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Stable carbocations

XXIII *. Generation and isolation of salts of ferrocenyl(alkoxy)methylium cations and their intermediacy in acid-promoted acetal hydrolysis **

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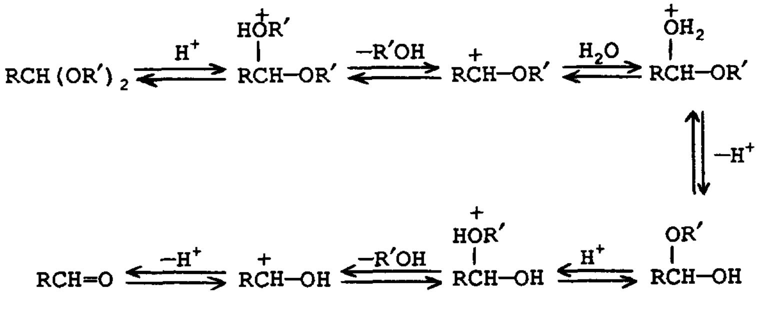
Abstract

Ferrocenyl(alkoxy)methylium cations have been generated from (dialkoxymethyl)ferrocenes and isolated as tetrafluoroborate salts. Their structures and their reactivity towards nucleophiles have been investigated.

Introduction

The conversion of most simple aliphatic acetals into aldehydes in aqueous acid follows the A1 mechanism (Scheme 1) with hydronium-ion catalysis. The rate-limiting step is usually heterolysis of the conjugate acid of the acetal and, in consequence, the resulting alkoxycarbocation intermediate has only a fleeting existence in these reactions [2].



Scheme 1

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* For Part XXII, see ref. 1

** Dedicated to Professor Peter L. Pauson on the occasion of his retirement.

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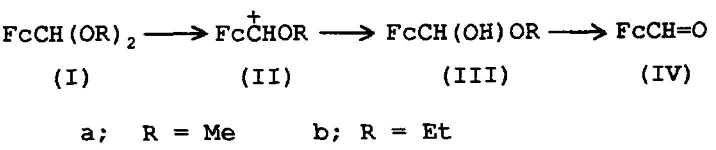


$$\underset{(I)}{FcCH(OR)_2} \longrightarrow \underset{(II)}{Fc\overset{+}{C}HOR} \longrightarrow \underset{(III)}{FcCH(OH)OR} \longrightarrow \underset{(IV)}{FcCH{=}O}$$

a; R = Me b; R = Et

Scheme 2

In connection with our interest in the kinetics and mechanisms of reactions of ferrocenyl-stabilised carbocations [3] and of hydrolysis of transition metal-complexed acetals [4], we wished to study the acid-promoted conversion of (dialkoxyalkyl)ferrocenes (I) into formylferrocene (IV) via the presumed intermediate alkoxycarbocations II and hemiacetals III (Scheme 2). Earlier work [5] had shown that, in aqueous acidic solutions, the acetal Ia is converted smoothly and quantitatively into the aldehyde IV, but salt effects on the overall reaction rate appear anomalous [6] and rates of reactions of the intermediates II and III cannot be measured under these conditions.

In this paper, we report the generation and observation in solution of ferrocenyl(alkoxy)methylium cations, their isolation as tetrafluoroborate salts, and some observations on their reactivities towards nucleophiles.

Results and discussion

The acetals Ia and Ib were prepared by treatment of formylferrocene (IV) with trialkyl orthoformate in acidified alkanol. These compounds are very susceptible to hydrolysis back to the aldehyde and require storage under strictly anhydrous conditions. Upon dissolution in trifluoroacetic acid, the acetals were converted instantaneously and quantitatively into the corresponding ferrocenyl(alkoxy)methylium cations (IIa,b) by protonation of an oxygen atom and elimination of alkanol. The ^{1}H NMR spectra of these solutions are complicated by the occurrence of slow esterification of the alkanol released (ROH → $ROCOCF_3$). However, we have studied [7] these reactions and their rates earlier (at 35 °C; R = Me, $t_{1/2} = 7.6$ min; R = Et, $t_{1/2} = 12.0$ min) and so identification of the resonances of the cations IIa and IIb was straightforward.

