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# NUCLEOPHILIC CATALYSIS IN DEOXYMERCURATION: THE BETA EFFECT OF MERCURY

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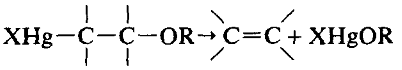
**Deoxymercuration was examined in the antiperiplanar stereochemistry of *trans*-2-acetoxycyclohexylmercury(II) acetate (6). The presence of the mercury group accelerates the departure of the beta leaving group by a factor of about $10^{10}$. This beta effect is larger than that of silicon and comparable to that of germanium. In contrast to these latter cases, the rate for 6 was found to increase with the nucleophilicity of the solvent. It is concluded that a molecule of solvent is coordinated with mercury in the transition state. This nucleophilic assistance raises the polarizability and nucleophilicity of the mercury group, enhancing its ability to stabilize the developing positive charge or to form a bridged intermediate.**

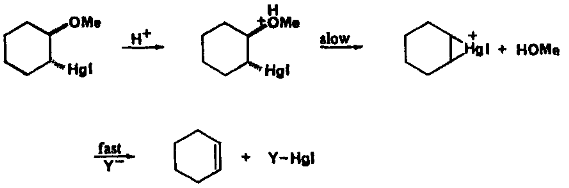
## INTRODUCTION

The deoxymercuration reaction [equation (1)] has long been studied[1] and illustrates many of the major mechanistic principles from the last half century: acid catalysis, intermediate vs transition state, *cis* vs *trans* addition, bridged vs open intermediate, extent of charge development, change in hybridization. The early work by Wright and co-workers[1,2] on the mechanism of oxymercuration suggested by the principle of microscopic reversibility that deoxymercuration occurs by a *cis* addition. Most of the elements of the currently accepted mechanism were developed by Kreevoy and co-workers in a series of papers.[3-5] The elimination of the elements of XHg—OR is attended by an enormous rate enhancement compared with the elimination of H—OR, a factor of $10^{11}$ by one estimation.[3] Thus mercury very effectively fulfils some sort of transition-state-stabilizing role. Nonetheless, acid catalysis is required to improve the leaving group ability of OR.[3] Kreevoy and Eisen[5] found that the *trans* (*anti*) relationship between nucleofuge (OMe in their study) and electrofuge (HgI) lowers the enthalpy of activation by 8·4 kcal mol$^{-1}$ (1 kcal = 4·184 kJ) compared with the *cis* (skew) stereochemistry. This observation supports closure to a bridged mercuronium ion that occurs most facilely from the antiperiplanar geometry available to a *trans* isomer. Alternatively, the faster rate for the *trans* isomer could be explained by an entirely concerted, *E*2-like mechanism,[6] whose microscopic reverse would be a termolecular addition (*Ad*$_E$3) to the double bond.



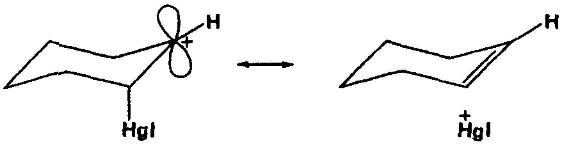
$$\mathrm{XHg{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}OR} \rightarrow \mathrm{{>}C{=}C{<}} + \mathrm{XHgOR} \qquad (1)$$

The Hammett $\rho$ value[4,7] and the secondary deuterium isotope effects,[5] however, are more in agreement with the hybridization and charge development of the mercuronium ion. Scheme 1 illustrates the overall mechanism for the cyclohexyl framework.



