Electronic Influence of Iron Tetracarbonyl Complexation on Unsaturated *N,N*-Diacyliminium Ion Precursors

Johan C. P. Hopman, Henk Hiemstra* and W. Nico Speckamp*

Laboratory of Organic Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands

Complexation with the $Fe(CO)_4$ group increases the electron density in the *N*-substituent of *N*-crotonoyl- and *N*-cinnamoyl-5-alkoxy-2-pyrrolidinones, making substitution reactions *via* formal *N*,*N*-diacyliminium ions possible.

We recently reported on the BF₃·OEt₂-induced substitution reactions on the Fe(CO)₄ complexes 1^1 and $2.^2$ Such reactions are not possible in the uncomplexed pyrrolinones, as it is known that the cation derived from alkoxypyrrolinones dimerises,³ whereas the cation from *N*-acyl alkoxypyrrolinones is not formed at all.²

Indeed, during investigations towards the reactivity of 5-alkoxy-3-pyrrolin-2-ones bearing a carbonyl substituent at nitrogen, we found it to be impossible to generate a *N*,*N*-diacyliminium ion from these compounds. Upon complexation of the double bond to Fe(CO)₄, substitution reactions *via* a cationic intermediate could be carried out. It was therefore clear that the complexation of iron to the double bond has a profound effect on the stability of this intermediate. The nature of the cation, however, is ambiguous. It can be described either as a *N*,*N*-diacyliminium ion or a π -allyliron cation (Scheme 1). Therefore, we decided to study the influence of Fe(CO)₄ complexation on the reactivity of 5-alkoxy-2-pyrrolidinones bearing an α , β -unsaturated *N*-acyl group, thus separating the effect of iron on the *N*-carbonyl moiety from the direct effect on the iminium ion.

N-Crotonoyl- and *N*-cinnamoyl-5-ethoxy-2-pyrrolidinone 3^{\dagger} and 4 were synthesized in excellent yields from 5-ethoxy-2-pyrrolidinone⁴ by acylation of the sodium salt with the appropriate acid chloride. The Fe(CO)₄ complexes were prepared by stirring 3 or 4 in toluene with Fe₂(CO)₉ (Scheme 2). Complexes 5^{\ddagger} and 6 were obtained as a 2:3 mixture of diastereoisomers in good yield.

Both 3 and 4 react with allyltrimethylsilane in the presence of $BF_3 \cdot OEt_2$, giving only traces of alkylation and Michael addition⁵ products. More than 90% of the starting material was recovered. However, when 5 and 6 were treated with allyl-





Scheme 2 Reagents and conditions: i, 1. NaH (1.4 equiv.), THF, 40 °C, 1 h; 2. RCH=CHC(O)Cl (1.5 equiv.); ii, Fe₂(CO)₉ (2.0 equiv.), toluene, room temp., 5.5 h

trimethylsilane and BF_3 ·OEt₂ the alkylation products 7§ and 8 were formed exclusively (Scheme 3). Obviously, the Fe(CO)₄ moiety allows *N*,*N*-diacyliminium reactions to proceed. The results of the substitution reactions are given in Table 1.

The reaction was improved greatly both in time and in yield by the addition of 1 equiv. of acetic anhydride. This probably leads to the formation of the 5-acetoxy derivative,¶ which is more reactive because of the presence of a better leaving group. The application of these modified conditions to **3** and **4** appeared not to have any effect on the outcome, 90% of starting material and only traces of products being obtained.

Apart from the effect on the reactivity, the influence of the Fe(CO)₄ group on the organic ligand is apparent in NMR and Xray studies. In all cases, the chemical shifts of the double bond protons in the ¹H NMR spectrum change by approximately 3 ppm (upfield).^{1,2,6} The carbon resonances of the double bond shift by 70–90 ppm in the ¹³C NMR spectrum. Furthermore, several X-ray studies established that the double bond is elongated by *ca*. 0.1 Å upon coordination to iron.^{1,2,7} All this evidence points to a significant amount of π -back donation in the iron–alkene bond.⁸ This makes the olefin and thereby the conjugated carbonyl group much more electron-rich, thus reducing its destabilizing effect on the cation.

