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Driven equilibria: a strategy for the regioconvergent preparation of tricarbonyl(η^5-cyclohexadienyl)iron(1 +) complexes by hydride abstraction

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Abstract

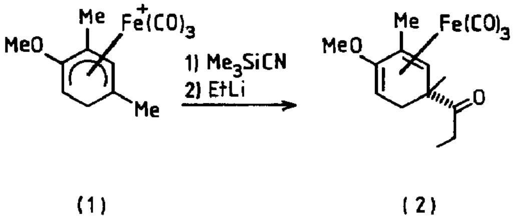
The regioconvergent preparation of a tricarbonyl(η^5-cyclohexadienyl)iron(1 +) complex has been achieved by hydride abstraction from an interconverting mixture of organometallic intermediates. The process is sensitive both to temperature and to reagent stoichiometries, with the best selectivity observed at higher temperatures, with moderate quantities of acid, and an excess of triphenylcarbenium tetrafluoroborate.

Introduction

Complexation of dienes by reaction with $Fe(CO)_5$, whilst a simple and convenient procedure, suffers from a major disadvantage, the formation of mixtures of regioisomers. This poses problems in the conversion of neutral η^4-diene complexes into the synthetically more important cationic η^5-dienyl complexes. Unless cumbersome separations are to be performed, special methods are needed, either to control the regiochemistry of complexation, or for the regioconvergent conversion of mixtures of diene complexes into a single dienyl complex. Acid-catalysed demethoxylation [1] has been particularly successful as a regioconvergent method, allowing a series of interconverting diene complexes to react in a single irreversible loss of OMe. In contrast, hydride abstraction, a common and complementary alternative to demethoxylation, lacks regiocontrol [2] and frequently produces mixtures of dienyl complexes. This paper describes an investigation of modified procedures for hydride abstraction by triphenylcarbenium ion reagents that seek to improve product ratios by use of a similar kinetic control approach, driving equilibrium reactions with a dominant, irreversible step. Previous attempts [3,4] at kinetic control in hydride abstractions have relied on the chemical *separation* of products through the exploitation of different rates of reaction. In such cases, the yield of the required product is limited by the proportion of its precursor in the mixture of substrate complexes.

By use of kinetic control to drive an equilibrium system, complete conversion of the substrate can be achieved, with products formed in a ratio determined by the relative rates of the steps in which they are produced. This product ratio reflects neither the ratio of starting materials arising from the complexation conditions, nor the equilibrium ratios of the products or starting materials themselves.

Recently we described preliminary work [5] in which the cationic dienyl complex **1** was converted into the ethyl ketone **2** in a series of model studies for organometallic routes towards the synthesis of biologically active tridachiapyrones such as tridachione (**3**). For this investigation, the dienyl complex **1** had been obtained [3] by selective partial conversion of a mixture of diene complexes, which necessarily resulted in a rather low yield, since only 40% of the substrate mixture was taken through to the required product. In contrast, treatment of the same mixture in strong concentrated acid promoted equilibration of the diene complexes and complete conversion in to a single demethoxylated cation (**8**). The objective of the present study was to examine milder conditions for the interconversion of diene complexes, performed in the presence of triphenylcarbenium tetrafluoroborate, in an attempt to improve the yield of complexes retaining the OMe substituent. By use of dilute acid and an excess of the triphenylcarbenium reagent, it has proved possible to promote the conversion of the majority of the starting material into the dienyl complex required for our synthetic programme. Our results indicate that the choice of stoichiometry and conditions is critical if regioconvergence is to be attained in work of this type.



