signals closely resemble a Gaussian curve.

TABLE 2

COUPLING CONSTANTS USED IN THE CALCULATED SPECTRA OF CINNAMYL- AND ALLYLMERCURIC ACETATE[a]

| Compound	Coupling constants (Hz)						
	$J(1, 2)$	$J(1, 3)$	$J(1, 4)$	$J(1, 5)$	$J(2, 3)$	$J(2, 4)$ and $J(2, 5)$	$J(3, 4)$ and $J(3, 5)$
C_6H_5 C=C $H_{(1)}$ / $H_{(2)}$ CH_2-HgOAc (3,4)	17.80	9.00	9.00		−1.30	−1.30	0.00
$H_{(2)}$ C=C $H_{(1)}$ / $H_{(3)}$ CH_2-HgOAc (4,5)	10.00	17.00	8.00	8.00	2.00	−1.20	−1.70
[$H_{(2)}$ C=C $H_{(1)}$ / $H_{(3)}$ CH_2 (4,5)]$_2$ Hg	9.43	17.09	8.81	8.81	2.21	−0.63	−0.98

[a] The data for diallylmercury is taken from H. E. Ziegler and J. D. Roberts see ref. 3.

stants are seen to be unexceptional for allylic systems, and compare very well with those employed by Ziegler and Roberts[3]. The value of $J(1, 2)$ of 17.80 Hz would seem to confirm the *trans* nature of the cinnamylmercurial.

^{199}Hg–^1H spin coupling. We were initially interested in determining the magnitude of such couplings to aid in decisions concerning the inter- or intra-molecular nature of certain rearrangement processes in allylmercury systems. The four allylmercuric acetates investigated showed in their spectra sharp satellites of appropriate intensity (ca. 16 % of total signal intensity) about the main proton resonance (*i.e.* due to molecules containing mercury isotopes other than ^{199}Hg). For crotyl and allylmercuric acetates couplings to the vinyl as well as to the methylene protons were observed and are condensed below (and see Fig. 1, 2). Little variation in these magnitudes was detected for the other mercurials. In the crotyl case coupling to the CH_3 protons was also identified, being 104 Hz.

$$J_4 = J_5 = 286 \text{ Hz}$$
$$J_1 = 104 \text{ Hz}$$
$$J_2 \approx J_3 = 95 \text{ Hz}$$
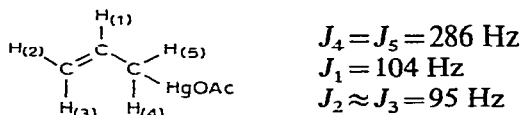
Perhaps the most noteworthy feature of these couplings is that J_2 and J_3 are only marginally smaller than J_1 and this could be due to a substantial contribution from a conformation in which the mercury atom is located quite near the region of the double bond *e.g.*:
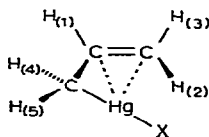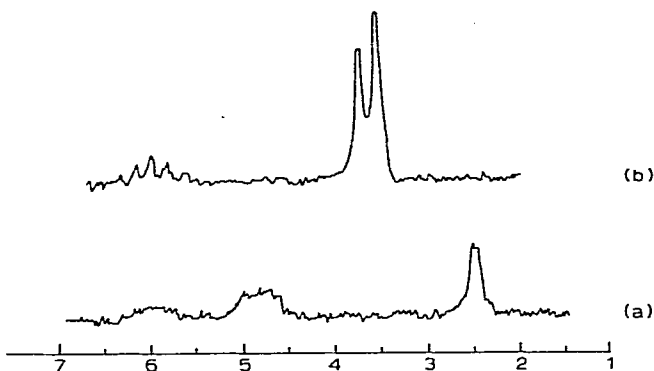
Fig. 3. (a), The 60 MHz spectrum of CH_2=CH–CH_2HgCl in DMSO-d_6, showing three broad absorptions; (b), Spectrum after addition of ca. 20 mg of $HgCl_2$, with the emergence of a one-proton quintet and four-proton doublet, and no ^{199}Hg coupling was visible.

Alternatively, the strong coupling may in part be due to a π-component in the C_1–C_2 bond as a result of extensive polarisation of the C_1–Hg bond, permitting "σ–π conjugation". The conformation below would then be most favored for the allylmercury system*.

In comparison with the data for diallylmercury[3], the J values (*i.e.* to ^{199}Hg) for the acetate are approximately twice as great, *e.g.* J_4 in $(C_3H_5)_2$Hg is 144.30 Hz and J_1 45.8 Hz and this is in line with the behaviour of J values for the change R_2Hg→ RHgX[10]. The close similarity between J_1 and J_2 and J_3 is also observed in the diallyl-mercury case[3]. The presence of satellites confirms the long life (on the NMR time scale) of the C–Hg bond in allylmercuric acetates.

Allylmercuric halides

Initial attempts to obtain spectra of these compounds were difficult, due to poor solubility in typical NMR solvents such as carbon tetrachloride, chloroform or carbon disulfide. Acetone, dioxane, tetrahydrofuran or DMSO, which presumably coordinate with mercury are more satisfactory.