Scheme 1

There is considerable latitude for mechanistic discussion of the slow step in Scheme 1. If C—O bond breaking is well advanced in the transition state without appreciable movement of the mercury atom toward the bridged position (vertical stabilization), then the stabilizing effect of mercury can best be described in terms of hyperconjugation in a carbocation (1). Closure to the



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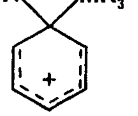
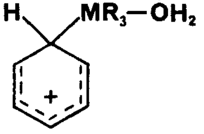
mercuronium ion then follows formation of **1**, and the *cis*/*trans* rate difference for cyclohexyl is explained because the skew geometry (60° dihedral angle) of the *cis* system does not permit effective orbital overlap. On the other hand, if movement of mercury occurs simultaneously with C—O bond breaking (non-vertical stabilization, analogous to traditional neighboring group participation or anchimeric assistance), the transition state resembles the bridged mercuronium ion of Scheme 1 and stabilization derives entirely from the nucleophilicity of the mercury group. Backside displacement is effective in the *trans* but not the *cis* cyclohexyl geometry. Kreevoy and Eisen[5] found an $\alpha$ secondary deuterium isotope effect of $1{\cdot}12$ for $PhMeOCH(D)CH_2HgI$, which supports some build-up of positive charge in the transition state and requires some C—O bond breaking prior to the transition state. The $\rho$ value[4,7] of about $-2{\cdot}8$ is consistent with partial positive charge on the $\alpha$ carbon, either in a very early transition state with only partial C—O cleavage or in a transition state with partial mercury bridging, which is intermediate between the carbocation **1** and the mercuronium ion in Scheme 1. These matters of timing have not been clarified to date.

The mechanism of Scheme 1 is unclear about the nature of the mercury electrofuge. The attachment of the second group to mercury (Y in Scheme 1) can occur at several different times. The questions are analogous to the situation with silicon ($Me_3Si$ replacing HgI in Scheme 1).[8] In this case the electrofuge is a silyl cation $Me_3Si^+$, which is destroyed by reaction with solvent or another nucleophile, although the matter of timing again has never been clarified. For the case of tin, several workers have suggested that attack of the nucleophile occurs prior to C—Sn cleavage and in fact is instrumental in bringing about the rate acceleration.

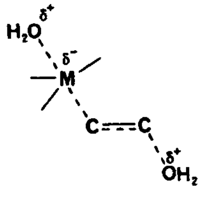
Eaborn and Pande's study[9] of protiodemetalation in $C_6H_5MR_3$ found approximate relative rates for $M = Si, Ge, Sn, Pb$ of $1:36:10^5:10^8$. They suggested that the sigma intermediate resembles **2** for Si and Ge but **3** for Sn and Pb in order to rationalize the much stronger accelerating effect of the latter pair of elements, although there was no direct evidence for transition state hydration. Baekelmans *et al.*[10] used this precedent to explain stereochemistry and solvent effects in iododemetalation. Davis and Gray[11] found that the rates of deoxystannylation and of deoxyplumbylation ($R_3M—C—C—OH \rightarrow C{=}C + R_3M—OH$ formally) increased more rapidly with water concentration than was predicted by $H_0$ and concluded that water was present in a transition state such as **4**, which is reminiscent of the discredited *E*2-like transition state of Bentham *et al.*[6] The study of Davis and Gray,[11] however, did not demonstrate that $H_0$ was an appropriate acidity function for these substrates, so there is some question about the validity of the approach.



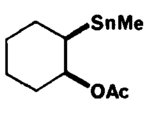
**2**



**3**



**4**



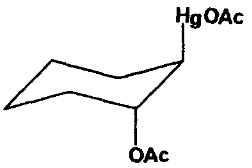
**5**

In a solvent effect study[12] we found that *cis*-2-(trimethylstannyl)cyclohexyl acetate (**5**) reacted in aqueous ethanol and trifluoroethanol to form cyclohexene without an appreciable dependence on solvent nucleophilicity. The rate acceleration of this *cis* substrate ($10^{11}$ compared with cyclohexyl) is much less than that of the *trans* substrate (at least $10^{14}$), for which the effect of solvent nucleophilicity could not be explored. These observations were more in line with vertical assistance, analogous to **1**, with neither solvent assistance nor movement of tin. These studies, however, were preliminary and remain to be confirmed, particularly by kinetic studies of a fully *anti* stereochemistry. The role of water in the transition state ('nucleophiliation') and its effect on the kinetic acceleration for tin therefore remain largely uncertain, and the situation for lead has been even less studied. In contrast, the case of silicon now seems relatively clear, as the rate shows no sensitivity to solvent nucleophilicity (no transition state hydration)[13] and the rate is strongly dependent on solvent ionizing power (C—OR bond breaking). The secondary isotope effect of $1{\cdot}17$ is indicative of almost full charge development (vertical stabilization with a carbocation rather than non-vertical stabilization leading to a siliconium ion).[14]

To bring our understanding of transition state nucleophiliation of mercury up to the level of the Group IV (14) elements, we carried out a study of the dependence of the rate of deoxymercuration on the ionizing power and nucleophilicity of the solvent. We found a strong dependence on solvent nucleophilicity that requires transition state nucleophiliation not observed for silicon.

