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NOTE

SULFUR DIOXIDE INSERTION: ALLYLIC AND BENZYLIC MERCURIALS

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A number of recent reports[1-3] have described the preparation and properties of sulfinato complexes of divalent mercury. These have been prepared by redistribution between mercuric sulfinates and the appropriate diorganomercury compound[3], or by insertion[1-3] of sulfur dioxide into carbon–mercury bonds. In the latter connection, we wish to report our observations on the reactions between sulfur dioxide and allylmercuric acetate, dibenzylmercury and benzylmercuric acetate, and comment on the mechanism of insertion.

The proton spectra of allylmercuric acetate in typical NMR solvents correspond to σ-allyl species[4,5] and ^{199}Hg–^{1}H spin coupling is clearly evident[6]. Dissolution in liquid SO_2 at $-35°$ occurs readily, but the general features of the spectra (recorded immediately) are now very different, and insertion of SO_2 into the C–Hg bond has apparently occurred. The lower field resonances (which lack ^{199}Hg satellites) centred at τ 4.42 (3; multiplet) and τ 6.17 (2; doublet, $J \sim 6$–7 Hz) are in accord with a gross structure (II) for the insertion product.

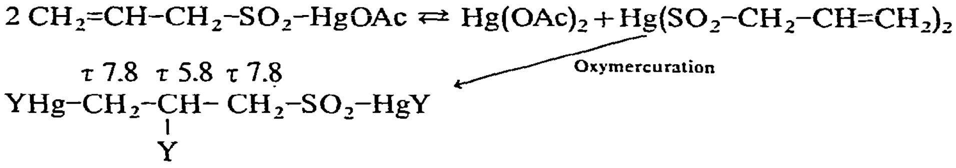
$$\begin{array}{lllll} & CH_2= & CH— & CH_2–HgOAc & \\ & \tau\ 5.15 & \tau\ 4.23 & \tau\ 7.12 & (I) \\ J(^{199}Hg–^{1}H) & 90 & 100 & 286 & \end{array} \qquad \begin{array}{ll} \underbrace{CH_2{=}CH}_{\tau\ 4.42}–\underset{\tau\ 6.17}{CH_2}–SO_2–HgOAc & (II) \\ \text{None observable} & \end{array}$$

$$\underbrace{CH_2{=}CH}_{\tau\ 4.45}–\underset{\tau\ 6.92}{CH_2}–SO_2–Sn(CH_3)_3 \qquad (III)$$

These resonances values, and signal multiplicities agree well with those for the insertion product (III) of allyltrimethylstannane, which has been fully characterised[7].

Removal of solvent (SO_2) left a solid product, which very rapidly decomposed so that analytical and IR data could not be obtained. Thus it is not clear how the SO_2 group is actually incorporated in the insertion product *i.e.* *O*-sulfinato or *S*-sulfinato.

Other features of the PMR spectrum are acetate resonance (τ 8.05), a broad smeared resonance at τ 5.8 and a complex band centred at τ 7.8. These latter resonances have intensity ratio 1/4, and correspond to the presence of substantial amounts of an oxymercurial of type (IV), according to the following scheme.



$$2\,CH_2{=}CH{-}CH_2{-}SO_2{-}HgOAc \rightleftharpoons Hg(OAc)_2 + Hg(SO_2{-}CH_2{-}CH{=}CH_2)_2$$

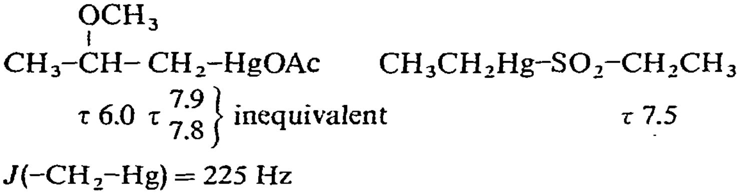
Oxymercuration

$$\begin{array}{l} \tau\ 7.8\quad \tau\ 5.8\quad \tau\ 7.8 \\ YHg{-}CH_2{-}\underset{\displaystyle Y}{\underset{|}{CH}}{-}\,CH_2{-}SO_2{-}HgY \end{array}$$