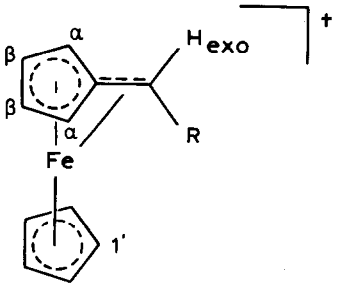
In the ^{1}H NMR spectra of these cations, the chemical shifts of the cyclopentadienyl ring protons (Table 1) are similar to those of secondary ferrocenylalkylium cations [8] such as $Fc\overset{+}{C}H(p\text{-anisyl})$, indicating that the contribution of oxonium-ion

Table 1

^{1}H NMR spectra of carbocations [a]

Protons [b]	$Fc\overset{+}{C}HOMe$ (IIa)	$Fc\overset{+}{C}HOEt$ (IIb)	$Fc\overset{+}{C}HAn$ [c]
H_α	4.53, 5.25	4.67, 5.35	4.83, 5.58
H_β	5.77, 6.09	5.88, 6.18	6.18, 6.40
$H_{1'}$	4.82 (s)	4.89 (s)	4.80 (s)
H_{exo}	9.08 (s)	9.28 (s)	8.30 (s)
Other	4.31 (s, OMe)	1.64 (t, Me) 4.76 (q, CH_2)	4.00 (s, OMe) 7.1–8.1 (A_2B_2q, aryl)

[a] For solutions in CF_3CO_2H with Me_4Si as internal reference; δ-values; multiplets unless indicated otherwise; (s) singlet, (t) triplet, (q) quartet. [b] Locations are shown in the structure of V. [c] Data from ref. 10; An = p-anisyl (C_6H_4OMe).



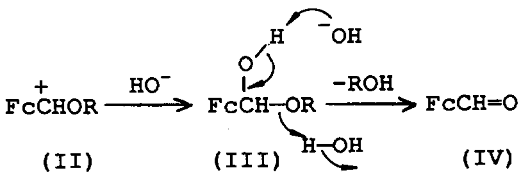
(V)

character (FcCH=$\overset{+}{O}$R) to their electronic structures is not substantial. In particular, the non-equivalence of the protons of the α- and β-pairs of the substituted cyclopentadienyl ring shows that rotation around the Fc–$\overset{+}{C}$ bond is restricted, a consequence of electron donation from the ferrocenyl group to the carbocation centre and a fulvenoid-like ligand structure (V). Such a property is typical of secondary carbocations of the type Fc$\overset{+}{C}$HR (R = alkyl, aryl) [8] in which the barriers (E_a) to rotation around the exocyclic bond are around 85 kJ mol^{-1} [9].

Treatment of the acetals Ia and Ib in CH_2Cl_2 solution with triphenylmethyl tetrafluoroborate resulted in transfer of an alkoxy group and production of the cations IIa and IIb which could be isolated as their deep-blue BF_4^- salts by precipitation with ether. These salts are extremely reactive but could be stored for limited periods in the dark under dry N_2 in a deep-freeze. Their ^1H NMR spectra in CF_3CO_2H showed identical resonances to those in the spectra of the acetals in the same solvent (Table 1), thus confirming their structure. The reactions of the acetals with trityl cation therefore proceed by alkoxide- rather than hydride-transfer which would have produced dialkoxycarbocations Fc$\overset{+}{C}$(OR)$_2$.

Reactions of the salts [IIa,b][BF_4^-] with dilute aqueous sodium hydroxide solution gave formylferrocene (IV) as the sole product. The presumed intermediate hemiacetals III were not isolated, showing that base-catalysed elimination of alkanol occurs readily (Scheme 3).

The quantitative hydroxide-promoted conversion of the salts [II][BF_4^-] into the aldehyde IV provides further structural corroboration. Under the reaction conditions, any Fc$\overset{+}{C}$(OR)$_2$ present would have been converted into the corresponding known esters $FcCO_2R$ (R = Me, Et) which were not detected. Furthermore, the salts [IIa,b][BF_4^-] reacted instantaneously with solutions of NaOR in ROH to give the



Scheme 3

corresponding acetals Ia and Ib as the sole products. The success of these reactions opens up the possibility of synthesis of mixed acetals of the type FcCH(OR')OR.

We are now investigating rates of reactions of cations of the type II with various nucleophiles in order to compare their reactivities with those of other ferrocenylalkylium ions [3] and related ferrocenyliminium ions $\mathrm{FcCH{=}\overset{+}{N}R_2}$ [11].

Experimental

For general remarks, see ref. 12. Formylferrocene (i.e. ferrocenecarboxaldehyde) was used as supplied by Aldrich Chemical Co. Ltd.

