Insertion of Sulphur Trioxide into the Metal–Carbon Bond of Dimethylmercury

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Summary The reaction between dimethylmercury and sulphur trioxide in methylene chloride solution gives methylmercuric methanesulphonate, and upon further addition of sulphur trioxide, a soluble product in which one mercury–carbon bond remains intact.

ALTHOUGH much work has been done on insertion reactions of sulphur dioxide with organometallic compounds, almost the only reports of similar reactions of sulphur trioxide have been of insertions into the bonds between carbon and other elements of main-Group IV.[1–3] Otto[4] reported that sulphur trioxide reacted violently with diphenylmercury, cleaving both mercury–carbon bonds to yield mercuric benzenesulphonate.

We found that when equimolar amounts of sulphur trioxide and dimethylmercury, in methylene chloride solution at $-70°$, were mixed, a white precipitate, of composition $C_2H_6SO_3Hg$, was formed immediately in an exothermic reaction. By removal of most of the solvent, the product was obtained in almost quantitative yield. The precipitate was identified as methylmercuric methanesulphonate, $MeHgOSO_2Me$ (I) as follows. The product was soluble in water, and reacted with sodium chloride in aqueous solution to give a precipitate of methylmercuric chloride, and sodium methanesulphonate by evaporation of the supernatant liquid. The i.r.† and n.m.r. spectra and X-ray powder diffraction pattern were identical with those of an authentic sample of (I) prepared by the reaction of silver methanesulphonate and methylmercuric chloride in aqueous methanol solution. The ^1H n.m.r. spectrum consisted of a singlet at τ 8·92 (D_2O) or 8·73 (CH_2Cl_2) accompanied by small, symmetrically placed satellites, and a singlet of equal intensity at τ 7·22 (D_2O) or 7·08 (CH_2Cl_2). The high-field peak is assigned to the methyl group bonded to mercury, and the satellites to ^1H–^{199}Hg coupling (J = 238 Hz). The low-field peak is assigned to the methanesulphonate methyl group.

Upon the slow addition of a solution of sulphur trioxide to a solution of dimethylmercury in methylene chloride, to a mole ratio $SO_3 : Me_2Hg = 2{\cdot}0$, at $-70°$, the precipitate initially formed was redissolved. The n.m.r. spectrum of the resulting solution again consisted of two singlets of equal intensity, one (τ 8·62) with ^{199}Hg satellites (J = 259 Hz), the other at τ 6·77. Thus addition of the second SO_3 group did not result in cleavage of the remaining C–Hg bond. We suggest that the product is methylmercuric methanedisulphonate, $MeHgS_2O_6Me$ (II) since Robinson and Silberberg[5] have shown that methanedisulphonic acid, MeS_2O_6H, is formed by the addition of sulphur trioxide to methanesulphonic acid, and observed a similar downfield shift in the methyl proton resonance upon its formation. Attempts to isolate (II) by removal of solvent under vacuum resulted in the loss of some sulphur trioxide, leaving a light brown oil of uncertain composition.

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† The complete i.r. and Raman spectra have been obtained and may be assigned on the basis of the postulated structure.