(IV)

where $Y = OAc$ or $SO_2CH_2{-}CH{=}CH_2$

The complexity of the τ 7.8 resonance is consistent with (IV), since both sets of methylene protons being adjacent to an asymmetric centre constitute AB sets of ABX type spectra*. Similarly the methine proton (τ 5.8) will be complex, and deshielded by the Y group, be it acetate or allylsulfinate. ^{199}Hg satellites about the $Hg{-}CH_2$ resonance are observable ($J \sim 234$ Hz), such a value being consistent with other studies[8,9] which indicate that $J(\alpha\text{-}CH_2{-}Hg) = 210\text{–}240$ Hz in oxymercurials, essentially independent of adjacent substituents. Comparison of the resonances for (IV) agree well with those for suitable model compounds, as below[8,1]. Markovnikov addition is confirmed by these resonance positions.



$$CH_3{-}\overset{\displaystyle OCH_3}{\overset{|}{CH}}{-}\,CH_2{-}HgOAc \qquad CH_3CH_2Hg{-}SO_2{-}CH_2CH_3$$

$$\tau\ 6.0\ \ \tau \left.\begin{matrix}7.9\\7.8\end{matrix}\right\}\text{ inequivalent} \qquad\qquad \tau\ 7.5$$

$$J({-}CH_2{-}Hg) = 225\text{ Hz}$$

Thus the features of the spectrum of allylmercuric acetate in SO_2 are consistent with insertion and oxymercuration processes, the product distribution at apparent equilibrium being 1/1. Passage of SO_2 into solutions (*e.g.* acetone, $CHCl_3$) of allylmercuric acetate at room temperature led to the formation of an instantaneous white precipitate of very limited stability.

Dibenzylmercury has only limited solubility in liquid SO_2, but initially after dissolution (to produce a yellow solution) resonances at τ 7.58 [$J(CH_2{-}^{199}Hg) = 144$ Hz] and τ 2.88 (2/5) are observed. After standing for *ca.* 30 min at −70°, the solution yielded PMR spectra (obtained at −25°) which established that reaction was occurring, in that two equi-intense signals (at τ 7.15 and τ 6.23) were emerging as the benzylic resonance of dibenzylmercury was diminishing in intensity. Only one of these emerging signals (τ 7.15) was coupled with ^{199}Hg ($J = 302$ Hz) making signal assignments unambiguous. Commensurate changes were occurring in the aromatic region of the spectrum. Thus the spectral features are consistent with

$$(C_6H_5CH_2)_2Hg + SO_2 \rightarrow C_6H_5CH_2HgSO_2CH_2C_6H_5$$

The product (evaporation of SO_2 in nitrogen) although still rather unstable, is more readily characterised than the insertion product of allylmercuric acetate, and

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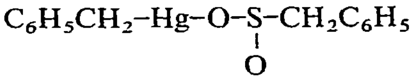
* See ref. 8 for a spectrum of 2-methoxy-1-(chloromercurio)propane with inequivalent methylene protons.

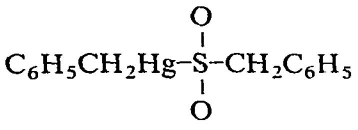
has m.p. 94° (reported[1] 95°). Satisfactory analyses have been obtained[1], and the compound is reported[1] to be monomeric in dichloroethane. The NMR spectrum for $CDCl_3$ solution is very similar to that in liquid SO_2.

