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Preliminary communication

THE REACTION OF SALTS OF THALLIUM(III) WITH TRICARBONYL(CYCLOHEXA-1,3-DIENE)IRON

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Summary

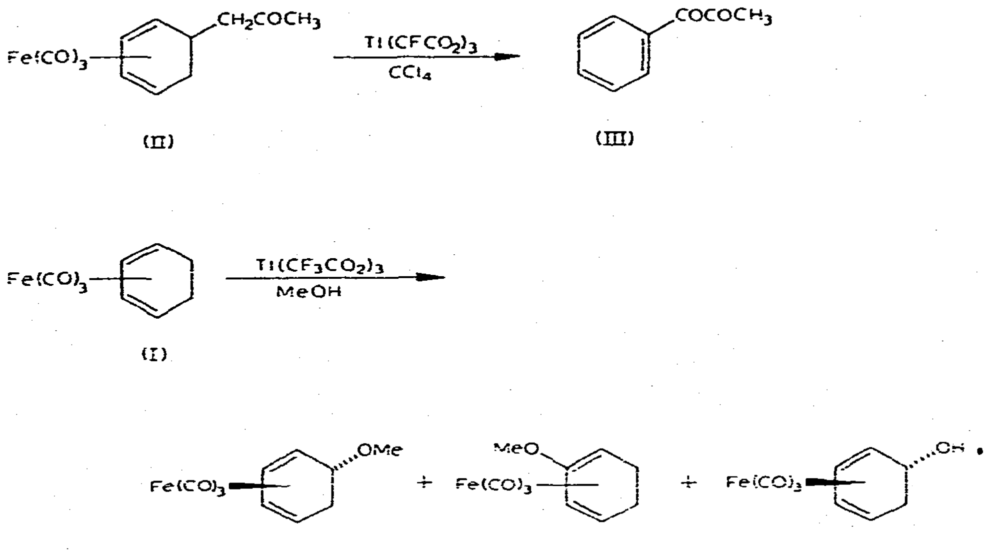
Reactions initiated by electrophilic attack of thallium(III) salts on tricarbonyl(cyclohexa-1,3-diene)iron in methanol are described.

Electrophilic substitution reactions of tricarbonyl(cyclohexa-1,3-diene)iron (I) have received scant attention, reaction of I with deuterons [1] and acetyl cations [2] being the only reported examples. Thallium(III) salts are powerful electrophiles [3], and we report below the reaction of such salts with I.

Thallium(III) trifluoroacetate was used by Birch [4] to oxidatively cleave the iron carbonyl moiety from tricarbonyl(5-acetonylcyclohexa-1,3-diene)iron (II) (Scheme 1). However, the organic ligand was also oxidised, yielding 1-phenylpropan-1,2-dione (III). Indeed, when I was refluxed in carbon tetrachloride with thallium(III) trifluoroacetate, benzene was the main product, together with lesser amounts of cyclohexa-1,3-diene.

However, when the reaction is carried out in a polar solvent, a more useful reaction occurs. Thus when a methanol solution of I was added to a well stirred solution of thallium(III) trifluoroacetate in methanol under dinitrogen, there was immediate formation (TLC analysis) of tricarbonyl(5-*exo*-methoxycyclohexa-1,3-diene)iron (IV) and tricarbonyl(2-methoxycyclohexa-1,3-diene)iron (V) [5] (Scheme 1). Quenching the reaction with water, followed by ether extraction led to isolation of I (40%), IV (30%), V (5%), and tricarbonyl(5-*exo*-hydroxycyclohexa-1,3-diene)iron (VI) 25% [5]. Formation of VI is probably due to hydrolysis of IV on work up under the acidic conditions generated in the reaction, and could be suppressed by carrying out the reaction in the presence of base such as potassium carbonate [6].