(Dimethoxymethyl)ferrocene (Ia)

A solution of formylferrocene (1.0 g, 4.7 mmol), trimethyl orthoformate (20 ml) and conc. H_2SO_4 (1 drop) in dry MeOH (20 ml) was stirred under N_2 at room temperature for 24 h. The solution was then diluted with $NaHCO_3$ aq. (excess) and extracted with CH_2Cl_2. The extract was washed with $NaHCO_3$ aq., dried over anhydrous Na_2CO_3, and evaporated under reduced pressure giving the title compound (1.2 g, 95%) as a viscous orange-red oil (lit. [5] liquid). ^{1}H NMR (CS_2): δ 3.12 (6H, s, OMe); 3.96 (5H, s, C_5H_5); 3.96 and 4.12 (2H and 2H, 2t, C_5H_4); and 5.12 (1H, s, CH).

(Diethoxymethyl)ferrocene (Ib)

This compound was prepared from formylferrocene, triethyl orthoformate and conc. H_2SO_4 (1 drop) in dry EtOH (20 ml) by the same procedure as in the preceding experiment and isolated as a viscous orange-red oil (96% yield). Found: C, 62.7; H, 7.1. $C_{15}H_{20}FeO_2$ calc.: C, 62.5; H, 7.0%. ^{1}H NMR (CS_2): δ 1.12 (6H, t, Me); 3.39 (4H, q, CH_2); 3.95 (5H, s, C_5H_5); 3.94 and 4.01 (2H and 2H, 2t, C_5H_4); 5.32 (1H, s, CH).

Ferrocenyl(methoxy)methylium tetrafluoroborate [IIa][BF_4^-]

A solution of triphenylmethyl tetrafluoroborate [13] (330 mg, 1 mmol) in dry, alcohol-free CH_2Cl_2 (2 ml) was added dropwise to a stirred solution of the acetal Ia (260 mg, 1 mmol) in the same solvent (5 ml) under N_2 at room temperature. The resulting deep-blue solution was stirred for a few min, then added dropwise with stirring to chilled dry ether. The precipitated title salt was allowed to settle and the supernatant solvent was decanted. The precipitate was washed several times with dry ether, decanting the washings each time, and the residual product (185 mg, 58%) was dried under vacuum. ^{1}H NMR (CF_3CO_2H): see Table 1.

Ferrocenyl(ethoxy)methylium tetrafluoroborate [IIb][BF_4^-]

This salt was prepared from the acetal Ib by the same procedure as described in the preceding experiment and was isolated in 55% yield as a deep-blue gummy solid. ^{1}H NMR (CF_3CO_2H): see Table 1.

Reactions of acetals with CF_3CO_2H

The acetals Ia and Ib each dissolved readily in CF_3CO_2H. The ^{1}H NMR spectra of the resulting dark-blue solutions contained the resonances of the cations IIa and IIb, respectively (see Table 1), together with those of the corresponding liberated alcohol (ROH) and derived ester ($ROCOCF_3$): viz. Me resonances, δ 3.60 (s, MeOH) and 4.00 (s, $MeOCOCF_3$); Et resonances, δ 1.32 and 3.90 (t and q, EtOH), 1.40 and 4.45 (t and q, $EtOCOCF_3$). At time progressed, the alcohol signal(s) diminished and the ester signal(s) increased (see ref. 7).

Reactions of salts with hydroxide ion

The salt [IIa][BF_4^-] (150 mg, 0.47 mmol) was added to an aqueous solution of NaOH (0.1 *M*, 50 ml) which was stirred at room temperature in a two-phase system over CH_2Cl_2 (50 ml). After 30 min, the lower layer was separated and combined with CH_2Cl_2 extracts of the aqueous layer. The total extract was washed with water, dried over anhydrous $MgSO_4$, and evaporated giving as the sole product formylferrocene (94 mg, 92%), identical with an authentic specimen. ^1H NMR (CS_2): δ 4.13 (5H, s, C_5H_5); 4.42 and 4.62 (2H and 2H, 2t, C_5H_4); and 9.81 (1H, s, CH).

Similar treatment of the salt [IIb][BF_4^-] gave the aldehyde IV in 90% yield.

Reactions of salts with alkoxide ions

The salt [IIa][BF_4^-] (150 mg, 0.47 mmol) was added to a solution of a NaOMe in MeOH (0.1 *M*, 50 ml). The mixture was stirred at room temperature for a few min, then diluted with water and extracted with CH_2Cl_2. The extract was washed with $NaHCO_3$ aq., dried over anhydrous Na_2CO_3, and evaporated, giving as the sole product the acetal Ia (111 mg, 91%), identical with the compound described earlier.

Similar treatment of the salt [IIb][BF_4^-] with NaOEt in EtOH gave the acetal Ib in 89% yield as the sole product.

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