## RESULTS

The *trans*-1,2 relationship between mercury and the nucleofuge within the cyclohexyl framework corre-



**6**

sponds to the antiperiplanar relationship in the diaxial conformation **6**. We were able to prepare this material from cyclohexene by reaction with one equivalent of mercury(II) acetate in dry tetrahydrofuran containing 1–3 equivalents of acetic acid. Use of alternative acids yielded analogous structures with other nucleofuges. We found that the compounds with tosyloxy, trifluoroacetoxy or dichloroacetoxy (in place of acetoxy on carbon in **6**) were either too reactive or unstable; *p*-nitrobenzoyloxy was stable but poorly soluble. *trans*-2-Acetoxycyclohexylmercury(II) acetate (**6**) was stable and reacted at convenient rates for kinetic measurements.

The $A$ value of AcOHg may be unique in being negative, which is indicative of an axial preference in cyclohexane.[15] Moreover, *trans*-2-methoxycyclohexylmercury(II) chloride (analogous to **6** but with Cl in place of AcO on Hg and MeO in place of AcO on C) exists to a large extent in the diaxial conformation.[16] The similarity of the NMR parameters of this material to those of **6** suggests that the latter also has substantial contributions from the illustrated diaxial conformation. Hence there is no appreciable thermodynamic impediment to reaction of **6** from the antiperiplanar geometry.

Rate constants were obtained by monitoring the increase and decrease, respectively, of product and starting material $^1$H NMR resonances. The average rate constants from triplicate runs are presented in Table 1 for six solvents at 50 °C. Additional rate constants in 97% trifluoroethanol at 42·2 and 35 °C yielded an Arrhenius plot ($r = 0{\cdot}96$) from which activation parameters were calculated: $E_a = 17{\cdot}4\ \text{kcal mol}^{-1}$, $\log A = 8{\cdot}0$, $\Delta H^\ddagger = 16{\cdot}8\ \text{kcal mol}^{-1}$, $\Delta S^\ddagger = -24\ \text{cal K}^{-1}\text{mol}^{-1}$.

Table 1. Rate constants for **6**

| Solvent[a] | Temperature (°C) | $k$ (s$^{-1}$) |
|---|---|---|
| 80% ethanol | 50 | $5{\cdot}45 \times 10^{-4}$ |
| 70% ethanol | 50 | $1{\cdot}37 \times 10^{-3}$ |
| 60% ethanol | 50 | $2{\cdot}24 \times 10^{-3}$ |
| 97% TFE | 25 | $1{\cdot}75 \times 10^{-5}$[b] |
| | 35 | $5{\cdot}04 \times 10^{-5}$ |
| | 42·2 | $7{\cdot}02 \times 10^{-5}$ |
| | 50 | $1{\cdot}88 \times 10^{-4}$ |
| 80% TFE | 50 | $3{\cdot}21 \times 10^{-4}$ |
| 60% TFE | 50 | $1{\cdot}60 \times 10^{-3}$ |

[a] Percentages are v/v for ethanol and w/w for TFE.
[b] Extrapolated from the other values.

Product studies were carried out in 80% ethanol and 97% trifluoroethanol (TFE), which are the least and most ionizing, respectively, of the solvents used. In ethanol, cyclohexene (45%), cyclohexyl ethyl ether (5%), 2-hydroxycyclohexylmercury(II) hydroxide (10%), 2-ethoxycyclohexylmercury(II) hydroxide (28%), cyclohexanone (trace) and cyclohexene oxide (5%) were found. In TFE, cyclohexene (72%), cyclohexyl trifluoroethyl ether (trace), 2-hydroxycyclohexylmercury(II) hydroxide (14%), 2-(trifluoroethoxy)-cyclohexylmercury(II) hydroxide (5%), cyclohexanone (1%) and cyclohexene oxide (6%) were found.

