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Preliminary communication

A SUPERIOR METHOD FOR THE ADDITION OF CYANIDE TO SUBSTITUTED TRICARBONYL(η^5-CYCLOHEXADIENYL)IRON(1+) SALTS

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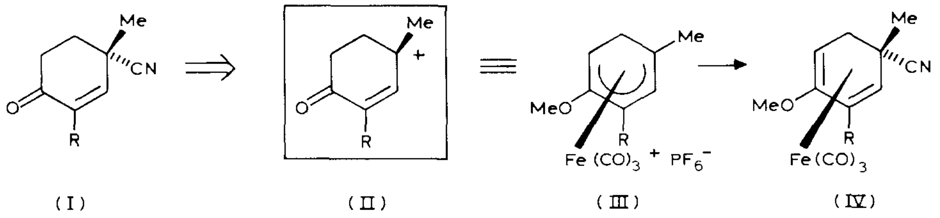
Summary

Nitrile adducts have been obtained in high yield from tricarbonyliron(1+) salts by the use of the reagents trimethylsilyl cyanide and tetra-n-butylammonium cyanide. Trimethylsilyl cyanide is a versatile reagent which is superior to sodium cyanide for this purpose, and its use is the method of choice in cases where a terminal alkyl group is present on the dienyl system. Tetra-n-butylammonium cyanide is a useful reagent only in cases where the site of reaction is unsubstituted.

Recent interest in the use of tricarbonyliron complexes as intermediates in a number of natural product syntheses [1] is reflected in their description [2] as the equivalents of cyclohexenone cations in retrosynthetic analysis. The validity of this equivalence relies on the availability of generally applicable alkylation reactions that permit the use of highly substituted complexes required for synthetic purposes. In this paper we describe the use of trimethylsilyl cyanide [3] to overcome a limitation in the introduction of nitrile groups to η^5-tricarbonyl salts that is encountered [4] when the site of intended alkylation is sterically hindered. In such cases competing deprotonation results in the formation of triene complex.



SCHEME 1. a: R = Me; b: R = H.

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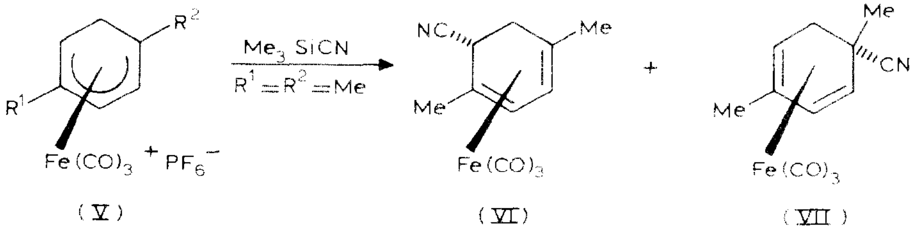
In the course of studies of natural product synthesis we required a masked synthon for the cyclohexenone Ia. An approach (Scheme 1) based on the use of the dimethyl substituted 2-methoxy salt IIIa [5], the synthetic equivalent of the enone cation IIa, was adopted. Introduction of the nitrile group by reaction with sodium cyanide following a procedure successfully employed by Pearson [6] for the salt IIIb, however, was unsuccessful, and the product, an unstable oil, appeared to arise from deprotonation of the terminal methyl group. Our requirement for a less basic source of cyanide was met by the use of trimethylsilyl cyanide [3] for this alkylation. Reaction with an excess of the reagent in acetonitrile at reflux produced the nitrile adduct IVa in 95% yield.

TABLE 1

Substrate	Yield of nitrile adduct		
	Me_3SiCN	Bu_4NCN	NaCN [Ref]
IIIa	95%	0	0
IIIb	86%	—	52% [6]
Va	69%	75%	58% [11]
Vb	97% [a]	—	—

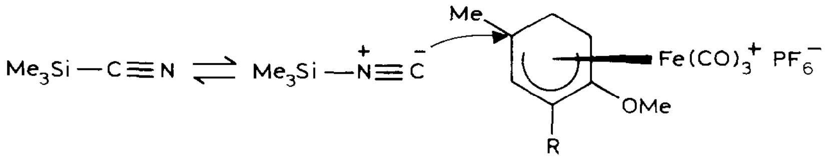
[a] 2/1 mixture of VI and VII.

In the course of this work the alkylation of a number of tricarbonyliron salts has been examined. The silicon reagent appears, in general, to be superior to conventional methods for the reaction, as shown by the yields indicated in Table 1. The alkylation of the 1,4-dimethyl salt Vb was examined to determine the regioselectivity of the reagent in cases where no strong directing group was present in the molecule. Alkylation in this case occurred predominantly at the less hindered end of the dienyl system. A 2/1 mixture of the regioisomers VI and VII shown in Scheme 2 was obtained in 97% yield.



SCHEME 2. a: R^1 = OMe; R^2 = H; b: R^1 = R^2 = Me.

These results show that trimethylsilyl cyanide should be considered the reagent of first choice for the introduction of a nitrile group to complexes such as III and V. In common with the reactions of other silyl reagents, such as silyl enol ethers [7] and allylsilanes [8], with complexes of this type, no catalyst was needed to promote the alkylation, provided a considerable excess of the alkylating agent was employed. The greatly reduced tendency to de-



SCHEME 3

(VIII)

protonate sensitive substrates suggests that the cyanide anion itself is not the alkylating species. IR evidence [9] has shown that trimethylsilyl cyanide exists in solution as an equilibrium mixture of C- and N-bound isomers. A possible explanation for the non-basic character of the reagent would thus be the direct reaction (Scheme 3) of the N-bound isomer VIII with the tricarbonyliron salt.

The use of the organic soluble cyanide salt, tetra-n-butylammonium cyanide [10], as the reagent for this reaction has also been examined. While good results were obtained for the alkylation of the salt Va, this reagent is not suitable for use with complexes bearing a terminal methyl substituent. Attempted reaction with IIIa, for example, produced none of the required nitrile adduct.

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