Methylation of Mercury by Common Nuclear Magnetic Resonance Reference Compounds

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Summary Inorganic mercury salts are methylated, in aqueous solution, by trimethylsilyl salts commonly used as n.m.r. reference compounds.

DURING a study[1] of the chemical methylation of mercury by methylcobalamin (vitamin B_{12}), a new, unusual, and interesting reaction was observed. The formation of MeHgOAc was observed *via* n.m.r. spectroscopy to occur with a control sample of aquocobalamin, presumably containing no transferrable methyl groups. This implicated the n.m.r. reference compound sodium 3-trimethylsilypropionate (TSP) which proved to be reacting very readily with mercury(II) acetate, quantitatively yielding MeHgOAc [$\delta \approx 1{\cdot}0$ p.p.m.; J (^{199}Hg–^{1}H) *ca.* 240 Hz]. A similar reaction was also observed with sodium 2,2-dimethyl-2-silapentane-5-sulphonate (DSS) (Figure). The reaction of DSS with mercury(II) acetate may be formulated as in (1).

$$\mathrm{Me_3Si[CH_2]_3SO_3Na + Hg(OAc)_2 \rightarrow [CH_3]_2Si(OAc)[CH_2]_3SO_3Na + MeHgOAc} \quad (1)$$

It is clear that care must be taken when using these water-soluble trimethylsilyl derivatives. Unexpected reactions may occur to produce spurious sharp resonances easily mistaken for the intended reference. Mercury-containing solutions should not be left in contact with these references for longer than absolutely necessary, if at all. The methyl resonance due to 'demethylated DSS,' presumably the dimethylsilyl salt containing the anion of the mercury(II) salt co-ordinated to silicon, occurs at 0·15 p.p.m. downfield from DSS.

It is unusual and surprising that this reaction occurs upon simply mixing two water-soluble salts at room temperature, *i.e.*, under very mild conditions. Previous reactions[2,3] which are most similar to those reported here involve exchange between alkylsilanes and dialkylmercurials or between silylmercurials and alkyl mercury(II) halides. Much more vigorous conditions are required,

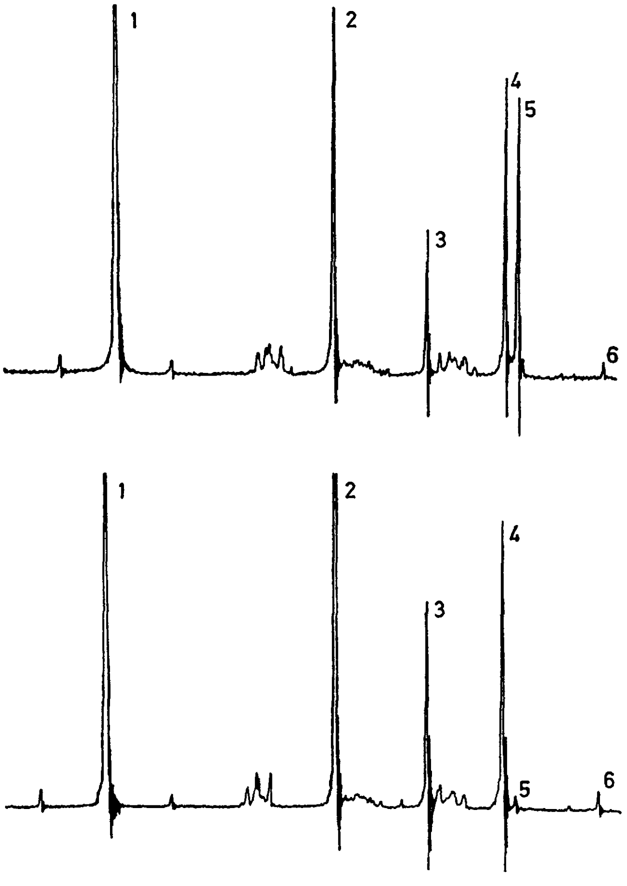

FIGURE. 60MHz *N.m.r. spectra: upper trace:* $\mathrm{Hg(OAc)_2 + DSS}$ *in* $\mathrm{D_2O}$ 10 *min after mixing. Lower trace: same, after* 1 *h.* (1) HOD. (2) $\mathrm{MeCO_2^-}$. (3) MeHgOAc. (4) 'Demethylated' DSS. (5) DSS. (6) ^{199}Hg satellite of MeHgOAc.

however, and even in these cases a direct transfer of an alkyl group from silicon to mercury is not observed. Further, other metal salts which might undergo similar reactions, $TlNO_3$, $Pb(NO_3)_2$, $Pb(OAc)_2$, $Cd(OAc)_2$, $Zn(OAc)_2$, and $SnCl_2$, do not seem to react at all under these conditions.

In aqueous solution, mercury(II) nitrate reacts much more rapidly than mercury(II) acetate. In methanol–water the rates are slower and increase in the order $HgCl_2 << Hg(OAc)_2 < Hg(NO_3)_2$. (The length of time needed for a reaction to go to completion upon mixing equimolar concentrations of reactants is taken as a qualitative measure of relative reaction rates.) This is as would be expected if the methyl group were abstracted as a carbanion, Me^-, the rate being determined by the Lewis acidity of the attacking mercury(II) species. In methanol, however, only $Hg(NO_3)_2$ reacts, indicating that solvent polarity may be significant in determining the effective Lewis acidity of the mercury(II) salt and its ability to demethylate silicon. A possible mechanism might involve the SO_3 or CO_2 group acting intramolecularly as Lewis bases to weaken the Si–C bond, enabling abstraction by the mercury(II) species. However, as with DSS, tetramethylsilane in methanol reacts only with $Hg(NO_3)_2$, at about the same rate. This does not preclude the above possibility, but it does not seem a very likely mechanism.

Finally, integration of mercury- and silicon-bound methyl n.m.r. resonances shows reaction of DSS and $Hg(OAc)_2$ in aqueous solution results in transfer of only one methyl group from silicon to mercury. The acetate methyl resonances of both products are accidentally degenerate; however when MeHgOAc is extracted into $CHCl_3$, the other product can be readily isolated and integration of the n.m.r. resonances shows two silicon-bound methyl groups for each acetate methyl group, indicating that the acetate group is bonded to silicon. The reaction with $Hg(NO_3)_2$, as opposed to that with $Hg(OAc)_2$, goes to completion, with all three methyl groups being removed from silicon, apparently as a result of two effects: the acetate deactivates the silicon to further attack more effectively than the nitrate, a much poorer co-ordinating group, and, secondly, acid catalysis is likely to be involved since $Hg(NO_3)_2$ gives a more acidic solution than $Hg(OAc)_2$. Addition of $HClO_4$ to lower the pH of the acetate solution brings about further reaction, but still not the complete reaction observed with $Hg(NO_3)_2$. Similarly reaction of $Hg(NO_3)_2$ with TMS produces more than one product.

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