## DISCUSSION

The extreme rapidity of the deoxymercuration reaction was recognized by Kreevoy and Eisen[5] and earlier workers.[1] The present data permit the rate acceleration to be placed on a common basis with other beta accelerating groups. The widely used point of comparison is cyclohexyl, in which only hydrogen is beta to the leaving group, reacting in 97% trifluoroethanol at 25 °C. This substrate solvolyzes by a $k_S$ mechanism (solvent participation), so that comparisons are not necessarily apt if the substituted cyclohexyl system solvolyzes by a different mechanism. For the same *trans* stereochemistry as found in **6**, we previously determined[12] for the trifluoroacetate leaving group that neighboring $Me_3Si$, $Me_3Ge$ and $Me_3Sn$ provide accelerations of $5{\cdot}7 \times 10^9$, $1{\cdot}0 \times 10^{11}$ and $>10^{14}$, respectively. For this basis, we need a conversion factor between the acetate leaving group used in the current study and the trifluoroacetate leaving group used previously. We determined[12] this value to be at least $1{\cdot}5 \times 10^6$, on which basis the rate constant at 25 °C in 97% TFE in Table 1 becomes at least 26·3, a value that is $3{\cdot}7 \times 10^{10}$ times faster than that of cyclohexyl trifluoroacetate under the same conditions. A similar calculation for the tosylate leaving group, using the conversion factor from acetate to tosylate of $2{\cdot}64 \times 10^{10}$ measured by Noyce and Virgilio,[17] gives an acceleration of $2{\cdot}7 \times 10^{11}$ compared with cyclohexyl. These comparisons indicate that mercury provides a larger beta effect acceleration than silicon, a comparable acceleration to germanium and a smaller acceleration than tin. These results provide a quantitative assessment of the already well known ability of mercury to provide a beta acceleration.

Such simple comparisons are not entirely useful unless there is a good understanding of the mechanism. The data in Table 1 include variation of the rate with both solvent ionizing power (which would enhance a carbocation or $k_c$ mechanism) and solvent nucleophilicity (which would enhance solvent assistance or $k_S$). The aqueous ethanol mixtures vary the solvent ionizing power while keeping the nucleophilicity relatively constant, whereas the aqueous TFE mixtures vary the nucleophilicity while keeping the ionizing power relatively constant.[18] Raber, Harris and their co-workers[18] suggested that plotting solvolytic kinetic data in these solvents against the rate of a known $k_c$ substrate, 1-adamantyl bromide, in the same solvents produces a visual distinction between $k_S$ and $k_c$. A substrate with a $k_c$ mechanism produces a single straight line, as both *x* and *y* axes are responding to the same phenomena. In such plots the TFE points show little variation with water content (little dependence on nucleophilicity) and tend to bunch in the upper right-hand corner of the plot. When the substrate along the *y* axis reacts by a $k_S$ mechanism, however, the two solvents produce distinct, non-parallel lines.

The data for **6** are plotted in Figure 1, which has the classic two-line form for a $k_S$ reaction. The triangles are the points for TFE. There is little variation along the *x* axis, as 1-adamantyl bromide is not responsive to solvent nucleophilicity in its $k_c$ reaction. There is, however, variation of about an order of magnitude along the *y* axis, as **6** exhibits considerable sensitivity to solvent nucleophilicity. In turn, the ethanol points show more variation for 1-adamantyl than for **6**. We can conclude from Figure 1 that **6** reacts with solvent participation, in contrast to the analogous *trans* silicon[13] and germanium[12] substrates (plots of this type were not constructed[12] for the *trans* tin compound because of its extremely rapid rate). The large, negative entropy of activation of **6** ($-24\,\mathrm{cal\,K^{-1}\,mol^{-1}}$) also is similar to that for cyclohexyl trifluoroacetate ($-27\,\mathrm{cal\,K^{-1}\,mol^{-1}}$) (a $k_S$ substrate) and different from those measured for the *trans* silicon dinitrobenzoate ($-1\,\mathrm{cal\,K^{-1}\,mol^{-1}}$)[13] and the germanium dinitrobenzoate ($-12\,\mathrm{cal\,K^{-1}\,mol^{-1}}$).[12] The larger negative value for **6** is consistent with the greater order expected by the addition of solvent to the transition state.