In Fig. 3 is the spectrum of allylmercuric chloride in DMSO-d_6. The lower spectrum is broad and poorly resolved, although three absorptions at ca. 2.5, 4.9 and 6.00 ppm can be discerned. The upper spectrum is after the addition of ca. 20 mg of $HgCl_2$ which produces a remarkable change in that a quintet and doublet (1/4 rel. intensity) (J 11 $\pm$ 1 Hz) emerge. It is clear from Fig. 3 that the quintet is essentially in the same resonance position as the original 6.00 ppm signal, while the doublet is at the average (ca. 3.7 ppm) of the original 4.9 and 2.5 ppm signals. These characteristics define an AX_4 system. Allylmercuric chloride in chloroform behaves similarly although the spectrum is very weak. Similar observations apply to the bromide and iodide. The data obtained are collected in Table 3.
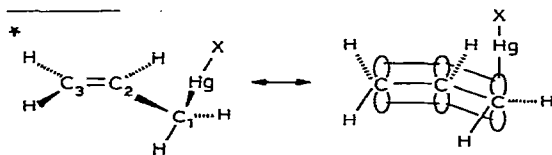
TABLE 3

NMR DATA FOR ALLYL–MX COMPOUNDS SHOWING AX_4 PATTERN

MX	Solvent	Chemical shift (ppm)		$J(AX)$ (Hz)	Ref.
		H_A	H_X		
HgCl	DMSO-d_6	6.02	3.64	11 ± 1	This work
HgBr	DMSO-d_6	6.15	3.74	11 ± 1	This work
HgI	DMSO-d_6	6.18	3.74	11 ± 1	This work
HgCl	CHCl$_3$	6.01	3.91	11 ± 1	This work
MgBr	Ether	6.38	2.50	12 ± 1	11
Li	Ether	6.84	2.57	12 ± 1	12
PdCl	DMSO	6.82	4.77	9.8	13

There appears to be a growing body of data favoring the idea that metalloene interaction in σ-allyl metallics where the metal center has acceptor orbitals, is a quite significant factor determining spectroscopic and reactivity properties[7-9].

β-Methallylmercuric halides

These mercurials are soluble in a greater variety of solvents suitable for NMR work. Fig. 4 shows the spectrum of β-methallylmercuric chloride in CHCl$_3$ with and without added HgCl$_2$. Again a very broad spectrum is sharpened by this addition and the signal areas are in the expected 4/3 (low/high) ratio, assignable to the four equivalent CH$_2$ protons and the C–CH$_3$ group. The data are collected in Table 4.
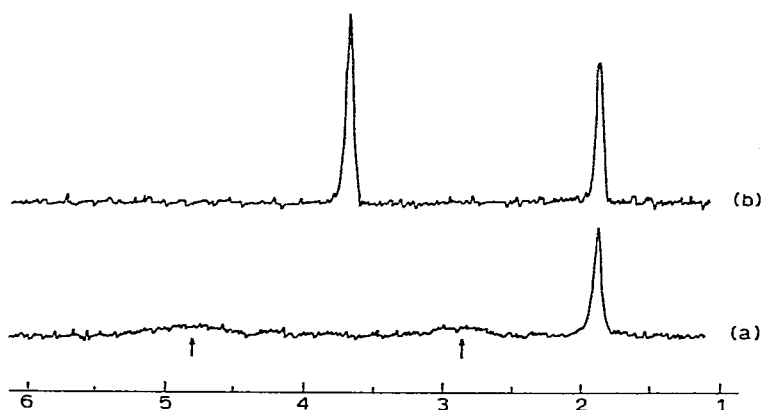

Fig. 4. (a), The 100 MHz spectrum of CH$_2$=C(CH$_3$)–CH$_2$HgCl in CDCl$_3$, showing broad resonances for vinyl and methylene protons; (b), The effect of added HgCl$_2$, with the emergence of a four-proton singlet. The C–CH$_3$ resonance is essentially unaffected, and no ^{199}Hg coupling is visible.

The possibility of small amounts of impurities in the mercurial (β-methallyl) was tested. Freshly recrystallized compound (in which conceivable impurities might be Hg^{II} or Hg^{I} halides) was treated with potassium hydroxide which yielded no precipitate, and with H$_2$S which precipitated HgS only after thirty seconds. These tests readily detected 0.1 % of deliberately added HgCl$_2$, and consequently the β-methallylmercuric chloride contained no detectable inorganic mercury salts. The spectrum of this sample was the same as that of the others.

TABLE 4

CHEMICAL SHIFTS (PPM) FOR $CH_2=C(CH_3)-CH_2HgX$

X	Solvent	C–CH$_3$	H$_x$ and H$_y$	Added salt
Cl	CHCl$_3$	1.81	3.72	HgCl$_2$
Cl	DMSO-d_6	1.77	3.55	HgCl$_2$
		1.8	3.2	NaI
Br	CHCl$_3$	1.81	3.7 (v. broad)	
	Benzene	1.38	3.19	HgBr$_2$
	DMSO-d_6	1.74	3.55	HgBr$_2$

Salts other than Hg^{II} were also examined, but only halides affected the spectra in a similar way. Whereas catalytic quantities of the former sufficed, increasing amounts of NaI were required to produce the same effect. The anions that coordinate well to mercury, *e.g.* I$^-$, were most effective.
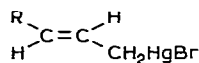
Crotyl and cinnamyl mercuric bromides

These mercurials yielded well resolved spectra in DMSO-d_6 in sharp contrast to the symmetrical allylmercuric halides just discussed. The addition of mercuric bromide or sodium bromide in trace, equimolar or excess amounts, caused no discernible change in the NMR spectra of crotylmercuric bromide in either DMSO-d_6 or CHCl$_3$. The compound was recovered unchanged in 91 % yield after refluxing for thirty minutes in chloroform with added equimolar HgBr$_2$.

