

REACTION OF DI-IRON ENNEACARBONYL WITH *N*-SULPHINYLPHENYLHYDRAZINE

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(Received March 19th, 1980)

Summary

When *N*-sulphinylphenylhydrazine is reacted with $\text{Fe}_2(\text{CO})_9$ in benzene at room temperature, $[\text{Fe}(\text{CO})_3\text{SPh}]_2$ and thiophenol are produced.

Introduction

When *N*-sulphinyl aniline, $\text{PhN}=\text{S}=\text{O}$, was heated [1] with $\text{Fe}_2(\text{CO})_9$ in benzene for three hours at 40–45°C, $\text{Fe}_2(\text{CO})_6\text{PhNS}$ was produced in 1.6% yield. Sulphurdiimines, $\text{R}-\text{N}=\text{S}=\text{N}-\text{R}$, reacted [2] with $\text{Fe}_2(\text{CO})_9$ split across one or two $\text{N}=\text{S}$ bonds giving complexes containing $\text{R}-\text{NS}$, $\text{R}-\text{N}$ and S fragments. These results prompt us to report the reaction of $\text{Fe}_2(\text{CO})_9$ with *N*-sulphinylphenylhydrazine, $\text{Ph}-\text{NH}-\text{N}=\text{S}=\text{O}$, a related cumulated bond system.

Experimental

To 1.5 g (4.1 mmol) of $\text{Fe}_2(\text{CO})_9$ in 30 ml of sodium dried benzene was added 0.75 g (4.2 mmol) of PhNHNSO in 20 ml of dry benzene under a nitrogen atmosphere and with constant stirring at room temperature. After seven hours stirring, the reaction mixture had changed from yellow to very dark red; however, unreacted $\text{Fe}_2(\text{CO})_9$ was still present.

The reaction was continued for a further twelve hours, at which stage all $\text{Fe}_2(\text{CO})_9$ had disappeared. A reddish oil, obtained after vacuum distillation, was dissolved in *n*-hexane, passed down a silica gel column and eluted with *n*-hexane. The red chromatographic band crystallized out as a red solid, yield 76 mg (3.7%), elemental analysis corresponding to $[\text{Fe}(\text{CO})_3\text{SPh}]_2$. Thiophenol was also isolated.

Discussion

In *n*-heptane, the infrared spectrum of this red solid showed four carbonyl peaks at 2077m, 2040vs, 2008s and 2001s cm^{-1} . The band profile was identical

to that of the sulphur bridged binuclear complex, $[\text{Fe}(\text{CO})_3\text{SPh}]_2$, previously prepared by [3] the reaction of refluxing thiophenol with iron carbonyl under nitrogen ($\nu(\text{CO})$ 2078, 2041, 2009, 2001 cm^{-1} in CCl_4).

The reaction mechanism for our products is not yet clear. It presumably involves initial addition across the $\text{N}=\text{S}$ band of *N*-sulphinylphenylhydrazine, followed by rearrangements. However, the sodium salt of thiophenol has been obtained previously [4] when *N*-sulphinylphenylhydrazine was reacted with sodium.

References

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