

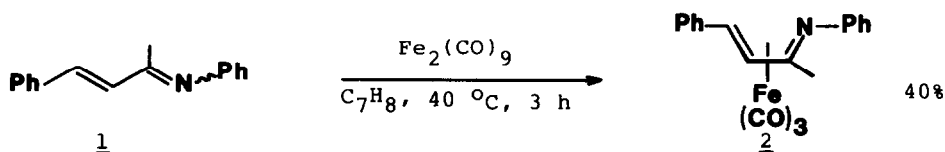
PYRROLE FORMATION FROM A (1-AZABUTADIENE)TRICARBONYLIRON(0) COMPLEX

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Summary : The (1-azabutadiene)tricarbonyliron(0) complex 2 formed by selective complexation of the  $E_{CN}$  isomer of the stereoisomeric mixture of 1-azabutadienes 1 reacts smoothly with methyl-lithium to give the 1,2,3,5-tetra substituted pyrrole 3.

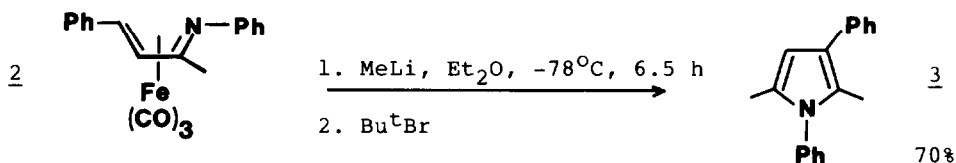
The number of investigations into the reactivity of hydrocarbon ligands attached to transition metals greatly exceeds the number of investigations into the reactivity of ligands containing heteroatoms. As part of a programme designed to discover the effect on reactivity of introducing heteroatoms into ligands of transition metal complexes, we recently reported the first example of nucleophilic attack on iron tricarbonyl complexes of  $\alpha, \beta$ -unsaturated ketones. Addition of a range of hard nucleophiles to iron tricarbonyl complexes of benzylideneacetone and analogues resulted in the clean production of 1,4-diketones.<sup>1,2</sup> This Letter reports that nucleophilic addition to an iron tricarbonyl complex of an imine of benzylideneacetone results in pyrrole production. As far as we are aware, this represents the first example of nucleophilic attack on an iron tricarbonyl complex of an azadiene.

Condensation of aniline with benzylideneacetone under zinc chloride catalysis<sup>3</sup> produced a mixture of the two stereoisomeric imines 1. Heating this mixture with  $Fe_2(CO)_9$  in toluene at 40 °C for 3 h under a nitrogen atmosphere followed by filtration and concentration of the reaction mixture gave red crystals which were identified as the novel complex (1,4-diphenyl-2-methyl-1-azabutadiene)tricarbonyliron(0) 2 on the basis of spectroscopic and analytical data.

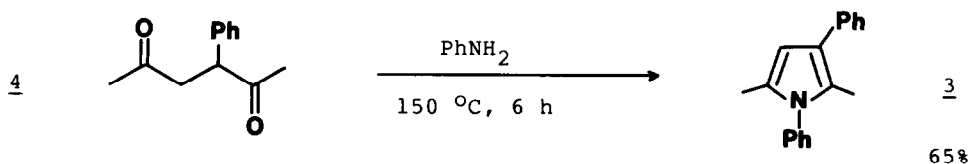


The stereochemistry about the carbon-nitrogen bond of 2 was assigned as E by n.o.e. difference spectroscopy - irradiation of the methyl protons of 2 enhanced the signals due to the ortho-protons of the N-phenyl group (9%) and the C(3) proton (7%). There was no evidence for the formation of the Z<sub>CN</sub> isomer of 2 which is presumably unstable due to a strong steric interaction between an ortho-proton of the N-phenyl group and the C(4) proton.

Complex 2 was treated with methyl-lithium at  $-78^{\circ}\text{C}$  for 6.5 h and the reaction mixture quenched with a proton source. Chromatography led to the isolation of the major reaction product which was identified as the novel pyrrole 3 on the basis of spectroscopic and analytical data.



This identification was confirmed by an independent synthesis of 3. The 1,4-diketone 4 was synthesised by adding methyl-lithium to the iron tricarbonyl complex of benzylideneacetone.<sup>1,2</sup> Heating 4 with aniline at  $150^{\circ}\text{C}$  for 5.5 h gave a product which was spectroscopically identical with 3.



It is of note that attempts to perform this classical pyrrole synthesis at temperatures lower than  $150^{\circ}\text{C}$  failed to produce any evidence for the formation of 3 (as detected by 220 MHz  $^1\text{H}$  n.m.r. spectroscopy) within 6.5 h. The low temperature used in the formation of 3 from the complex 2 strongly suggests that the iron moiety not only acts as a carbonylating agent in the reaction but also is intimately involved in the ring closure step of the pyrrole formation.<sup>4</sup> The nature of this involvement is currently under investigation.

#### References

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