Close examination of a concentrated pyridine solution of crotylmercuric bromide showed the presence of ^{199}Hg satellites* about the CH$_2$–Hg resonance ($J \sim 280$ Hz) and these survived on the addition of HgBr$_2$, and other features of the spectrum were unchanged, *i.e.*, no significant changes in chemical shift. The implications of these results will be discussed shortly, but it should be emphasised that in the allyl and β-methallyl cases, no ^{199}Hg satellites were observed about the proton resonances in the presence of added HgX$_2$, indicating rapid breaking and reforming of C–Hg bonds. The spectral parameters for crotyl- and cinnamylmercuric bromides are assembled in Table 5. All spectra integrated correctly, and in resonance positions and general absorption patterns, closely resemble the corresponding acetates.

It is convenient to discuss certain features of the spectra of the halides, in the

TABLE 5

CHEMICAL SHIFT DATA (PPM) FOR $\underset{H}{\overset{R}{>}}C=C\underset{CH_2HgBr}{\overset{H}{<}}$

| R	Solvent	$\underset{H}{>}C=C\overset{H}{<}$	–CH$_2$–	CH$_3$	C$_6$H$_5$
CH$_3$	CHCl$_3$	5.45^a	2.73	1.68	
CH$_3$	DMSO-d_6	5.42^a	2.5	1.62	
C$_6$H$_5$	DMSO-d_6	6.57^a	2.8		7.44
C$_6$H$_5$	CHCl$_3$	6.41	2.96		7.3

^{a} Center of complex multiplet.

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* ^{199}Hg coupling to the CH$_3$ group was also visible being ca. 108 Hz, very similar to that in the acetate.

absence of added HgX_2, first. For cinnamyl- and crotylmercuric bromides there seems no doubt that the σ-allyl description with extremely small amounts (if any) of the α-methallyl isomer present, is appropriate*. The presence of ^{199}Hg satellites implies a relatively long life (on the NMR time scale) for the C–Hg bond.

The data for allyl- and 2-methallylmercuric chlorides strongly suggest the operation of an equilibrating process even in the absence of HgX_2 (see Fig. 3, 4). The rate of rearrangement is fast enough to broaden and obliterate fine structure, but not fast enough to cause coalescence or sharpening. This suggests a rate constant ca. 10^{-2} times that estimated for the lower limit of exchange in the presence of added salt (*vide infre*). Two plausible mechanisms may be advanced for the averaging process in the absence of added HgX_2.
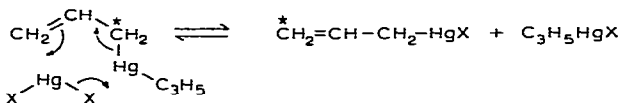
Firstly, a mechanism involving symmetrisation and subsequent cleavage by HgX_2 as shown below.

$$2\ CH_2{=}CH{-}CH_2{-}HgX \overset{K}{\rightleftharpoons} (CH_2{=}CH{-}CH_2)_2Hg + HgX_2$$
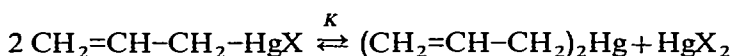
Although K as written is quite small, the rate constants k_f and k_r $(K = k_f/k_r)$ may be sufficiently rapid to produce slow exchange. The forward step is really cleavage of allylmercuric halide by allylmercuric halide, symbolised below as S_Ei'.
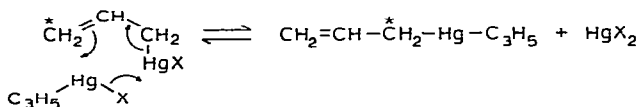

Note the interchange of the asterisked group in the forward step, while further interchange occurs in the reverse step below, since S_Ei' cleavage is again highly favored.

An essential feature of this mechanism involves the stability of HgX_2 produced in the forward symmetrisation, and this may account for the rate sequence I > Br > Cl. Thus the above mechanism would require minor modification to account for catalysis by iodide and other coordinating ligands which favor the symmetrisation step by stabilising Hg^{II} as HgI_3^- or HgI_4^-.

Secondly, rearrangement not involving the formation of diallylmercury could proceed as below, and any steric problems might be relieved by the length of the C–Hg bond and near planarity of the allyl group.

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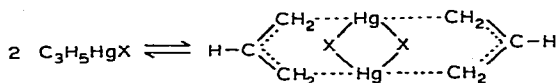
* Solution IR spectra (which provide a faster snap-shot of the system) are most definitely in favor of primary structures, and no absorptions appropriate for the secondary structure are detectable.

The mercury may be almost tetracoordinated here and the stronger Hg–I bond may be a critical factor in the exchange rates of the halides. Consequently it is not surprising that the acetates, which lack a strong bridging (even some π-bonding to Hg) capability exchange very slowly, and not evident by NMR.

