

## Insertion of Sulphur Dioxide into a Tin-Carbon Bond

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THE study of insertion reactions has recently become a topic of considerable interest in organo-metallic chemistry. A large variety of addends has been found to insert into tin-nitrogen and tin-oxygen bonds,<sup>1</sup> while olefins have been inserted

into metal-metal bonds,<sup>2</sup> and carbon monoxide and sulphur dioxide into transition metal-carbon bonds.<sup>3</sup> The whole range of insertion reactions has recently been reviewed.<sup>4</sup>

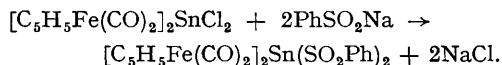
In an attempt to insert sulphur dioxide into a

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tin-iron bond as part of a general study of tin-iron compounds,<sup>5</sup> we found that sulphur dioxide will insert into a tin-carbon bond. This appears to be the first insertion of sulphur dioxide into a tin-carbon bond and provides a new method for forming carbon-sulphur bonds.

The compound  $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{Sn}(\text{SO}_2\text{Ph})_2$  was obtained as orange-yellow crystals in 70% yield by passing sulphur dioxide into bis-( $\pi$ -cyclopentadienyldicarbonyliron)diphenyltin in benzene at room temperature. The product has  $\nu(\text{C}=\text{O})$  at 2020, 2000, 1941, and 1919  $\text{cm}^{-1}$ , probable  $\nu(\text{S}-\text{O})^{\text{sb}}$  at 1103 and 1088  $\text{cm}^{-1}$ , probable  $\nu(\text{S}=\text{O})^{\text{e}}$  at 869 and 853  $\text{cm}^{-1}$ , and  $^1\text{H}$  resonances at  $\tau$  2.27 (complex) and 4.82 (singlet) of equal intensity.

The structure of the insertion product was confirmed by an independent synthesis from bis-( $\pi$ -cyclopentadienyldicarbonyliron)dichlorotin and sodium benzenesulphinate in methanol:



The insertion product could have a C-S-Sn or a C-S-O-Sn bond system. It has recently been

found that insertion of carbonyl sulphide into a tin-nitrogen bond gives a tin-sulphur rather than a tin-oxygen bond.<sup>7</sup> The application of the hard-soft acid-base concept<sup>8</sup> would also favour the formation of Sn-S rather than Sn-O-S bonds. Finally, the reaction of sodium benzenesulphinate with organic halides gives compounds containing only carbon-sulphur bonds.<sup>9</sup> The presence of bands at 869 and 853  $\text{cm}^{-1}$ , however, indicates that the compound contains  $\text{PhS}(\text{O})\text{OSn}$  groupings. Professor Bryan has now carried out a full X-ray crystallographic study<sup>10</sup> which shows unambiguously that sulphur dioxide inserts into the phenyl-tin bonds to give a compound containing C-S(O)-O-Sn units.

H. C. Clark and N. A. D. Carey<sup>11</sup> have reported some reactions of organometallic compounds with liquid sulphur dioxide. Their interpretations of their results indicate insertion of  $\text{SO}_2$  into Sn-Sn and Sn-Mn bonds. We found no evidence of insertion into Sn-Fe bonds.

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