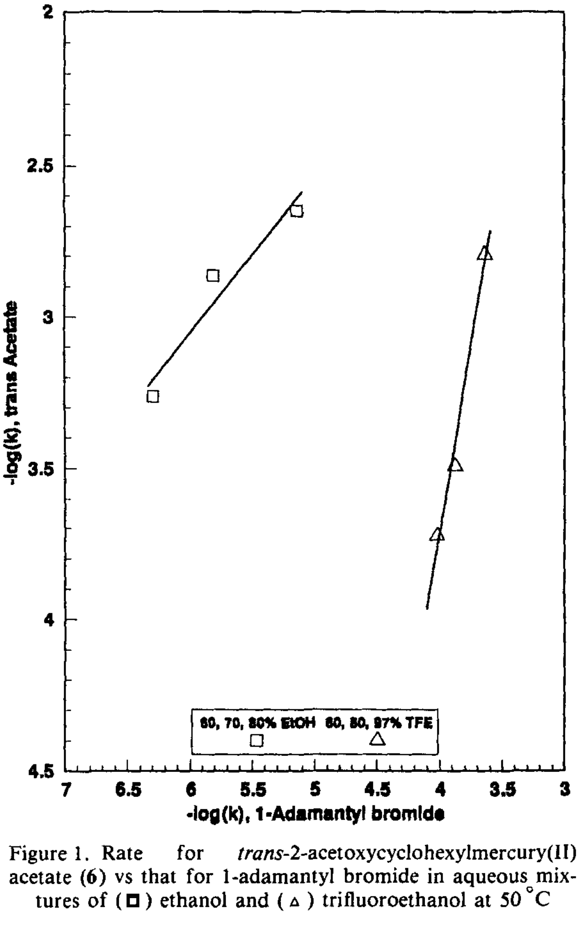
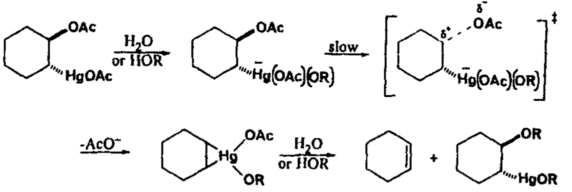


Figure 1. Rate for *trans*-2-acetoxycyclohexylmercury(II) acetate (**6**) vs that for 1-adamantyl bromide in aqueous mixtures of (□) ethanol and (△) trifluoroethanol at 50 °C

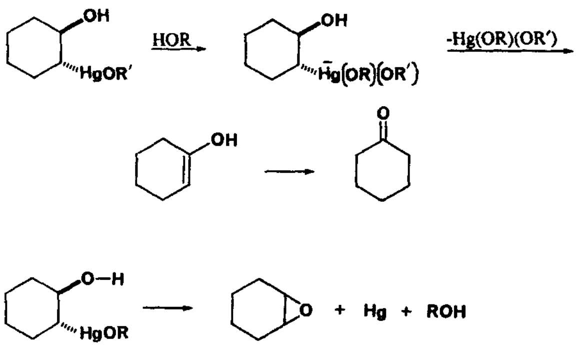
These results indicate that under the current conditions the mechanism of Scheme 1 must be modified. We did not explore acid catalysis, as earlier workers had examined this aspect thoroughly.[3–5] The nucleophile that comprises the second ligand to mercury, represented by $Y^-$ in Scheme 1, however, must be introduced prior to or in the rate-determining step. We cannot define the exact point, but one such scenario is given in Scheme 2. This mechanism takes into account the previous work[3–5,7] that indicated C—O bond breaking and partial positive charge build-up from the $\rho$ value and the secondary $\alpha$ deuterium isotope effect. Since the transition state resembles a carbocation, closure of the mercuronium ring has not been completed. Hence much of the strong kinetic acceleration could derive from the ability of the C—Hg bond to hyperconjugate in the transition state when the O—C—C—Hg geometry is antiperiplanar. The presence of the solvent molecule on mercury must increase the polarizability of the C—Hg bond and increase the nucleophilicity of mercury. Both factors would lead to an enhanced beta effect. The data do not define whether the transition state more closely resembles an open carbocation (vertical participation) or the closed mercuronium ion (nonvertical participation).