There is convincing analogy for the suggested inter-molecular transfer of allyl groups in the chemistry of the σ-cyclopentadienylmercuric halides, where *intra*- and *inter*-molecular processes compete[14]*, and we have demonstrated that the line shapes of β-methallylmercuric chloride in CHCl$_3$, at constant temperature, are quite dependent on concentration, with faster exchange at higher concentration. On cooling to $-60°$, the observed spectrum of β-methallylmercuric chloride closely resembles that of the acetate, in both line positions and ¹⁹⁹Hg couplings. The latter however, vanish as the temperature is raised. By analogy with the *intra*-molecular rearrangement ("fluxional") of cyclopentadienylmercuric chloride[14], an *intra*-molecular route as below can be envisaged:
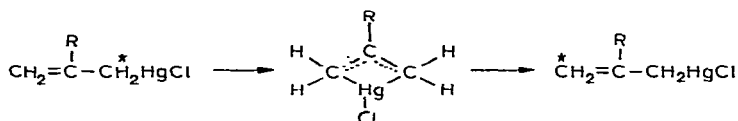
but in view of the above data, this appears highly unlikely, as a major mechanistic component.

The remarkable effect of added HgX$_2$ on the spectra of allyl- and 2-methallyl-mercuric halides requires the incursion of a separate mechanism. Examination of the data in Table 6 reveals very strong evidence that a true averaging process is occurring. Since allylmercuric acetates are not involved in rearrangement at finite rates, the chemical shifts can be taken as a good approximation of the signals of the halides, were they not executing some averaging process**. Thus averaging the positions of

TABLE 6

CHEMICAL SHIFT (PPM) OF ALLYLIC MERCURIC HALIDES ($+$ HgX$_2$) COMPARED TO THE AVERAGE OF VINYL AND METHYLENE SHIFTS FOR CORRESPONDING ALLYLIC MERCURIC ACETATES

Compound	Solvent	H$_2$C=	–CH$_2$–	Average
H₂C=C(CH₃)CH₂HgOAc	Chloroform	4.74	2.73	3.74
	DMSO-d_6	4.57	2.45	3.51
				H$_z$ and H$_y$
H₂C=C(CH₃)CH₂HgCl	Chloroform			3.72
	DMSO-d_6			3.55
H₂C=C(H)CH₂HgOAc	DMSO-d_6	4.92	2.52	3.72
				H$_z$ and H$_y$
H₂C=C(H)CH₂HgBr	DMSO-d_6			3.74

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* Concomitant allylic rearrangement and intermolecular exchange has been suggested in the case of diallylmercury (ref. 4).
** This proposition is validated by the observation that the low temperature, non-averaged spectrum of β-methallylmercuric chloride is essentially the same as that of the corresponding acetate.

the vinyl and methylene resonances of the acetates should yield the chemical shift of the four equivalent protons under conditions of rapid rearrangement of the halides. This is what is found.

Also, the signal position for the β-proton (or β-methyl group) is essentially unchanged, since the magnetic environment of such groups is unchanged by the equilibration between symmetrical species. Further evidence for an exchange process comes from examination of $^1\text{H}-^1\text{H}$ coupling constants. In allylmercuric acetate, coupling constants to H_1 (β-proton) of $+10$, $+17$, $+8.0$ and $+8.0$ Hz were found to reproduce the spectra. The average of these $(43/4 \sim 11 \text{ Hz})$ is what is found for allylmercuric chloride in the presence of HgCl_2, *i.e.*, J_{AX} 11 Hz for the AX_4 system.

For the case of exchange between two sites, having equal life-times and populations, $\tau_{\frac{1}{2}}$ is the half-life for the exchange process. The two signals will just coalesce when $\tau_{\frac{1}{2}} = \sqrt{2}/2\pi \cdot (\nu_A - \nu_B)$ where ν_A and ν_B are the frequencies in Hz of A and B in the absence of exchange. The shape of the doublet for allylmercuric chloride is sharp, and use of calculated curves can indicate a lower limit on exchange in the presence of added salts. The observed signal corresponds best to that for a half-life, $\tau_{\frac{1}{2}} < \frac{1}{2}\pi \cdot (\nu_A - \nu_B)$. Taking 146 Hz as the separation of the vinyl and methylene resonances in allylmercuric acetate, gives $\tau_{\frac{1}{2}} < 1.1 \times 10^{-3}$ sec, yielding $k \; (= \tau_{\frac{1}{2}}^{-1}) \geqslant 10^3$ sec^{-1}. Thus the protons are exchanging their environments at least one thousand times per second.

The lack of ^{199}Hg satellites under conditions of exchange induced by HgX_2, confirms the *inter*molecular nature of the exchange. The most likely mechanism appears to be as below.
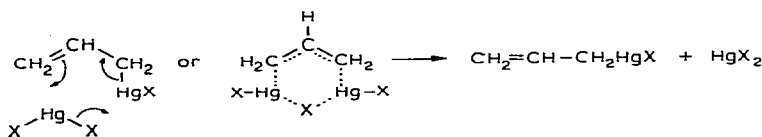
This mechanism is consistent with the absence of satellites, the catalytic effect of HgX_2 (far less than equimolar quantities are needed since each act of substitution produces a replacement molecule of HgX_2) and the bridging role of X in the transition state above may partly account for the ordinal reactivity $\text{HgI}_2 > \text{HgCl}_2$.

