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DIRECT ACCESS TO FERROCENYLIMINIUM SALTS AND THEIR USE IN SYNTHESIS

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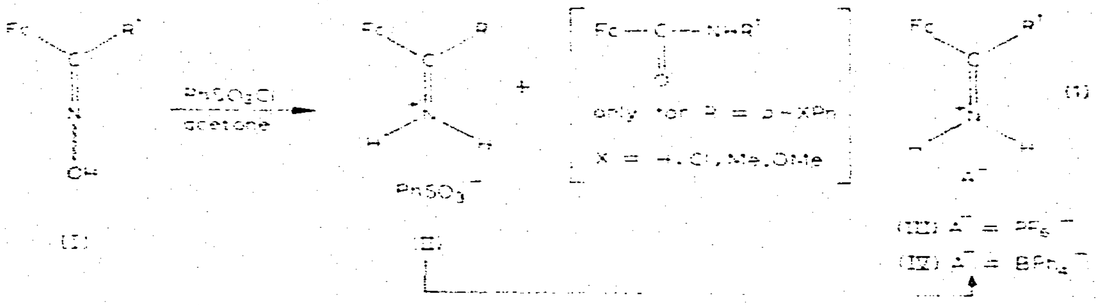
Summary

Reduction of ferrocenylketoximes by titanium trichloride provides a convenient route for the preparation of ferrocenyliminium salts, which have been shown to be useful for the synthesis of new derivatives.

Introduction

We have previously shown [1,2] that Beckmann rearrangement of ferrocenylketoximes, [FcC(R^1)=NOH] (I), via their benzenesulfonic esters, occurs only when R^1 = *p*-XPh. The migration of the aryl group is in accord with a previous observation [3]. When $R^1 \neq$ Ph, migration of either the ferrocenyl or the aliphatic group was never detected, rather we obtained good yields of benzenesulfonate salts II. Replacement of the benzenesulfonate anion can be achieved by adding hexafluorophosphate (or tetraphenylborate) to an aqueous solution to give the iminium salt III (or IV). These salts are obtained in moderate yield when $R^1 \neq$ Ph but only in low yield when R^1 = *p*-XPh (eq. 1). In order to study the



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* Part of the "thèse de 3me cycle" of D. Mourot.

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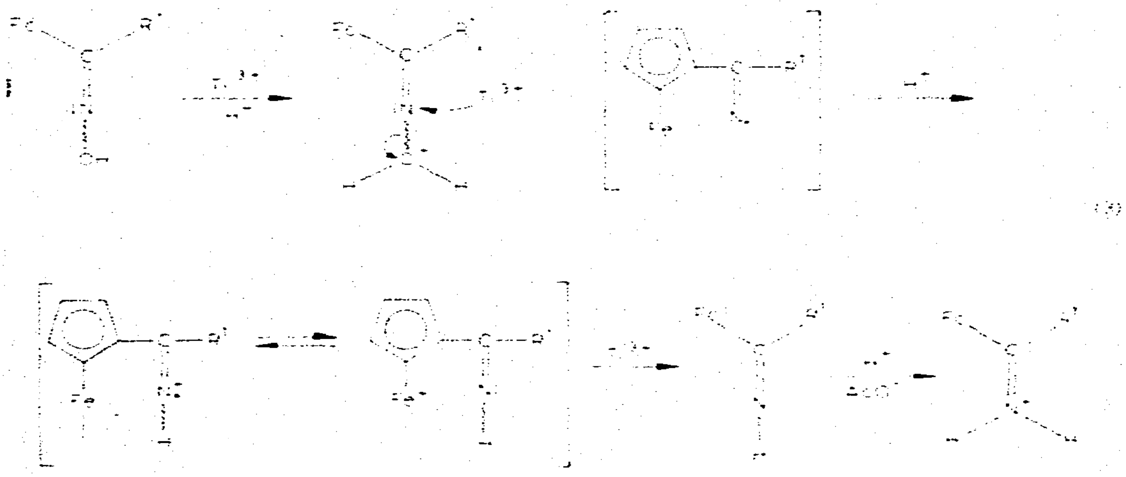
diacy of a possible iminyl radical. Such radicals have recently been observed [5]. Rapid protonation of the iminyl radical yields a radical cation which would be stabilized by the ferrocenyl moiety [6]. Further reduction gives the imine and hence the iminium salt (3).

