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THE REVERSAL OF SULPHUR DIOXIDE INSERTION INTO METAL-CARBON BONDS

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There have been several recent reports of the preparation of sulphinato complexes by insertion of sulphur dioxide into metal-carbon bonds (1-7). Although the formation of metal-carbon bonds by sulphur dioxide elimination reactions of metal sulphinate complexes is also known (8, 9), attempts to reverse the sulphur dioxide insertion reactions have so far proved unsuccessful (2,3,5). In particular, the compounds $EtHg(SO_2Et)$ and $PhCH_2Hg(SO_2CH_2Ph)$, prepared by reaction of sulphur dioxide and diethyl- or dibenzyl-mercury, do not lose sulphur dioxide on ultraviolet irradiation or on heating in dioxane (3). We now report that two sulphinato complexes, which can be prepared by sulphur dioxide insertion, decompose on heating by the reverse of the formation reaction.

Phenylmercuric benzenesulphinate can be prepared by reaction of diphenylmercury and liquid sulphur dioxide (3,7), and exists as two linkage isomers, the S-sulphinate and the O-sulphinate (7). On heating either isomer under vacuum, sulphur dioxide elimination occurs and diphenylmercury sublimes from the reaction mixture in high yield (Table). When the decompositions are carried out at atmospheric pressure, a more complex reaction occurs. Mercury is formed, and diphenylmercury is obtained in lower yield. There is no evidence for interconversion of the isomers prior to loss of sulphur dioxide. Each isomer is recovered after heating to just below the decomposition temperature. Reaction of di-p-tolymercury and liquid sulphur dioxide yields p-tolylmercuric p-toluenesulphinate [previously obtained from reaction of di-p-tolyl-

TABLE

Desulphonylation Reactions of some Sulphinato Complexes

Complex	Reaction Conditions	Reaction Temperature (°C)	Product	Yield (%)
O-$\mathrm{PhHg(SO_2Ph)}$	a	110	$\mathrm{Ph_2Hg}$	88
	b	125	$\mathrm{Ph_2Hg}$	44
S-$\mathrm{PhHg(SO_2Ph)}$	a	115	$\mathrm{Ph_2Hg}$	91
	b	125	$\mathrm{Ph_2Hg}$	45
p-$\mathrm{MeC_6H_4Hg(SO_2}$-*p*-$\mathrm{MeC_6H_4)}$	a	155-170	(*p*-$\mathrm{MeC_6H_4)_2Hg}$	85
$\mathrm{PhHg(SO_2}$-*p*-$\mathrm{MeC_6H_4)}$	a	120	PhHg-*p*-$\mathrm{MeC_6H_4}$	91
p-$\mathrm{MeC_6H_4Hg(SO_2Ph)}$	a	130	PhHg-*p*-$\mathrm{MeC_6H_4}$	66

a Heated under vacuum in a sublimator until no further sublimate collected.

b Heated at atmospheric pressure until gas evolution ceased, the product being recovered by hexane extraction of the reaction mixture.

mercury with mercuric *p*-toluenesulphinate (7)]. This compound also eliminates sulphur dioxide on heating, di-*p*-tolylmercury being formed (Table). The mercurials were identified by their melting points and infrared spectra, and the liberated sulphur dioxide by its infrared spectrum.

Phenyl-*p*-tolylmercury can also be prepared by sulphur dioxide elimination reactions. Decomposition of either phenylmercuric *p*-toluenesulphinate or *p*-tolylmercuric benzenesulphinate, prepared by reaction of the appropriate diarylmercurial and mercuric arenesulphinate (7), gives phenyl-*p*-tolylmercury in good yield (Table). The compound was obtained analytically pure on sublimation, and the absence of diphenyl- or di-*p*-tolyl- mercury in the product was established by X-ray powder photography.

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