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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 Me₃NO [2]. We describe in this paper the liberation of the organic ligand from Fe(CO)₃ complexes using CuCl₂ 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 Me₃NO, gave a mixture of products none of which corresponded to the expected product. Reaction of complex V with CuCl₂, 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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$$\frac{\text{Cucl}_2/\text{EtOH}}{2 \, h_i \, \text{r.t.}} = 90 \% \text{ yield}$$

$$(CO)_3 \text{Fe} \qquad \qquad (II) \qquad (II)$$

$$(CO)_3 \text{Fe} \qquad \qquad (IV)$$

$$(CO)_3 \text{Fe} \qquad \qquad (V) \qquad (VVI)$$

$$(CO)_3 \text{Fe} \qquad \qquad (VVI)$$

$$(CO)_3 \text{Fe} \qquad \qquad (VVII)$$

$$(CO)_3 \text{Fe} \qquad (VVII) \qquad (VVIII)$$

$$(CO)_3 \text{Fe} \qquad (VVII) \qquad (VVIII)$$

$$(CO)_3 \text{Fe} \qquad (VVIII) \qquad (VVIII)$$

$$(CO)_3 \text{Fe} \qquad (VVIII) \qquad (VVIII)$$

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$$(CO)_3 \text{Fe} \qquad (VVIII) \qquad (VVIII) \qquad (VVIII)$$

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 CuCl₂ gave compound VIII as the only product.

Reaction of complexes of the type IX with CuCl₂ 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 CuCl₂ 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). ν_{max} . (CHCl₃) 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/CHCl₃), 2-(4-methoxyphenyl)cyclohexanone (XII), m.p. 86–88°C (lit. [5] 89°C), δ (CDCl₃) (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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References

- 1 A.J. Birch, K.B. Chamberlain, M.A. Haas and D.J. Thompson, J. Chem. Soc. Perkin I, (1973) 1882.
- 2 Y. Shvo and E. Hazum, Chem. Commun., (1974) 336.
- 3 A.J. Birch, K.B. Chamberlain and D.J. Thompson, J. Chem. Soc. Perkin I, (1973) 1900.
- 4 T.G. Clarke, N.A. Hampson, J.B. Lee, J.R. Morley and B. Scanlon, Canad. J. Chem., 47 (1969) 1649.
- 5 E.R. Clark and J.G.B. Howes, J. Chem. Soc., (1956) 1152.