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MERCURIC ACETATE CLEAVAGE OF SULFUR-DONOR LIGAND ORTHO-METALATED COMPLEXES

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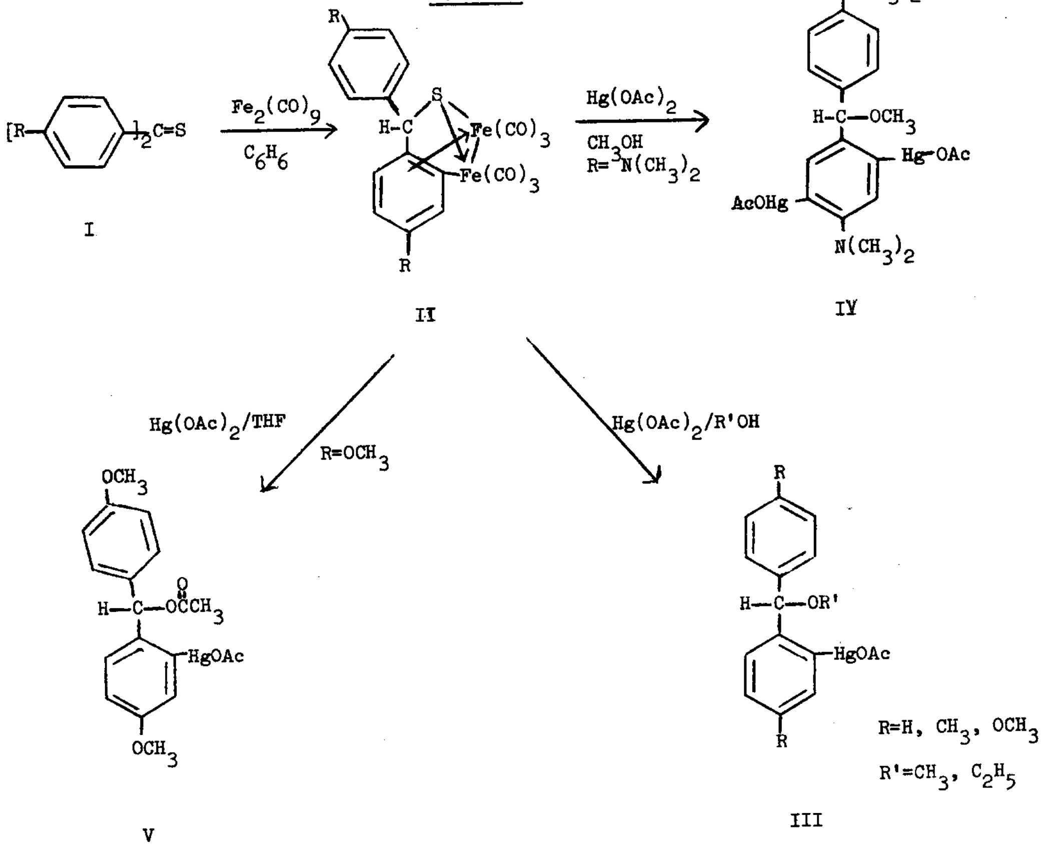
Treatment of thiobenzophenones [I - Scheme 1] with diiron enneacarbonyl at room temperature gives sulfur-donor ligand ortho-metalated complexes [II] in very good yields.[1] Isobenzothiophene derivatives were obtained by oxidative or photolytic cleavage of II. We now wish to report that cleavage of II by mercuric acetate results in ortho-mercuration. In addition, desulfurization occurs to give ethers, or esters, subject to the reaction conditions.

Exposure of II, R=CH_3, OCH_3, H, to mercuric acetate in dry methanol [5-6:1 mole ratio of $Hg(OAc)_2$: II] for 24 hr. at room temperature gave the corresponding methyl ethers III, R'=CH_3, in 36-68% yield. The ethoxy analog, III, R'=C_2H_5, was obtained in reasonable yield when ethanol was employed as the solvent. The yields and melting points for these new compounds are listed in Table I. When the dimethylamino substituted complex II,R=$N(CH_3)_2$, was used as reactant, mercuration occurred ortho to the benzylic carbon atom and to one of the dimethylamino groups to give IV.

In an aprotic solvent such as tetrahydrofuran (THF), mercuric acetate cleavage gave the acetate in good yield. Therefore, ortho-metalation and subsequent mercuric acetate treatment enables one to convert a thione function to an ether or an ester, and to effect ortho-mercuration, in generally good overall yield. Since the mercuric acetate group can be readily displaced by a variety of functionalities (e.g., halogen)[2], the described cleavage reaction of II thus provides an entry into aromatics difficult or impossible to obtain by other means.

Scheme 1



Scheme 2

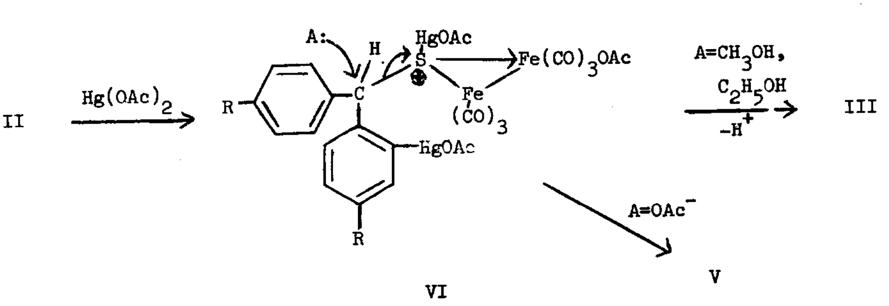


TABLE I

Products Obtained from Reaction of II with Mercuric Acetate

II,R=	Solvent	Product[a]	Yield (%)[b]	Mp(°C)
OCH_3	CH_3OH	III,R=OCH_3R'=CH_3	59	73-74
CH_3[c]	CH_3OH	III,R=R'=CH_3	36	114.5-115.0
H	CH_3OH	III,R=H,R'=CH_3	68	oil
OCH_3	C_2H_5OH	III,R=OCH_3,R'=C_2H_5	69	oil
$N(CH_3)_2$	CH_3OH	IV	39	95-98
OCH_3	THF	V	81	41-45

[a] Products were characterized by elemental analyses, and on the basis of infrared, nuclear magnetic resonance, and mass spectral results. [b] Yields are of pure materials. [c] Prepared from 4,4'-dimethylthiobenzophenone and $Fe_2(CO)_9$, m.p.104°C(dec.).

A possible pathway for these reactions is outlined in Scheme 2. Mercuric acetate probably serves two functions in reaction with II - cleavage of the carbon-iron sigma bond and mercuration at sulfur to give VI. In an alcohol solvent, attack by the solvent at the benzylic carbon of VI, and subsequent proton loss, would afford the ether. In THF, the ester would result from attack of acetate ion on VI.

The following procedure is typical for the mercuric acetate reactions. A mixture of II,R=OCH_3[2.05g.,3.8mmol] and mercuric acetate [6.88g.,21.6mmol] in dry methanol [60ml.] was stirred at room temperature for 24 hr. under a blanket of nitrogen. The solution was filtered, and the filtrate was flash evaporated (~30 mm.). The residue obtained from evaporation was treated with benzene (100-150 ml.), filtered, and flash evaporation of the filtrate gave an oil which was crystallized from carbon tetrachloride-hexane. Recrystallization from carbon tetrachloride-hexane afforded 1.15g. (59%) of pure III,R=OCH_3,R'=CH_3.

ACKNOWLEDGMENTS

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