The mechanism of Scheme 2 explains about 90% of



Scheme 2

the product in TFE and 85% of the product in ethanol, i.e. cyclohexene, 2-hydroxycyclohexylmercury(II) hydroxide (R = H in Scheme 2), 2-ethoxycyclohexylmercury(II) hydroxide (R = Et), and 2-(trifluoroethoxy)-cyclohexylmercury(II) hydroxide ($R = CF_3CH_2$). The remaining, unexpected products were demercurated in some way. The ethers may be explained by protonolysis of the C—Hg bond in the expected ether products of Scheme 2 ($R = C_2H_5$ or $CF_3CH_2$). Mercury(II) oxide, which would form in such protonolysis reactions, was observed qualitatively by its yellow color. The alcohol product (R = H) of Scheme 2 could produce cyclohexanone and cyclohexene oxide by the mechanism of Scheme 3. These are minor products that are not central to the mechanistic questions.



Scheme 3

## CONCLUSIONS

A mercury(II) acetate group in the *trans* geometry within the cyclohexyl framework greatly accelerates the departure of a beta nucleofuge, about $10^{10}$ for trifluoroacetate or $10^{11}$ for tosylate. These values are similar to those for beta silicon, germanium, and tin, and place mercury among the strongest beta effect atoms known. In contrast to the cases of silicon and germanium, the beta effect reaction of mercury is subject to acceleration by increased nucleophilicity of the solvent and hence qualifies as a $k_S$ mechanism. The solvent (HOR in Scheme 2) serves to heighten the polarizability and nucleophilicity of mercury, thereby improving its ability to stabilize the developing positive charge in the transition state and eventually to form the three-membered ring. Although solvent nucleophilic catalysis of the deoxymercuration reaction has not previously been documented, similar phenomena have been reported in analogous reactions of tin.[9–11] Ichikawa *et al.*[7] always included an extra chloride ion on mercury in their mechanisms, which would fulfil the same role as $RO^-$ in Scheme 2, and Kreevoy and Turner[19] observed catalysis by iodide ion.

## EXPERIMENTAL

*NMR kinetic experiments.* Each of 24 oven-dried, 5 mm NMR tubes was charged with approximately 50 mg of **6**. To each tube was added sufficient solvent to yield a solution 0·08 M in substrate. The mixture was sonicated in a Bransonic 220 ultrasonic bath for a few seconds to aid in the dissolution of the substrate. The tube was sealed at room temperature and immediately inserted into the NMR probe for analysis. Reactions were followed by observing the decrease in intensity of the aliphatic resonances (C*H*OAc or C*H*Hg) and, when possible, the increase in the alkenic resonance of cyclohexene. The integral ratios were used to determine the extent of the reaction. Points were collected at various elapsed times. A point was defined as a 16 transient spectrum taken with an acquisition time of 2·675 s and a pulse delay of 2 s. The initial time zero was defined as the point at which the NMR probe had returned to thermal equilibrium after a new sample was inserted. Points were collected without removing the sample from the probe for at least two half-lives. Kinetic data were analyzed with the LOTUS 123 package, and graphical presentations were prepared via the transmission of that data to the LOTUS FREELANCE PLUS program. The actual temperature in the NMR probe was determined and calibrated by means of the methanol calibration graph. The software of the Varian XLA-400 includes a program, TEMCAL(M), which determines the temperature from the frequency difference between the two peaks of a neat sample of methanol. By running several temperatures, a calibration graph can be generated. In practice, however, it was simpler to use the graph only as a guide and to determine the actual temperature each day with the methanol sample.