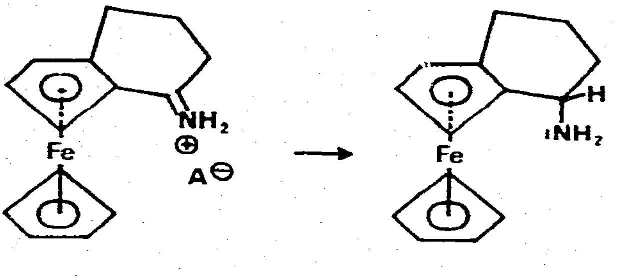


Reactivity of the iminium salts

We have compared the reactivity of the ferrocenyliminium species with the known behaviour of other such salts [7]. It was surprising to find that they failed to react in a similar fashion with diazomethane or Grignard reagents. Their reactivity towards other nucleophiles, however, can be rationalized as an attack of the nucleophile on the electron-deficient carbon centre. In some examples elimination of a nitrogen-containing fragment was observed.

1. Reaction with hydroxide ion (deoximation procedure). Addition of NaOH to a solution of iminium salt in ethanol/water quickly gives in excellent yield, the corresponding acylferrocenes. This method provides a very convenient way of removing the oximino protecting group.

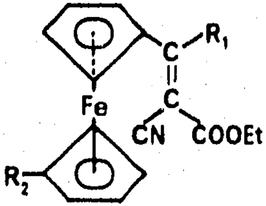
2. Reduction in α-ferrocenylalkylamines. Reducing agents (KBH_4 or $LiAlH_4$) convert, in good yield, the iminium salts to primary amines and the stereospecific reduction of compound IX leads to the 1,2-*endo*-[α-aminotetramethylene)-ferrocene. The first amino alcohols and amino 1,1'-esters in this series are easily obtained from compounds VII and VIII.



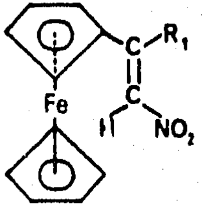
(IX)

TABLE 2

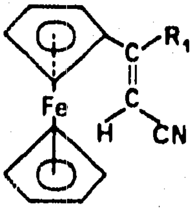
CHARACTERISTICS OF THE COMPLEXES [a].



(X) (*E*)



(XI) (*E*)



(XII) (*E*)

Compound	R^1	R^2	δ(ferrocenyl protons) (ppm)	δ(olefinic or other characteristic protons) (ppm)	M.p. (°C)
X	Me	H	5.00(2H)t; 4.60(2H)t; 4.15(5H)s	Me(*E*) 2.53; Me(*Z*) 2.60	98
X	Et	H	5.19(2H)t; 4.73(2H)t; 4.28(5H)s		61
X	Pr	H	5.16(2H)t; 4.68(2H)t; 4.25(5H)s		39
X	(2)-(CH$_2$)$_3$ (1)-C	H	5.78(1H)m; 4.50(2H)m; 4.19(5H)s		118
X	Ph	H	4.80(2H)t; 4.60(2H)t; 4.20(5H)s		137
X	*p*-MePh	H	4.88(2H)t; 4.63(2H)t; 4.30(5H)s		123
X	Me	CO$_2$Me	4.53(2H)t; 4.70(2H)t; 4.90(2H)t; 5.13(2H)t		79
XI	Me	—	4.46(4H)m; 4.21(5H)s	*E*(52%)Me 2.50; *Z*(48%)Me 2.47; H 4.91 and 4.94[13]	122[14]
XI	Ph	—	4.54(2H)t; 4.33(2H)t; 4.22(5H)s		160
XI	*p*-MePh	—	4.52(2H)t; 4.33(2H)t; 4.22(5H)s	*E*(84%)Me 2.42; *Z*(16%)Me 2.34	137
XII	Me	—	4.48(4H)m; 4.17(5H)m	5.42(1H) broad peak	98[15]
(XII)	(2)-(CH$_2$)$_3$ (1)-C	—	4.28(1H)m; 4.16(2H)m; 3.83(5H)s	5.00(1H) broad peak	57
(XII)	Ph *Z*	—	4.60(2H)t; 4.23(2H)t; 3.97(5H)s	5.00(1H)s	68[15]
	E	—	4.18(4H)m; 3.92(5H)s	5.36(1H)s	97
(XII)	*p*-MePh *Z*	—	4.95(2H)t; 4.58(2H)t; 4.31(5H)s	5.39(1H)s	102
	E	—	4.43(4H)m; 4.17(5H)s	5.63(1H)s	81

[a] CDCl$_3$ solution.