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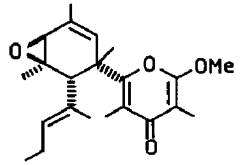
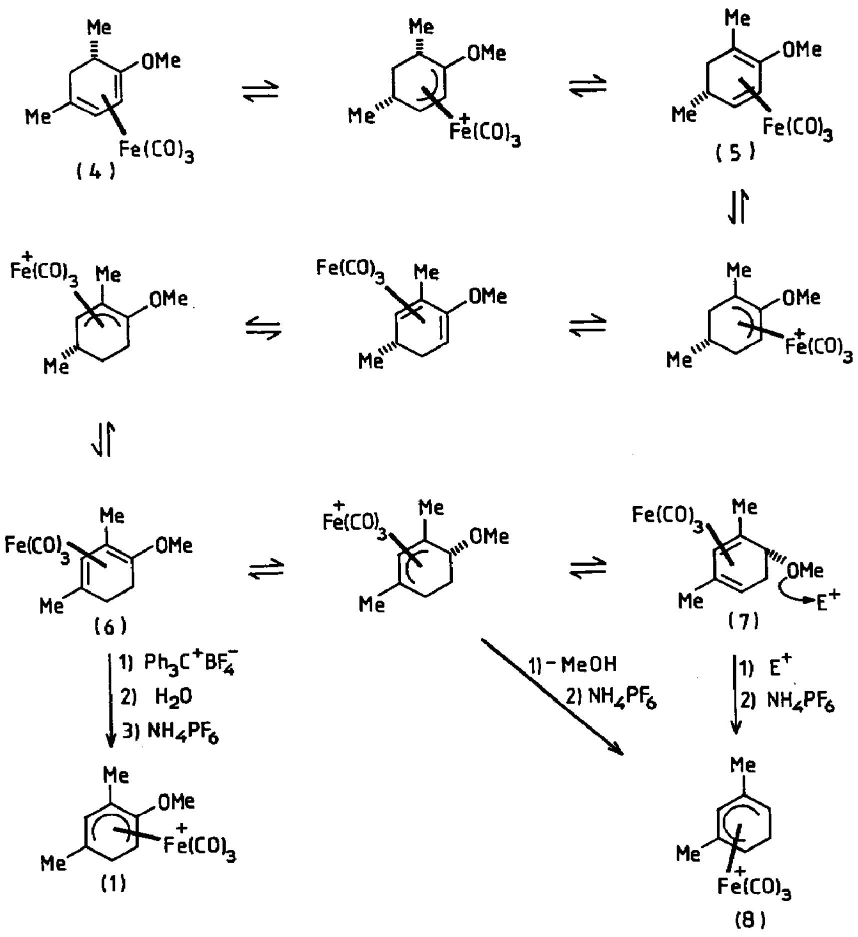


(3)

Results and discussion

The mixtures of complexes **4**, **5**, and **6** were prepared as previously described [3,5]. Hydride abstraction with triphenylcarbenium tetrafluoroborate can be performed under acid-free conditions by pre-treatment of the carbenium ion reagent with anhydrous potassium carbonate. Of the three complexes, only **6** can undergo hydride abstraction. The isomers **4** and **5** are inert because they carry α-methyl substituents. In this way the expected cation **1** was obtained in 24% yield based on the three complexes in the starting material, a result consistent with our previous experience with this reaction. Addition of a small quantity of HBF_4 had a marked effect on the yield of dienyl complexes. A 7/3 mixture of **1** and **8** (**8** is the known [3] product from acid-catalysed demethoxylation of **4**, **5**, and **6**) was obtained in 61% yield. This indicates an increase in the efficiency of production of **1** from 24 to 43%. This result can be accounted for in terms of an acid-catalysed isomerisation process involving interconversion of **4**, **5** and **6** via a series of allyl, and diene intermediates



Scheme 1. Interconversion of intermediates in acid.

[6*] (see Scheme 1). The isomer **6** is intercepted in the equilibrating mixture by the triphenylcarbenium reagent and converted by hydride abstraction into the salt **1**. Formation of **8** could arise either from the acid-catalysed demethoxylation reaction or by triphenylcarbenium ion mediated demethoxylation from **7**.

In order to investigate the relative importance of these two possibilities, the reaction was repeated with twice the quantity of the triphenylcarbenium ion reagent. If acid-catalysed demethoxylation were interfering, an improved yield of **1** would be expected under these conditions, since the relative contribution of hydride abstraction should be increased. In the event (entry 3), conversion into **1** was improved to 51% in a reaction that also showed improved selectivity, giving a 4/1 mixture of products. The improvement in yield of **1** from 43 to 51% by use of a greater excess of the hydride abstraction reagent suggests that hydride abstraction and *acid*-catalysed demethoxylation are in competition under the conditions used. Reaction with a four-fold excess of the triphenylcarbenium reagent further improved the selectivity

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* Reference number with asterisk indicates a note in the list of references.

for **1** to better than 95% (entry 4). Only traces of the minor product **8** could be seen in the high field ^{1}H NMR spectrum of the product.

Efficient conversion into **1** requires the conversion promoted by the triphenylcarbenium ion reagent to dominate the reaction. This should be easier to achieve at lower acid concentrations. A 25-fold reduction of the quantity of acid used (entry 5) did indeed improve the ratio of **1** and **8** from 4/1 to 19/1.

The effect of temperature on the reaction was also examined (entries 5, 6, and 7). When the reaction was performed under the same conditions but at 40 °C, a 93/7 ratio of products was obtained in 51% overall yield. Lowering the temperature further to room temperature gave the products in a poorer ratio of about 9/1, in a similar yield.