Use of thallium(III) nitrate trihydrate or thallium(III) triacetate sesquihydrate led to a product distribution identical with that described above; the former reacted to the same extent as thallium (III) trifluoroacetate while the latter reacted to the extent of ~15%. This reflects the trend encountered in

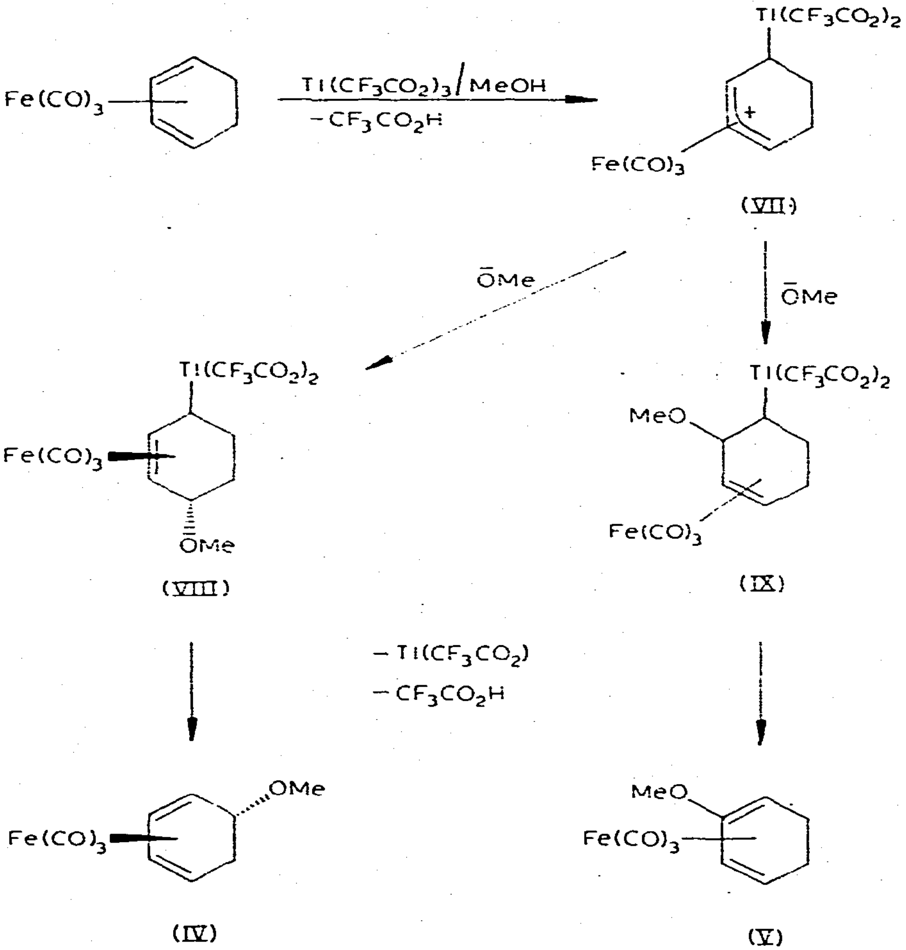


Scheme 1

other work [7]. The reaction mechanism is thought to be that depicted in Scheme 2. The initial step is formation of the expected intermediate for electrophilic substitution (VII), and then attack by methoxyl occurs at either C(1) or C(3) of the allyl cation, leading to VIII or IX, respectively. Elimination of [$HTl(CF_3CO_2)_2$] yields the observed products IV and V. Attack by methoxyl at C(1) in VII is almost certainly *exo* (with respect to $Fe(CO)_3$) since this is the orientation found in the product IV. However, the stereochemistry of addition of thallium(III) trifluoroacetate to I and methoxyl at C(3) in VII is not known. Some support for *exo* orientation of the thallium adduct comes from the fact that treatment of I with thallium(III) trifluoroacetate in ethanol results in formation of tricarbonyl(5-*exo*-ethoxycyclohexa-1,3-diene)iron [8] as the sole product, attack at C(3) in VII being inhibited by the increased bulk of the ethoxy anion. Furthermore, it seems plausible that the methoxy group in IX will also be *exo* since then the product V results from a *trans* elimination, and loss of *endo*-hydrogen from C(3) in VIII may well be metal assisted [1].

Previously it has been shown that reagents which are fast oxidising agents preferentially oxidise the organic ligand rather than the coordinated iron tricarbonyl [9]. This suggests, for the reaction of I in alcoholic solvents, that electrophilic attack by a thallium(III) species with subsequent nucleophilic quenching of the cationic intermediate VII is kinetically favoured over oxidation of the iron tricarbonyl moiety.

We are currently extending the reaction of thallium(III) salts to other coordinated diene systems in order to investigate the potential synthetic usefulness of the reaction.



Scheme 2

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