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Article

Direct One Step Preparation and ^{13}C-NMR Spectroscopic Characterization of α-Ferrocenyl Carbocations Derived from Ferrocene and Carbonyl Compounds in Trifluoroacetic Acid Medium[1a]

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A reação de aldeídos e cetonas com ferroceno, na presença de ácido trifluoroacético, gera uma série de α-ferrocenoalquil carbocátions estáveis por longo tempo que foram caracterizados por espectroscopia de Ressonância Magnética Nuclear de ^{13}C. De forma inesperada, quando esta reação foi realizada usando tetrafenilciclopentadienona, o correspondente dihidro derivado **3** foi isolado com muito bom rendimento. A formação deste composto pode requerer ferroceno atuando como agente redutor.

Reaction of aldehydes and ketones with ferrocene, in the presence of trifluoroacetic acid, afforded a series of stable long lived α-ferrocenylalkyl carbocations which were characterized by ^{13}C-NMR spectroscopy. When this reaction was attempted using tetraphenylcyclopentadienone, quite unexpectedly the corresponding dihydro derivative **3** was isolated, in very good yield. Formation of this compound may require ferrocene acting as a reducing agent.

Keywords: *ferrocene, α-ferrocenyl carbocations, ^{13}C-NMR of α-ferrocenylalkyl carbocations*

Introduction

Since the preparation of bis-(cyclopentadienyl)iron, ferrocene, in 1951[1b] the number of its reported derivatives is vast and the highly nucleophilic character of the aromatic cyclopentadienyl rings makes the Friedel-Crafts reaction one of the most common functionalization methods[2]. In fact, ferrocene is 3.3 x 10^6 times more reactive than benzene and about 1 x 10^3 times more reactive than mesitylene in Friedel-Crafts acetylations[3]. Direct electrophilic substitution of ferrocene by protonated carbonyl compounds followed by further reactions has attracted the interest of a large number of researchers[4]. Herrmann and Ugi, in 1981, reported[4] conditions wherein α-ferrocenyl carbocations formed as intermediates in the Friedel-Crafts reaction of ferrocene with carbonyl compounds using mixtures of trifluoroacetic acid/fluorosulfuric acid or trichloroacetic acid/fluorosulfuric acid solvent mixtures were directly reacted with nucleophiles or bases to give isolable α-substituted ferrocenyl alkanes and ferrocenylethene derivatives, respectively. However, the carbocation intermediates from these reactions were not spectroscopically characterized. Herein, we report the direct preparation and ^{13}C-NMR spectroscopic characterization of a number of stable α-ferrocenyl carbocations by reacting a number of cyclic, polycyclic and acyclic carbonyl compounds with ferrocene in trifluoroacetic acid medium. Trifluoroacetic acid appears to be in the right acidity range to stabilze α-ferrocenyl carbocations as long lived species at room temperature[4,5].

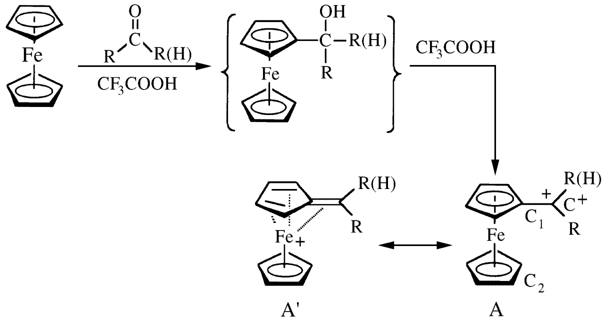
Results and Discussion

In a typical experiment, ferrocene was added to an excess of the aldehyde or ketone, under an argon atmosphere, and then treated with a large excess of trifluoroacetic acid, at 0 °C. After warming to ambient temperature, the green solutions were carefully transferred to an NMR tube and characterised by ^{13}C-NMR spectroscopy (using a capillary containing deuterated acetone as an external reference). Accordingly, dissolution of ferrocene (18.6 mg, 1 mmol) in dry acetone (29 mg, 5 mmol) in 1.5 mL of freshly distilled trifluoroactetic acid in a 5 mm NMR tube at 0 °C gave a greenish colored solution. The solution was brought to room temperature and characterized. The 75 MHz ^{13}C-NMR spectrum showed absorptions due to α,α-dimethylferrocenylmethyl carbocation **A** (R, R=CH_3) at δ ^{13}C 156.9 (s), 99.8 (s), 78.6 (d), 93.9 (d), 82.2 (d) and 24.8 (q) along with signals due to excess acetone as well as the trifluoroacetic acid. No unreacted ferrocene was detected in this case. The data obtained is in accordance with the studies of Olah and Liang carried out in sulfuric acid medium[6]. Formation of any significant concentration of paramagnetic species did not occur in the trifluoroacetic acid medium and NMR characterization was quite straightforward. When superacidic[7] fluorosulfuric acid (FSO_3H) was used significant line broadening was observed due to paramagnetic ferrocenyl radical cation easily generated under the oxidizing conditions. Scheme 1 shows a generalized reaction wherein the carbocation is obtained through the intermediately formed alcohol (by the reaction of the protonated carbonyl with the ferrocene in a typical Friedel Crafts type reaction) and subsequent ionization in the trifluoroacetic acid medium. In no case disubstitution of the second ring was observed even with large excess of the carbonyl compounds present under these conditions.