*General procedure for the mercuration of cyclohexene.* A dried, nitrogen-flushed, 10 ml, round-bottomed flask fitted with a magnetic stirring bar, a gas inlet adapter with a stopcock and a rubber septum was charged with cyclohexene (0·51 ml, 5·0 mmol), dry tetrahydrofuran (5·0 ml) and mercury(II) acetate (1·67 g, 5·25 mmol). To this rapidly stirred suspension was added the appropriate acid such as acetic acid (5·0 mmol). In some early model reactions, 3 equiv. of the acid were used with no change in the yield of product. The reaction was stirred until all of the mercury(II) acetate had dissolved, and the volatiles were removed at 0·2 mmHg to produce the crude material as a colored semi-solid (**6** when the acid was acetic acid). Specific yields and purifications are detailed below.

*trans*-2-(Tosyloxy)cyclohexylmercury(II) acetate was recrystallized from chloroform–hexane in 67% yield: $^1$H NMR ($CDCl_3$), $\delta$ 1·05–1·90 (m, 8H), 2·08 (s, 3H), 2·40 (s, 3H), 2·81 (m, $J_{\mathrm{HHg}} = 192$ Hz, 1H), 4·85 (m, $J_{\mathrm{HHg}} = 128$ Hz, 1H), 7·26 (d, 2H), 7·82 (d, 2H).

*trans*-2-(*p*-Nitrobenzoyloxy)cyclohexylmercury(II) acetate was triturated with hexane to yield a small amount of white sticky solid: $^1$H NMR ($CDCl_3$), $\delta$ 1·28–1·95 (m, 6H), 2·11 (s, 3H), 2·21 (m, 2H), 2·93 (m, $J_{\mathrm{HHg}} = 190$ Hz, 1H), 4·99 (m, $J_{\mathrm{HHg}} = 111$ Hz, 1H), 8·17 (d, 2H), 8·26 (d, 2H); $^{13}$C NMR ($CDCl_3$), $\delta$ 21·4, 24·3, 28·2, 31·1, 34·2, 49·4, 76·1, 124·0, 131·7, 141·5, 150·7, 169·5, 170·5.

*trans*-2-(Dichloroacetoxy)cyclohexylmercury(II) acetate was triturated with hexane to yield 78% of a gummy pink solid: $^1$H NMR ($CDCl_3$), $\delta$ 1·22–1·95 (m, 6H), 2·09 (s, 3H), 2·22 (m, 2H), 2·78 (m, $J_{\mathrm{HHg}} =$ 186 Hz, 1H), 4·93 (m, $J_{\mathrm{HHg}} =$ 116 Hz, 1H), 5·99 (s, 1H).

*trans*-2-Acetoxycyclohexylmercury(II) acetate (**6**) was triturated with hexane to yield a glassy solid that decomposed on heating above 100 °C: $^1$H NMR ($CDCl_3$), $\delta$ 1·30 (m, 1H), 1·45 (m, 2H), 1·66 (m, 1H), 1·82 (m, 2H), 2·02 (s, 3H), 2·08 (s, 3H), 2·17 (m, 2H), 2·61 (m, $J_{\mathrm{HHg}} = 182$ Hz, 1H), 4·92 (m, $J_{\mathrm{HHg}} =$ 104 Hz, 1H); $^{13}$C NMR ($CDCl_3$), $\delta$ 21·5 ($J_{\mathrm{CHg}} = 170$ Hz), 23·4, 23·7, 27·5 ($J_{\mathrm{CHg}} = 218$ Hz), 30·9 ($J_{\mathrm{CHg}} = 80$ Hz), 33·8 ($J_{\mathrm{CHg}} = 163$ Hz), 50·1 ($J_{\mathrm{CHg}} = 1699$ Hz), 75·9 ($J_{\mathrm{CHg}} = 42$ Hz), 170·9, 177·4; MS (EI), $m/z$ 403 (1%) ($[M+1]^+$), 342 (5), 321 (10), 303 (5), 279 (4), 261 (7), 217 (3), 202 (10), 141 (25), 99 (19), 81 (92), 67 (37), 54 (28), 43 (100); HRMS [$(M+1)^+$], calculated 403·0833, observed 403·0851.

## ACKNOWLEDGMENT

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