Finally, the use of a larger excess of the triphenylcarbenium reagent under the less acidic conditions was explored. No significant further improvement in product ratio was observed, (entries 5 and 8), a marked contrast to the results obtained at higher acid concentrations (entries 3 and 4).

Conclusions

Selectivity for the formation of **1** is best at higher temperatures. Reducing acid concentration also gives significant improvement in the product ratio. Under given conditions, selectivity can be improved to a limiting value of approximately 95/5 by increasing the concentration of the triphenylcarbenium ion reagent. This is consistent with a competition between rates of carbenium ion mediated salt formation and acid mediated salt formation. In order that the carbenium ion mediated reaction should dominate, a 2–4-fold excess of the reagent is required, depending on the quantity of acid used. Even under these conditions the formation of small amounts of demethoxylated products was observed. This may arise from some remaining, unselective, acid mediated reaction, or be due to demethoxylation by the triphenylcarbenium ion reagent itself. We have recently reported similar demethoxylation reactions of other complexes, promoted in this way by triphenylcarbenium hexafluorophosphate [7].

Table 1

Product ratios from hydride abstraction

Exp. no.	Equivalents $^+CPH_3$	HBF_4 (ml)	K_2CO_3 (g)	Temp.	Yield (%)	Ratio **1/8**
1	0.75	–	2	r.t.	24	100/0 [a]
2	1.00	0.5	–	Reflux	61	67/33
3	2.00	0.5	–	Reflux	66	78/22
4	4.00	0.5	–	Reflux	51	> 95/5
5	2.00	0.02	–	Reflux	54	95/5
6	2.00	0.02	–	40 °C	51	93/7
7	2.00	0.02	–	r.t.	52	88/12
8	4.00	0.02	–	Reflux	48	> 95/5

[a] No trace of **8** could be detected by ^{1}H NMR spectroscopy at 400 MHz.

Experimental

All reactions were performed under nitrogen. IR spectra were recorded with Perkin–Elmer 257 and 1720-X spectrometers. Routine NMR spectra were recorded with a JEOL PMX60 NMR spectrometer. All NMR spectra of mixtures in which product ratios were over 95/5 were measured at high field with a JEOL GX400 NMR spectrometer. Dichloromethane was distilled over calcium hydride under nitrogen. HBF_4 was used as an approximately 50% solution in diethyl ether. Petroleum ether refers to the fraction of b.p. 40–60 ° C, and ether refers to diethyl ether.

General procedure for the preparation of tricarbonyl(η^5-1-methoxy-2,4-dimethylcyclohexadienyl)iron(1 +) hexafluorophosphate(1 −) (1)

The mixture of complexes **4**, **5**, and **6** (2.0 g, 7 mmol) was stirred with triphenylcarbenium tetrafluoroborate (for quantity, see Table 1) in dichloromethane (30 ml) under a variety of conditions. The progress of the reaction was monitored by IR spectroscopy, completion being indicated by the absence of neutral carbonyl absorbances. The reaction solution was poured into ether (200 ml). The yellow precipitate was collected and heated with water (15 ml) on a steam bath for 15 min. The mixture was cooled and extracted with ether (2 × 25 ml), and the aqueous layer was added to a solution of ammonium hexafluorophosphate (1.5 g) in water (2 ml). The product was precipitated and collected from aqueous solution and purified by precipitation from acetone by addition of ether.

In the case of experiment 1, the triphenylcarbenium reagent was stirred with potassium carbonate (2 g) for 5 min before addition of the mixture of complexes.

Tricarbonyl(η^4-2,4-dimethylcyclohexa-2,4-dien-1-one)iron(0)

The ether extracts from the preparation of **1** were combined, dried over magnesium sulphate, and evaporated to afford the product, which was purified by chromatography on silica with petroleum ether/ether as eluent; (1/1 v/v) yield 0.13 g , 7%. (Found: C, 50.53; H, 3.91. $C_{11}H_{10}O_4Fe$ calc.: C, 50.42; H, 3.85%). ν_{max} 2057, 1996, 1985, 1686, and 1682 cm^{-1} (cyclohexane); δ(H) ($CDCl_3$), 1.50 (3H, s, C-4Me), 2.20 (3H, s, C-2Me); 2.36–2.52 (2H, t, H-6); 3.08–3.24 (1H, t, H-5); 5.78 (1H, d, H-3). m/z 262 (M^+).

Acknowledgements

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