A variant of the above, that involves the "mercurium ion" may also be considered. Attack at the double bond yields the ion (A) with collapses to the equivalent ion (B) which produces the rearranged product.
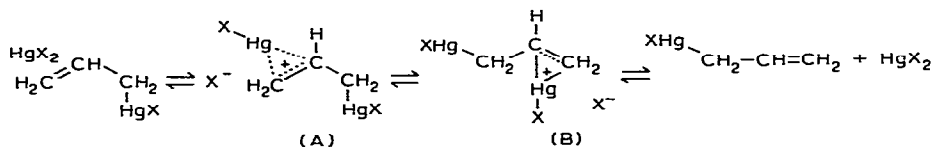
This type of scheme may be important for Hg(OAc)_2 which obliterated almost all signals, probably due to oxymercuration. Since "mercurium ion" formation is expected to be less important for the halides than acetates for example, and some halocoordination does seem to be important in the present observations, the $S_E i'$ mech-

anism above is more favored. However, both schemes provide the symmetrical energy profile for an exchange of this type.

The effect of $HgBr_2$ on the spectrum of crotylmercuric bromide is far less pronounced and at room temperature, ^{199}Hg satellites persisted indicating a much longer C–Hg pre-exchange time. We attribute this behaviour to the unfavorable aspects of the intermediate α-methallylmercuric bromide, which would be less favored thermodynamically. A similar situation obtains with the allylic mercurial, indenyl-mercuric chloride[3], where addition of $HgCl_2$ and heating are required to effect proton equilibration and satellite removal.
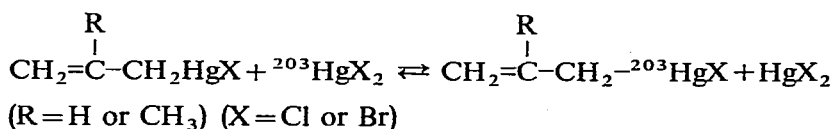
The inter-molecular nature of the mechanism for HgX_2 catalysis demands rapid exchange of mercury atoms between HgX_2 and allylHgX, and for this reason we have conducted a study of the exchange of mercury between allyl- and β-methallyl-mercuric halides (chloride or bromide) and the appropriate Hg^{II} halide, utilising radioactive ^{203}Hg as a tracer*.

The NMR observations alluded to above pertain to chloroform and DMSO, and the same spectral behaviour was also demonstrated for acetone. Chloroform is the least suitable for exchange studies due to its poor solubility of HgX_2. Therefore the exchange experiments were conducted in acetone and DMSO/methanol. β-Methallyl mercuric chloride appeared to suffer some decomposition in DMSO, and hence acetone was used for this compound.

Attempts to separate $CH_2=C(R)–CH_2HgX$ from HgX_2 (R = H or CH_3) by differential solubilities, while not completely discouraging, were nevertheless only marginally successful. A more promising procedure involved selective precipitation of HgX_2 with a nitrogen donor ligand. Bipyridine was employed and found to remove HgX_2 as HgX_2·Bipy from solutions of DMSO and acetone containing $CH_2=C(R)–CH_2HgX$. The IR spectrum of HgX_2·Bipy thus formed was identical in all respects with that of the authentic complex, and no bands due to $CH_2=C(R)–CH_2HgX$ or a complex with bipyridine were observed. As will become clear soon, precipitation from acetone, on addition of the calculated quantity of bipyridine, was essentially quantitative, but since HgX_2·Bipy has considerable solubility in DMSO (in fact this was the most suitable solvent for counting purposes) less than the theoretical amount of HgX_2·Bipy was precipitated when DMSO was employed as the exchange solvent, i.e. in the cases of $CH_2=CH–CH_2HgX$. This, however, does not prevent determination of the tag distribution since what is not precipitated must be left in solution and can be accounted for.

The results are condensed in Table 7 and actual details of preparation and manipulation of the radioactive materials are in the Experimental Section. Operationally the process is shown below:

$$CH_2=\overset{\overset{\displaystyle R}{|}}{C}-CH_2HgX + {}^{203}HgX_2 \rightleftarrows CH_2=\overset{\overset{\displaystyle R}{|}}{C}-CH_2-{}^{203}HgX + HgX_2$$

(R = H or CH_3) (X = Cl or Br)

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* At the time when a considerable amount of this work was complete (1964–1966) we were unaware of the very brief report by Reutov[15] who found that exchange between allylmercuric bromide and $HgBr_2$ was quite rapid in a number of solvents. However, none of the mechanistic implications were commented on, nor were any experimental results reported.

TABLE 7

R (CH₂=C–CH₂HgX (A))		HgX₂ (B)	Conc. (M) of		Solvent	Mg of Hg in		Time before separation (sec)	% of theoretical HgX₂·Bipy prec.	Calcd. (found) counts/minute for statistical exchange[a]	
R	X	X	(A)	(B)		(A)	(B)			(A)	(B)
H	Br	Br	0.025	0.016	DMSO/MeOH	122.3	78.6	72	79.7	126.7 (141.1)[b]	76.0 (78.7)[c]
H	Br	Br	0.022	0.008	DMSO/MeOH	111.2	43.7	120	70	84.3 (86.5)[b]	33.0 (36.9)[c]
H	Br	Br	0.03	0.026	DMSO/MeOH	154.3	133.5	108	79	171.6 (178.5)[b]	148.4 (141.1)[c]
CH₃	Cl	Cl	0.056	0.088	Acetone	89.1	141.6	90	99	108 (122)[b]	176 (165)[c]
CH₃	Cl	Cl	0.056	0.046	Acetone	90	73.8	72	98	81.3 (85.4)[b]	66.7 (59.2)[c]

[a] Based on count for known amount of tagged HgCl₂ in known volume in either acetone or DMSO. [b] Counted as residual solution to a known volume) after precipitation of HgX₂ as HgX₂·Bipy, and correction for unprecipitated HgX₂ in case of DMSO solvent. [c] Counted as HgX₂·Bipy dissolved in DMSO. Counting efficiency differences for DMSO and acetone solvents have been taken into account. See Experimental. Corrections for decay of ²⁰³Hg have not been applied since t₃ for ²⁰³Hg is of the order of 45 days and the base count on the HgX₂ employed in each run was conducted within an hour or two of the separated components,

and the results in the Table show that statistical distribution is established quite rapidly, and this defines one of the fastest one-alkylmercury exchanges yet reported*. Even at 10^{-3} M concentrations, statistical exchange is complete before separation is possible[15].