α-Ferrocenylalkylamines

To a solution of 0.5 g of salt III in 30 ml of a water/DME (20—80) mixture was added 0.5 g of KBH_4. After stirring for one hour at room temperature the solution was quenched with 300 ml of water. Extraction with ether followed by the usual work-up gave an oil which was dissolved in a few ml of anhydrous ether and filtered. Addition of a few drops of glacial acetic acid gave a yellow precipitate which was filtered and dried (yield 65—70%). A good yield of acetates was obtained by adding a THF solution of 10^{-3} mol of III or IV to a suspension of 10^{-2} mol of $LiAlH_4$ in dry THF. After 30 min at room temperature the reaction was worked-up in the usual way. For melting points of the ferrocenylalkylamines see Table 3.

Olefins X

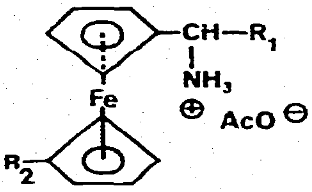
10^{-3} mol of salt III (or IV) was dissolved in a mixture of dichloroethane (10 ml) and ethylcyanacetate (5 ml) and to this stirred solution was added, at room temperature 10^{-3} mol of triethylamine. After 15 min water was added and the usual work-up gave a mixture which was separated by PLC (light petroleum/ether, 1 : 1). Crystallization from hexane/ether afforded olefins X in more than 90% yield (for melting points see Table 2).

Olefins XI

To a well-stirred solution of 10^{-2} mol of Triton-B in 20 ml of nitromethane

TABLE 3

CHARACTERISTICS OF THE COMPLEXES:



R^1	R^2	M.p. (°C)
Me	H	124 [9]
Et	H	117
CH_2Ph	H	113
(1)-$(CH_2)_3$-(2)		148 *endo* [11]
p-MePh	H	119
p-OMePh	H	113
p-ClPh	H	113
Me [a]	CHOHPh	128
Pr [a]	CHOHPh	143
CH_2Ph [a]	CHOHPh	139
Me	CO_2Me	95
Ph	CO_2Me	111

[a] The monooximes of 1-aryl 1′-benzoylferrocenes [12] are prepared by refluxing the diketones in EtOH with a five-fold excess of NH_2OH, HCl and ten-fold excess of KOH. The compounds were separated from the dioximes and diketone by chromatography on acidic alumina using light petroleum/ethanol (1000 : 1) as eluant.

was added a solution of 10^{-2} mol of salt III in 10 ml of nitromethane. Boiling was maintained until complete reaction of III (2 to 3 hours) was indicated by TLC. After cooling, the usual work-up gave by PLC (benzene) and crystallization, from a benzene/hexane mixture, the product in 55—65% yield (see Table 2 for melting points).

Olefins XII

To a solution of the crude olefin X, in ethanol (150 ml) was added 150 ml of 10% aqueous Na_2CO_3. After refluxing for 30 min the mixture was cooled, poured into water and extracted with ether. The solvent (without drying) was removed by vacuum and the red solid obtained was dried in a dessicator. The crude product was mixed with 15 ml of quinoline and 0.15 g of copper powder, and refluxed under nitrogen for 3 h. Usual work-up afforded a 70—80% yield of crude material which was purified (and eventually separated into *Z* and *E* isomers) by PLC (light petroleum/ether 80 : 20). See Table 2 for melting points.

β-Ferrocenylalkylamines

A solution of 10^{-3} mol of olefin XI, in dry THF, was added dropwise to a suspension of 10^{-2} mol of $LiAlH_4$ in THF. After one hour, at room temperature, hydrolysis followed by usual work-up afforded the amines as oils, which were characterized as their acetates (yields 75—80%). $FcCH(R^1)CH_2NH_3$ + AcO^-: R^1 = Me. m.p. 121° C: R^1 = Ph, m.p. 132° C; R^1 = *p*-MePh, m.p. 139° C.

γ-Ferrocenylalkylamines

A solution of 10^{-3} mol of olefin X in dry ether was added dropwise to 10^{-2} mol of a 1 : 1 mixture of $LiAlH_4/AlCl_3$ in ether. After complete addition the mixture was refluxed for 2 hours, cooled, and carefully quenched with water. Usual work-up gave oils which were transformed into their acetates (yields 70—80%) for purposes of characterization. $FcCH(R^1)(CH_2)_2NH_3^+AcO^-$: R^1 = Me, m.p. 129° C; R^1 = (2)-$(CH_2)_3$-(1), m.p. 148° C: R^1 = Ph, m.p. 137° C; R^1 = *p*-MePh, m.p. 144° C.

Acknowledgement

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