

Preliminary communication

AN ORGANOMETALLIC ROUTE TO TETRAHYDROCARBAZOLONES

G. RICHARD STEPHENSON

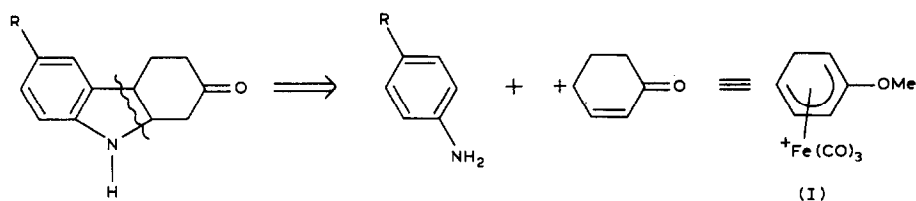
School of Chemical Sciences, University of East Anglia, Norwich, NR4 7TJ (Great Britain)

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Summary

Alkylation of tricarbonyl(2-methoxycyclohexadienyl)iron(1+) hexafluorophosphate(1-) by substituted anilines provides organometallic intermediates which can be converted into tetrahydrocarbazolones by reaction with trimethylamine *N*-oxide and hydrolysis of the product.

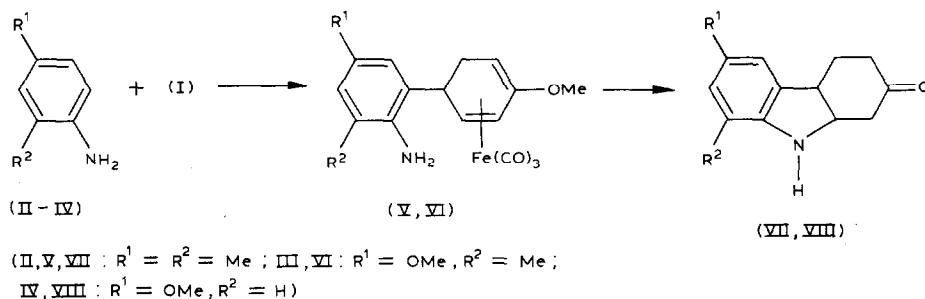
The established equivalence [1] of tricarbonyliron salts to cyclohexenone cations assists the design of synthetic routes based on their reactivity towards nucleophiles. In this paper I describe a successful three step synthesis of tetrahydrocarbazolones [2] from anilines, based on the simple retrosynthetic analysis shown in Scheme 1.



SCHEME 1

Previous experience [3] of the alkylation of aromatic amines by tricarbonyliron complexes has shown that the 4-position of the aniline must be blocked to ensure the *o*-alkylation that is required to allow eventual cyclisation by Michael addition to the enone. A small proportion of disubstituted products are also commonly formed. To avoid this latter complication in the initial investigations of the tetrahydrocarbazolone formation, doubly-blocked anilines were chosen. As expected, only a single complex was obtained from the reaction of an excess of 2,4-dimethylaniline (II) with the 2-methoxy substituted salt I.

The adduct V was isolated by flash chromatography (silica/ CHCl_3) in 63% yield. Similarly the adduct VI was obtained from III in 84% yield. The conversion of complex V to the product VII was achieved by treatment [4] with trimethylamine *N*-oxide to liberate the ligand which was not isolated but hydrolysed directly with dilute HCl. Cyclisation apparently occurred in situ when the solution was made alkaline, and the final product was tetrahydrocarbazolone (37% yield for the two steps).



The reaction need not be restricted to disubstituted anilines. Reaction of IV with the salt I, followed by flash chromatography, gave a major fraction which was treated with trimethylamine *N*-oxide without further purification to afford a crude product that was hydrolysed and cyclised as described above. Tetrahydrocarbazolone (VIII) was isolated by chromatography (Silica/5% EtOH in CHCl_3) in 26% yield overall from salt I.

The use of organometallic intermediates in synthetic routes of this type provides useful opportunities [5] for stereocontrol in enantiomer synthesis. The chirality at C(4) of the cyclohexanone ring is determined by that of salt I which contains a planar chiral element [6]. NMR spectra of the organometallic intermediates V and VI confirm the expected *trans* addition of the aromatic ring relative to the $\text{Fe}(\text{CO})_3$ group. The configuration at C(4), once established in the alkylation reaction, can then control the cyclisation to the tetrahydrocarbazolone, presumably by directing nitrogen addition to the same face of the enone. A PMR spectrum of VII recorded at 200 MHz confirmed the isolation of the product as a single stereoisomer.

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