Intermediate Compound in the Decomplexation of a Tricarbonyl Iron Complex Using Trimethylamine Oxide

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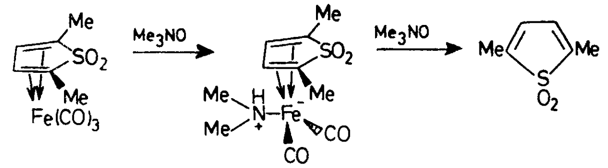
Summary In the decomplexation reaction of the tricarbonyl iron complex of 2,5-dimethylthiophen *SS*-dioxide by trimethylamine oxide in an aprotic solvent an intermediate containing a protonated dimethylamino-ligand has been isolated and identified.

The use of trimethylamine oxide as a mild and general reagent for decomplexing organic ligands from iron carbonyls has recently been demonstrated by Shvo and Hazum.[1] Under appropriate conditions and with suitable substrates this reagent can also be used to promote complexation reactions with pentacarbonyl iron.[2]

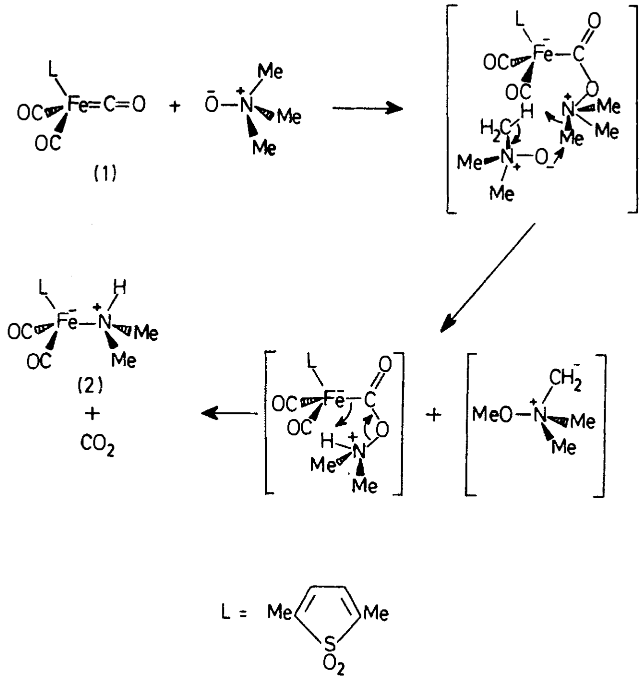


(1) (2) (3)

Scheme 1

We have intercepted and isolated a partially decomplexed compound from the reaction of Me_3NO with the tricarbonyl iron complex of 2,5-dimethylthiophen *SS*-dioxide (**1**), the structure of which sheds light on the mechanism of release of the iron carbonyl. When (**1**)[3] is treated with a four-fold excess of Me_3NO in benzene at 40 °C for 20 h (**2**) is obtained in 62 mol % yield (based on consumed starting material determined by n.m.r. spectroscopy) (Scheme 1). Addition of another four-fold excess of Me_3NO at the same temperature causes the conversion of (**2**), almost quantitatively, into 2,5-dimethylthiophen *SS*-dioxide (**3**) and inorganic products.

The structure of (**2**) was established from the following spectral data. ^1H N.m.r. spectrum: δ ($CDCl_3$, 40 °C) 4·47 (2H, s, H-3 and H-4), 2·71 (6H, d, *J* 6 Hz, NMe_2), and 1·68 (6H, s, 2×Me);† ^{13}C n.m.r. spectrum: δ ($CHCl_3$, 30 °C, relative to Me_4Si) 209·0 (s, CO), 73·4 (d, *J* 188·7 Hz, C-3 and C-4), 69·0 (s, ring C-2 and C-5), 48·7 (q, *J* 133·5 Hz, NMe_2), and 7·6 (q, *J* 129·9 Hz, 2- and 5-Me) p.p.m.; ν (Nujol) 3290sh (NH, indicating that there is no hydrogen bridge to the sulphone group),‡ 2090, 2000, 1940—1920 (CO), and 1160 (SO_2) cm^{-1}; and *m/e* 301·007 (M^+), calc. for $C_{10}H_{15}FeNO_4S$ 301·007. These data establish beyond doubt the proposed structure (**2**). In the ^{13}C n.m.r. spectrum, the carbonyl absorptions remain a singlet at −100 °C suggesting that these are in the equatorial position and that the $NHMe_2$ substituent is axial;[4] this agrees with earlier findings.[5] A possible mechanism leading to the formation of (**2**) is shown in Scheme 2 which is an extension of mechanisms suggested by other workers.[6]



Scheme 2

This investigation was supported by the Netherlands Foundation for Chemical Research (S.O.N.) with financial aid from the Netherlands Organization for the Advancement of Pure Science (Z.W.O.).

(*Received*, 24*th May* 1976; *Com.* 585.)

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† The strongly coupled nitrogen bound proton cannot be resolved even on proton decoupling.

‡ It has not been demonstrated conclusively that the sulphone and dimethylamino-groups are oriented *anti* as indicated in the drawing for (**2**).

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