In the absence of the information concerning the effect of HgX_2 on the PMR spectra of $CH_2=C(R)-CH_2HgX$, two basic mechanism could be considered for this one-alkyl exchange *viz.*:
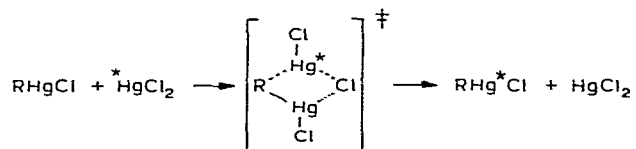

Closed transition state (S_Ei type but other variants are possible).

In contrast to this, a mechanism of the S_E' type (*i.e.* proceeding with allylic rearrangement) must also be strongly considered, *e.g.*:
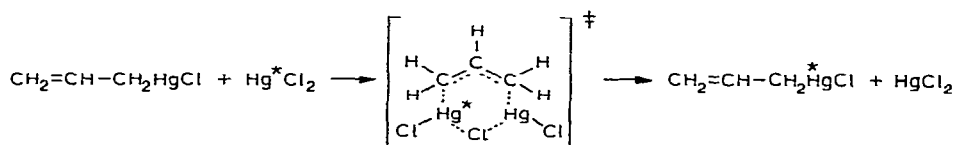
The available information on electrophilic substitution of allylic mercurials would favor the second of these mechanistic types most convincingly[4,5]. The knowledge of the effect of $HgCl_2$ on the PMR spectrum of $CH_2=CH-CH_2HgCl$ adds a new dimension to the considerations, since the AX_4 pattern requiring interchange (after rotation about the C-C bond) of terminal CH_2 groups at the rate of about 10^3 times per second, is inconsistent with any S_E2 or S_Ei mechanism, which would not produce CH_2 group interchange. That a substitution is occurring is evidenced by the absence of ^{199}Hg satellites. Thus the most plausible mechanism for the $HgCl_2$ promoted proton-equivalence in the PMR spectrum and the rapid Hg exchange would be along the following lines, although again fine details are not implied.
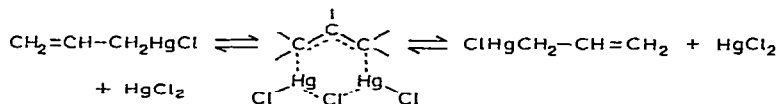
It is conceiveable that some acts of electrophilic substitution are occurring by other than S_E' routes, but these are unimportant from the viewpoint of proton equilibration, and are likely to be quite infrequent. The invocation of the S_E' mechanism

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* For a critical discussion of this whole area see ref. 16.

for proton equilibration necessarily demands that Hg exchange be also complete in a fraction of a second, but the physical problems of separation prevent confirmation. That exchange is complete in the times recorded in the Table is consistent with the above suggestions. If exchange was well removed from randomness in the times recorded, then serious problems regarding mechanistic identity for the two processes would be posed.

However, γ-substitution as in cinnamylmercuric bromide[15], reduces the exchange rate to such an extent that statistical distribution of the radio-tag requires at least five hours. This is in line with our PMR results on γ-methallylmercuric bromide (crotyl) in the presence of $HgBr_2$, where C—Hg bond cleavage and formation was relatively slow.

A comment on allylmercuric perchlorate

Treatment of crotylmercuric acetate in acetic acid with catalytic quantities of perchloric acid leads to the almost instantaneous production of finely divided mercury, and a mixture of α-methallyl and crotyl acetates[6]. However a quite different result is obtained when allylmercuric acetate is subjected to the same treatment. A sample of allylmercuric acetate on treatment with a 5% excess of perchloric acid produces a bright yellow precipitate which was washed well with pentane and dried under vacuum. The yield was of the order 90–95% based on the scheme:

$$C_3H_5HgOAc + HClO_4 \rightarrow C_3H_5HgClO_4 + HOAc$$
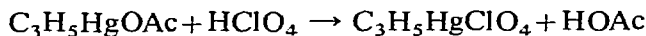
On heating, this yellow solid explodes, and an attempt to powder about 5 mg with a micro-ball mill produced a violent detonation. It is insoluble in water, nitromethane, tetrahydrofuran and liquid SO_2. Mulling for IR analysis was discouraged by the explosive nature of the compound, but the *bright yellow* compound is soluble in pyridine to produce a *colourless* solution (*vide infra*). The PMR spectrum of this solution is almost identical with that of allylmercuric acetate in the same solvent, except there is no resonance appropriate for acetate, and the $^{199}Hg-{}^1H$ coupling constants are somewhat (ca. 10%) larger. This parallels the behaviour of CH_3HgClO_4 and CH_3HgOAc, for example[10,17]. The above facts indicate this yellow compound is the perchlorate salt of allylmercuric cation. A similar yellow compound may be obtained from β-methallylmercuric acetate. Attempts to obtain a more tractable derivative, such as the BF_4^- derivative have not been successful.