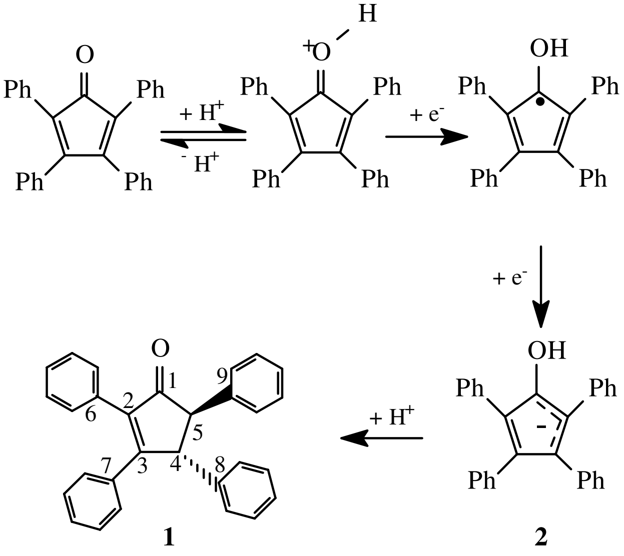
The selected ^{13}C-NMR shifts for the carbocationic centre (C^+), the ring carbon adjacent to C^+ (C_1) and the unsubstituted second cyclopentadienyl ring carbon (C_2), of a number of α-ferrocenyl carbocations generated by reacting the corresponding carbonyl compounds are shown in Table 1. The data indicates substantial shielding of the cationic center in **A** (R, R=CH_3) as compared to 2-phenyl-2-propyl cation (cumyl cation) (δ^{13}C 255.7)[8]. This is true with a variety of studied cyclic, polycyclic and acyclic systems. Earlier ^{13}C-NMR studies[9] on ferrocenyl stabilized carbocations have shown that ferrocene is an excellent stabilizer of an adjacent positive charge compared to a phenyl ring involving a resonance contributor wherein substantial positive charge is localized on the iron atom with significant double bond character between the carbocationic center and the ring (structure **A'**)[9,10]. Earlier, we have exploited the positive charge stabilizing ability of ferrocene by preparing even the α-ferrocenyl cyclopropyl cation.[11] Interestingly, the delocalization of positive charge into the metallocene is far less with tertiary derivatives than with the secondary or primary systems as indicated by the extent of the relative shielding of the carbocationic center as well as the tabulated Δ^{13}C (δC^+ - δC_1) criteria[10].

Dicyclopropylketone and benzophenone, however, did not react under these conditions. A reaction employing the procedure described above was also performed using tetraphenylcyclopentadienone. After quenching (sodium bicarbonate), extraction (dichloromethane) and chromatography (dichloromethane: hexane, 1:5, on silica) a pale yellow solid was isolated and identified as *trans*-tetraphenyl-2-cyclopent-1-enone **1** (60% based on recovered tetraphenylcyclopentadienone) by ^{1}H-NMR [300 MHz, $CDCl_3$: vicinal resonances; δ^{1}H 4.61 (d, $J_{H,H}$ 2.5 Hz) and 3.80 (d, $J_{H,H}$ 2.5 Hz)], ^{13}C-NMR and mass spectrometry.[12] The product of reduction was quite unexpected under these conditions. In Scheme 2 we suggest that, after protonation of the ketone, two electrons from ferrocene are accepted to form a six pi-electron aromatic system **2**. Protonation of **2** followed by enol-keto tautomerisation results in the monoenone **1**.

When the reaction was repeated using an excess of ferrocene (four equiv.), **1** was obtained in 97% yield after chromatography on silica. This compares well with, for example, the reduction of tetraphenylcyclopentadienone using tributylphosphine (93% of **1**)[13]. No reaction took place in the absence of ferrocene or while using weakly acidic methanol or acetic acid as the proton source. It is clear that the carbonyl oxygen of tetraphenylcyclopentadienone must be protonated for the reaction to proceed.

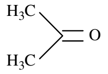
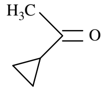
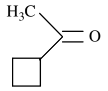
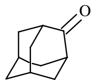
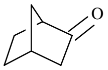
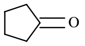
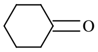
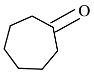
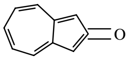
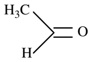
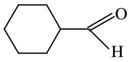
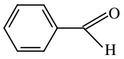


Scheme 1.



Scheme 2.

Table 1. ^{13}C-NMR data of selected carbons (in ppm.) of a number of α-Ferrocenylalkyl carbocations in Trifluoracetic acid medium at ambient temperature.

Carbonyl Compound	C^+	C_1	C_2	$\Delta^{13}C$*	Ref.
	156.9	99.8	82.2	57.1	6
	120.3	95.3	79.6	25.0	9
	165.9	98.8	80.0	67.1	
	145.6	92.4	77.3	53.2	
 †	144.5	99.3	79.9	45.2	
	142.1	94.2	80.6	47.9	
	164.2	97.2	81.2	67.0	
	165.8	99.6	80.8	66.2	
	158.4	99.5	81.2	58.9	
	118.4	105.3	81.8	13.1	6
$CH_3(CH_2)_5CHO$	122.3	104.6	81.3	17.7	
	132.3	102.9	79.9	29.4	
	123.7	101.5	82.7	22.2	

$\Delta^{13}C = \delta C^+ - \delta C_1$.

† Two isomers starting from the diastereomeric alcohols.

In conclusion, we have developed a mild and efficient procedure for the generation of long lived α-ferrocenyl carbocations in a one pot procedure by the reaction of aldehydes and ketones with ferrocene in trifluoroacetic acid medium.

Acknowledgement

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