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REACTION OF TRICARBONYLCYCLOHEXADIENEIRON COMPLEXES WITH CUPRIC CHLORIDE

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Summary

Ethanolic cupric chloride is a useful reagent for the efficient removal of the $Fe(CO)_3$ group from a variety of tricarbonylcyclohexadieneiron complexes. In one case removal of the $Fe(CO)_3$ group is accompanied by chlorination of the organic ligand.

Introduction

An essential step in organic synthesis using $Fe(CO)_3$ complexes is the efficient removal of the $Fe(CO)_3$ group under mild conditions. A variety of reagents have been described [1], the best of which appears to be Me_3NO [2]. We describe in this paper the liberation of the organic ligand from $Fe(CO)_3$ complexes using $CuCl_2$ under mild conditions.

Results and discussion

During our work on cyclohexadiene—$Fe(CO)_3$ complexes we found that the $Fe(CO)_3$ group could be removed from a variety of diene complexes under mild conditions using ethanolic cupric chloride to give the expected products e.g. II from I and IV from III.

One complex we were particularly interested in was V, since reaction of this complex with a variety of oxidising agents, including Me_3NO, gave a mixture of products none of which corresponded to the expected product. Reaction of complex V with $CuCl_2$, however, gave a single product in high yield which was identified as the chlorinated compound VI.

Although it could be envisaged that this product arose by a multi-step

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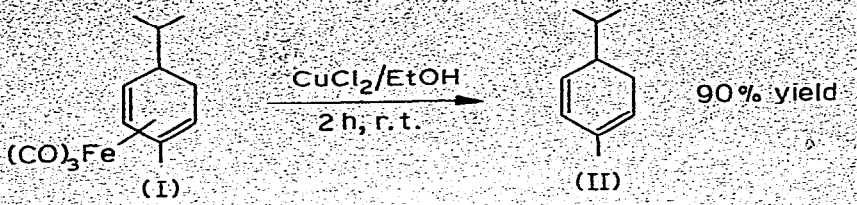
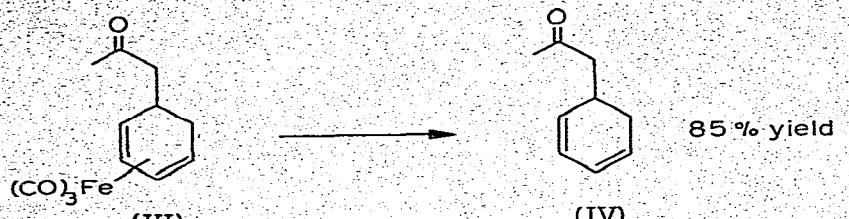


(I) (II)



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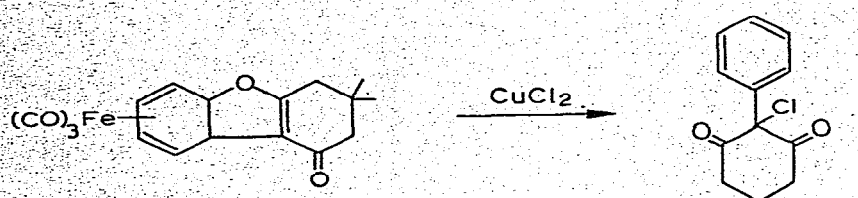

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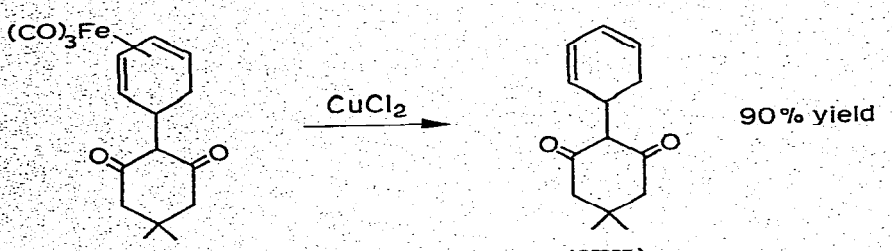
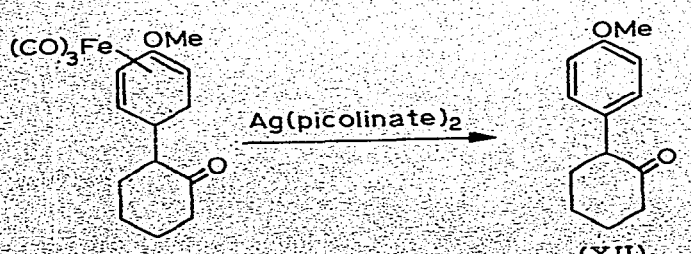


(VII) (VIII)

(IX) (X)



(XI) (XII)

mechanism, when the reaction was followed by thin layer chromatography only the starting material V and the product VI were observed. Furthermore, reaction of complex VII with $CuCl_2$ gave compound VIII as the only product.

Reaction of complexes of the type IX with $CuCl_2$ led to removal of the $Fe(CO)_3$ group but was usually followed by hydrolysis of the resulting enol ether to give compound X. This type of reaction has been observed before with other oxidising agents [1], but reaction of complex XI with silver picolinate gave compound XII in 25% yield.

Experimental

The complexes were synthesised as previously described [1,3].

Reaction of tricarbonyl-3,4,5a,9a-tetrahydro-3,3-dimethyldibenzofuran-1(2H)-oneiron (V) with cupric chloride

Complex V (0.2 g) [3] was stirred with a saturated solution of $CuCl_2$ in EtOH (40 ml) for 16 h. The mixture was poured into water and extracted with ether. The ethereal layer gave, after filtration through a plug of silica and removal of the solvent, 2-phenyl-2-chloro-5,5-dimethylcyclohexane-1,3-dione (VI) (80%), m.p. 103—105°C (Found: M^+, 252, 250. $C_{14}H_{15}O_2Cl$ calcd.: M^+, 252, 250). $\delta(CDCl_3)$ (ppm) 7.40 and 7.20 (5H, m), 2.76 (4H, s), 1.10 (3H, s) and 0.94 (3H, s). $\nu_{max.}$ ($CHCl_3$) 1790 and 1740 cm^{-1}.

Reaction of tricarbonyl-5-(2-oxocyclohexyl)-2-methoxycyclohexa-1,3-dieneiron (XI) with silver picolinate

Complex XI (0.2 g) [1] and silver picolinate (1 g) [4] in aqueous DMSO were stirred at 40°C for 15 min. The solution was filtered and the precipitate washed with water then ether. The two layers were separated and the ethereal layer washed with water. The ethereal layer gave, after chromatography (silica/$CHCl_3$), 2-(4-methoxyphenyl)cyclohexanone (XII), m.p. 86—88°C (lit. [5] 89°C), $\delta(CDCl_3)$ (ppm) 7.12 (2H, d, J 8 Hz), 6.92 (2H, d, J 8 Hz), 3.78 (3H, s), 3.56 (1H, m) and 2.6—1.7 (8H, m).

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