The structures of the compounds pose interesting questions. An unmodified σ-allyl structure seems incapable of explaining the yellow colour, and the fact that only the symmetrical allyl groups form insoluble compounds, while crotyl and saturated compounds readily demercurate. If the mercury atom carries a full positive charge, interaction with the double bond would be strongly favored, perhaps leading to a structure of type (I). Hg—ene interaction of an intermolecular nature may be occurring also, and such aggregation may be responsible for its poor solubility in non-coordinating solvents.

(I)
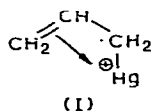
The marked difference between allyl and β-methallyl on the one hand and crotyl would appear to be associated with either the allyl group symmetry, or the ease of demercuration, which we would predict would be slower for the former by several powers of ten. This extended chromophore would also account for the low energy movement to the visible (allylmercuric acetate is colourless).

The reduced rate of demercuration could also favour rearrangement of the σ-allylHg$^{\oplus}$ to the π-allyl structure, which structurally might be favored by the symmetrical allyl groups. The yellow colour is certainly consistent with an extended π-allylmetal chromophore, but does not uniquely demand it. Bonding involving the π-molecular orbitals of the allyl anion and the $6s$ Hg orbital (predominantly) could be envisaged. Back donation from the filled $5d$ level of mercury could also occur.

The loss of colour on dissolution in pyridine, and reversal to a σ-allyl structure are consistent with either (I) or a π-allyl structure. The coordination about Hg is satisfied by pyridine, removing the necessity for double bond involvement. Irrespective of whether (I) or a π-allyl formulation is appropriate, the compound does appear to represent an extreme example of the situation in which the π bond in σ-allyl metallics interacts with the metal center[7,8]. This has previously been suggested for allylmercury halides on the basis of electronic spectra[7,8] but such interaction would be more favourable for the perchlorate. An interaction of this type is probably responsible for the yellowish colour of cyclopentadienylmercurials, which are known to be σ-C$_5$H$_5$ derivatives[14].

EXPERIMENTAL

Synthesis of allylic mercurials

Crotylmercuric bromide. In a dry 3 litre, 3 necked flask flushed with nitrogen and equipped with a Hershberg stirrer and reflux condenser, was placed mercuric bromide (190 g; 0.54 mole) dissolved in 250 ml dry tetrehydrofuran and 200 ml of dry ether. The flask was cooled in an ice-bath and protected from light. The Grignard solution (0.6 mole) prepared from freshly distilled butenyl bromide, was forced slowly over a 2 h period by N$_2$ pressure through a medium porosity sintered glass disk into the well-stirred mercuric bromide solution. There was immediate vigorous reaction producing a large amount of white precipitate which became grey as reaction progressed. After addition was complete, stirring was continued for two hours, and the mixture warmed to room temperature. Water (200 ml) was added, the ether separated and removed under vacuum. The solid remaining was dissolved in 500 ml of warm dichloromethane, which on cooling to 0° for several hours deposited 25 g of a fine powder m.p. 90–91°. Recrystallisation from 80/20 pentane/acetone at −80°, yielded pure crotylmercuric bromide, m.p. 90.8–91.2° (dec.). (Found: C, 14.16; H, 2.04. C$_4$H$_7$HgBr calcd.: C, 14.31; H, 2.10%.)

Crotylmercuric acetate. This compound was prepared by treating the above bromide (10 g; 0.03 mole) in ether (200 ml) with silver acetate (5 g; 0.03 mole) for about 8 h with exclusion of light. The filtered solution was evaporated (temperature < 40°) and the solid recrystallised from 120 ml of 80/20 pentane/acetone and dried 1 h at 3 mm. The overall yield was in excess of 90%; m.p. 76–77°. (Found: C, 22.66; H, 3.18. C$_6$H$_{10}$O$_2$Hg calcd.: C, 22.89; H, 3.20%.)

Cinnamylmercuric bromide. This compound was prepared directly from cin-

namyl bromide and mercury according to Nesmeyanov[18], and is a yellowish, waxy, mica-like solid which would be recrystallised from acetone. No definite m.p. was obtained. (Found: C, 27.04; H, 2.36. C_9H_9HgBr calcd.: C, 27.18; H, 2.28%.)

Very pure cinnamyl bromide appears to react very slowly (if at all) with mercury.

Cinnamylmercuric acetate. This compound was obtained from the bromide (1.50 g; 0.038 mole) and silver acetate (0.66 g; 0.039 mole) in acetone (30 ml) for 2 h. Crystallisation from acetone at $-15°$ gave a total yield in excess of 90%; m.p. 98°. (Found: C, 34.94; H, 3.25. $C_{11}H_{12}O_2Hg$ calcd.: C, 35.08; H, 3.21%.)

Allylmercuric chloride. This compound was prepared from the reaction of allylmagnesium chloride in THF with $HgCl_2$. Separation of the product from inorganic mercuric salts was difficult, being achieved by continuous ether extraction. A low yield of C_3H_5HgCl, m.p. 103–104° (from acetone) was obtained. Reported 110°[19] and 102–103°[20]. (Found: C, 12.58; H, 1.77; Cl, 12.66. C_3H_5HgCl calcd.: C, 12.99; H, 1.80; Cl, 12.80%.)