The IR spectra for both solid (Nujol) and solution phases ($CHCl_3$, $CDCl_3$) have been obtained*, to make possible a decision on the mode of bonding of the SO_2, as in (V) or (VI).



$$C_6H_5CH_2{-}Hg{-}O{-}\underset{\underset{O}{|}}{S}{-}CH_2C_6H_5$$

(V)



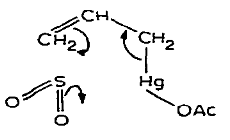
$$C_6H_5CH_2Hg{-}\overset{\overset{O}{|}}{\underset{\underset{O}{|}}{S}}{-}CH_2C_6H_5$$

(VI)

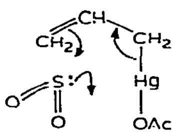
In both phases the S–O stretching frequencies deviated little from 1050 cm^{-1} (strong) and 878 cm^{-1} (strong), being $\nu_{as}(SO_2)$ and $\nu_s(SO_2)$ respectively**. In $CDCl_3$ particularly, which has a "window" in the appropriate region, there was no absorption near 1200 cm^{-1}, so that *S*-sulfinato product is essentially absent in both solid and solution. Structure (V) is thus heavily favoured***, but it is of interest that both O- and S-bonded forms have been identified under certain conditions for the insertion products of diphenylmercury and diethylmercury[1–3].

For the instantaneous chiral configuration (V), the methylene protons adjacent to the asymmetric sulfur centre are in principle magnetically inequivalent****, but not so in the achiral (VI). This argument has been considered before[1], but rapid (even slight) dissociation, and other phenomena[7] could render such protons equivalent. This approach to structure decisions requires caution.

Benzylmercuric acetate is quite soluble in SO_2 at $-70°$ but during a period of *ca.* 1 hour no reaction occurred as evidenced by the persistence of ^{199}Hg satellites ($J = 290$ Hz) about the benzylic resonance (τ 6.70), and the similarity of these parameters to those found for benzylmercuric acetate in chloroform [$J = 274$ Hz and $\tau(CH_2) = 6.80$]. Thus the order of reactivity is allylmercuric acetate ≫ dibenzylmercury > benzylmercuric acetate, which is the established order of electrophilic (protic) cleavage of C–Hg bonds[12,13]. The very high rate of reaction for the allyl compound suggests that it reacts by a mechanism peculiarly available to it. This would seem most likely to be either (VII) or (VIII) and is in line with rearrangements accompanying acid cleavage of allylmercury compounds[13].



(VII)



(VIII)

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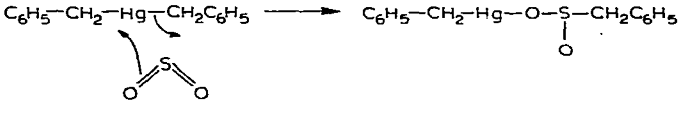
* We are grateful to Dr. G. Deacon and Mr. P. Felder of Monash University, Victoria, Australia, for obtaining this information for us.

** These absorption positions agree quite well with those reported in ref. 1 for Nujol mulls and bromoform solutions.

*** Much information on the position of S–O stretching bands has recently become available, and the above values fall nicely within the range for *O*-sulfinates. See ref. 3 for a concise coverage.

**** For an example of this type in sulfinate esters see ref. 10; see also ref. 11.

Evidence recently reported[7] strongly favours type (VII) for insertion into allylstannanes, but in the mercury case, the insertion product of crotylmercuric acetate[4,13] is very insoluble and highly unstable, so that a rearrangement path could not be confirmed. (VII) and (VIII) may be designated $S_E i'$ cleavages*, and correspond to formation of *O*- and *S*-sulfinato products respectively. Similarly (IX) would seem the best description for the dibenzylmercury case ($S_E i$).


(IX)

Recent data[3] are in line with these mechanistic suggestions. For example, sulfur dioxide appears to insert preferentially into the *p*-tolyl–mercury bond of phenyl-*p*-tolylmercury, and no reaction was observed with phenylmercuric chloride, bis(pentafluorophenyl)mercury and bis(pentachlorophenyl)mercury, which are highly deactivated as regards electrophilic carbon–mercury cleavage.

The very rapid insertion into allylic tin[7], lead[15] and mercury systems, suggests that care is required in the use of liquid SO_2 as a solvent for studies of fluxional σ-cyclopentadienyl and related metal systems.

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* In all cases reported the rates of $S_E i'$ en S_E' cleavages of carbon-metal bonds are much faster than the corresponding $S_E 2$ or $S_E i$ processes; see refs. 13 and 14.