On these grounds we conclude that the complexation of iron(0) to a carbon-carbon double bond can effectively cancel the electron-withdrawing effect of the conjugated carbonyl group. The nature of the intermediate in the substitution reactions of cis-1 and 2, however, remains ambiguous. Since in the cis-complex the iron cannot assist in the departure of the isopropoxide, the first stage in the reactions of cis-1 and 2 is likely to be an N,N-diacyliminium ion or an N-acyl-N-sulfonyl-iminium ion, respectively, the destabilizing effect of the carbonyl at C-2 being largely eliminated by the iron-to-alkene back donation. This iminium ion can subsequently rearrange



Scheme 3 Reagents and conditions: i, allyltrimethylsilane (3.0 equiv.), BF₃·OEt₂ (3.0 equiv.), CH₂Cl₂, room temp.; ii, Me₃NO·2H₂O (10 equiv.), room temp.

Table 1 Reactions of 3, 4, 5 and 6 with allyltrimethylsilane^a

Entry	Substrate	Reaction time	Products [yield (%)] ^b
1	3	8 d	7(3) + 9(5) + 3(20)
2	4 <i>c</i>	20 h	8 (8)
3	5	6 d	7(45) + 5(17)
4	5 ^c	8 h	7(66) + 5(14)
5	6	4 d	8(27)
6	6 ^c	5 h	8(42)
7	6 ^c	16 h	8(54)

^{*a*} Conditions: see Scheme 3. ^{*b*} After column chromatography ^{*c*} In the presence of 1.0 equiv. acetic anhydride.

electronically to a π -allyliron cation, which is likely to be more stable and presumably serves as the actual intermediate reacting with nucleophiles. In the case of *trans*-1 the π -allyliron cation can be formed directly.

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Footnotes

† Selected data for 3: IR v/cm⁻¹ (CHCl₃): 1735, 1680; ¹H NMR (CDCl₃; J/Hz): δ 1.16 (t, 3 H, J 7.0, OCH₂CH₃), 1.93 (d, 3 H, J 5.4, =CH–CH₃), 2.06 (m, 2 H, 4-H), 2.45 (ddd, 1 H, J 4.0, 6.3, 18.1, 3-H), 2.88 (dt, 1 H, J 10.1, 17.6, 3-H), 3.63 (q, 2 H, J 7.0, OCH₂), 5.75 (dd, 1 H, J 1.5, 3.4, 5-H), 7.03–7.18 (m, 2 H, –CH=CH–); ¹³C NMR (CDCl₃): δ 15.0, 18.2, 26.0, 31.4, 64.7, 86.2, 123.5, 146.0, 165.6, 175.4.

 \ddagger Selected data for 5: IR v/cm⁻¹ (pentane): 2100, 2020, 1990, 1735, 1670; ¹H NMR (C₆D₆; J/Hz): δ 1.03 (m, 3 H, OCH₂CH₃), 1.18–1.48 (m, 5 H, =CH–CH₃ and 4-H), 2.00 (dt, 1 H, J 8.4, 17.4, 3-H), 2.65 (m, 1 H, 3-H), 3.45 (m, 2 H, OCH₂), 4.08 (m, 1 H, β-H), 4.68 and 4.82 (d, 1 H, J 11.1, α-H), 5.40 and 5.52 (d, 1 H, J 4.6, 5-H); ¹³C NMR (C₆D₆): δ 16.1, 24.1, 26.5/27.1, 32.4/32.5, 55.1/55.5, 56.9/57.9, 65.6/65.8, 87.4/87.5, 172.2/173.5, 175.5/175.8, 209.9.

§ Selected data for 7: IR v/cm⁻¹ (CHCl₃): 1730, 1670; ¹H NMR (CDCl₃; *J*/Hz): δ 1.80–2.76 (m, 6 H), 1.91 (d, 3 H, *J* 5.7, =CHC*H*₃), 4.45 (m, 1 H, 5-H), 5.09 (dd, 2 H, *J* 0.8, 12.6, =CH₂), 5.74 (m, 1 H, =CH–), 6.99–7.18 (m, 2 H, -CH=CH–); ¹³C NMR (CDCl₃): δ 18.2, 21.4, 32.1, 37.0, 56.2, 118.5, 123.8, 133.0, 145.3, 165.6, 175.5.

¶ From an experiment with **3** in the presence of Ac₂O, 5-acetoxyl-1-crotonyl-2-pyrrolidinone was isolated, indicating the BF₃-mediated formation of 5-acetoxy compounds from 5-ethoxypyrrolidinones and acetic anhydride.

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