Allylmercuric bromide. This compound was obtained in about 50% yield from allylmagnesium bromide and mercuric bromide in THF. Recrystallisation from 1/1 ether/methanol gave material with m.p. 124–125° dec. Reported[20] 124–125°.

β-Methallylmercuric chloride. β-Methallylmercuric chloride from β-methallylmagnesium chloride and mercuric chloride in THF in 40% yield, had m.p. 76.7–77° (dec.) from ether/pentane or methylene chloride. (Found: C, 16.53; H, 2.38; Cl, 11.77. C_4H_7HgCl calcd.: C, 16.48; H, 2.44; Cl, 12.19%.)

β-Methallylmercuric bromide. β-Methallylmercuric bromide from β-methallylmagnesium bromide and mercuric bromide in THF, was obtained in 42% yield, and had m.p. 70.8–71.5°, from 1/1 pentane/ether. (Found: C, 14.33; H, 2.04; Br, 23.53. C_4H_7HgBr calcd.: C, 14.31; H, 2.10; Br, 23.81%.)

Allylmercuric iodide. This compound was prepared directly from allyl iodide and mercury in ethanol. Recrystallisation from acetone gave a cream solid which turned yellow on exposure to light particularly; m.p. 129–131°. Reported[21] 133–135°.

Allylmercuric acetate and 2-methallylmercuric acetate. These compounds, m.p. 77.5–78° and 61.8–62.6° respectively were obtained by the AgOAc route outlined above. (Found: C, 20.03; H, 2.61. $C_5H_8O_2Hg$ calcd.: C, 19.97; H, 2.68%.) (Found: C, 22.78; H, 3.28. $C_6H_{10}O_2Hg$ calcd.: C, 22.99; H, 3.20%.)

Structure of allylmercuric halides

The allylmercuric halides either in solution or as a KBr disk show $v(C=C)$ in the range 1620–1635 cm^{-1} which is higher than that found for ionic allyl systems, *e.g.* of sodium $v(C=C)$ 1535 cm^{-1}, but quite similar to these for σ-allylMn(CO)$_5$ where $v(C=C)$ 1620 cm^{-1} [22,23]. This is significantly higher than $v(C=C)$ for π-allyl-Mn(CO)$_4$[23], $v(C=C)$ being at 1505 cm^{-1}. These agreements are expected for an essentially covalent σ-allyl mercurial.

Examination of the vinyl C–H deformation frequencies shows bands at ca. 890 and 983 cm^{-1}, expected for the $CH_2=CH$-group[24]. The *trans* arrangement for

$$\underset{H}{\overset{}{\diagdown}}C{=}C\overset{H}{\diagup}$$
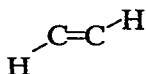
shows only one band[24] near 965 cm^{-1} generally, and in crotyl and cinnamyl mercurials

it lies at 963 and 972 cm^{-1} respectively.

The NMR spectra definitely confirm predominantly primary structures for the crotyl and cinnamyl compounds, and the UV spectrum of the latter with λ_{max} at 282 nm ($\varepsilon = 7,000$) for the bromide in cyclohexane is expected for the conjugated cinnamyl chromophore[25].

The isolation of primary product from the reaction of butenyl Grignard (which predominantly has a primary structure) contrasts with the results for carbonyl compounds[26]. However, rapid HgX$_2$ promoted isomerisation or equilibration as discussed fully in this paper, would lead to primary product.

NMR spectra

The NMR spectra were obtained on either Varian A-60 or JEOL-100 spectrometers, and solvents were the purest available commercial materials, or were purified by standard methods.

Preparation of radio-mercuric chloride

Radio-mercury was obtained in the form of Hg(NO$_3$)$_2$ in dilute HNO$_3$ from the New England Nuclear Corp., Boston, Mass., and had the following specifications: Isotope: ^{203}Hg. Amount: 2 mc. Concentration: 2.35 mc/ml. Volume: 0.85 ml. Purity $= 99+$ % (by γ spectrum). Solids: 4 mg/ml. Prepared: ^{202}Hg (n, γ) ^{203}Hg.

All radio samples were encased in lead blocks and lead shields were used in the normal way during manipulation.

The high activity material (25 micro-litres) was added to ca. 2 ml of 12 N HCl. This was then evaporated to dryness and 10 g of HgCl$_2$ and 30 ml of methanol added. The solution was boiled to ensure homogeneity and then filtered and set aside for crystallisation behind the lead shields. Crystals of HgCl$_2$ appeared and were filtered and dried.

In a similar way, radio-HgBr$_2$ was prepared.

An example of the procedure used in the exchange runs is given below for allylmercuric bromide and ratio-*HgBr$_2$. Counting rates etc. are given in Table 7 in the text, as are times before separation.

To *HgBr$_2$ (141.5 mg; 0.393 mmoles) and allylmercuric bromide (199.6 mg; 0.62 mmoles) in 24 ml of MeOH and 1 ml of DMSO at ca. 20°, was rapidly added bipyridine (52.8 mg; 0.393 mmoles) in DMSO (1 ml). At once a white precipitate of HgBr$_2$·Bipy formed which was filtered and washed thoroughly and dried. The washings were (together with the original solution) made up to a known volume for counting purposes, and the HgBr$_2$·Bipy was dissolved in DMSO, to a known concentration. Counting was conducted on solutions with a Nuclear Chicago Counter.

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