

REACTIONS OF β - FERROCENYLALLYL CATIONS
 Henryk ŻMUDA

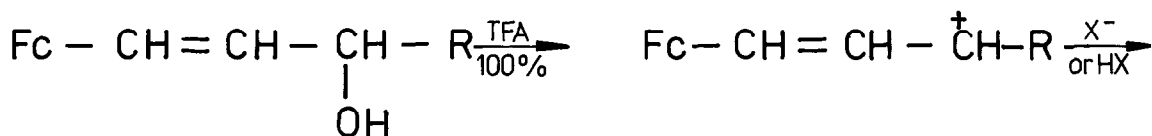
Department of Organic Chemistry, Silesian University
 40-006 Katowice, Szkolna 9, Poland

Summary: The formation of stable β - ferrocenylallyl cations which react with nucleophilic reagents yielding unrearranged products, was observed.

The unusual stability of 1-ferrocenylcarbonium ions is their very well known feature. It causes the non-typical course of the nucleophilic reactions involving the carbocations and is attributed to the diversity of ferrocene interactions¹.

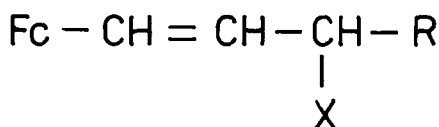
The range of the ferrocenyl substituent interaction seemed to be a very interesting problem. No interaction of such a character was found in β - ferrocenylalkyl alcohols². The earlier studies on 1-ferrocenyl-3-aryl cations have revealed the equilibrium between α -ferrocenylallyl and β -ferrocenylallyl cations³. Nesmeyanov et al⁴ came to the similar conclusions finding that the equilibrium is shifted towards the α - ferrocenylallyl cation.

This note presents preliminary results of the studies on carbocations formed from β - ferrocenylallyl alcohols, 1a and 1b, as well as their reactivity with nucleophilic reagents.



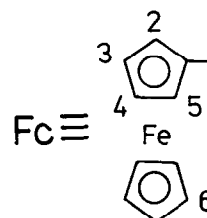
1

2



a) R = H

b) R = CH₃



A

The starting alcohols 1a and 1b were dissolved in 100% trifluoroacetic acid /TFA/ and the NMR spectra were determined at room temperature. It was found that the 2a and 2b carbocations are stable for several days. The NMR spectra for several cations are presented in Table I.

Table I. The PMR parameters of the β -ferrocenylallylcations
/ TFA, δ , ppm/

Carbo- cation	H ²	H ³	H ⁴	H ⁵	H ⁶	-CH=CH-	others
<u>2a</u>	4.25	5.78	6.02	4.75	4.52	6.20-7.10	5.85 / d, 2H, CH ₂ /
<u>2b</u>	4.18	5.55	5.75	4.70	4.38	6.50-7.25	1.60 / d, 3H, CH ₃ / 5.60 / m, 1H, CH/

Their structure, as well as chemical shifts of signals from protons indicate the location of the cation centre on the α -allyl carbon atom.

Dropwise adding of a suitable nucleophilic reagent to the 2a and 2b cations solution in TFA yielded several compounds, which have been identified after their separation by the preparative thin layer chromatography. The results of experiments were gathered in Table II.

No rearrangement products whatever were found and the analysis of the PMR spectra has revealed that the nucleophilic substitution occurs exclusively on the α -allyl carbon.

The thiosalicylic acid derivatives were desulphurized using mercuric chloride in the presence of a suitable nucleophilic reagent.

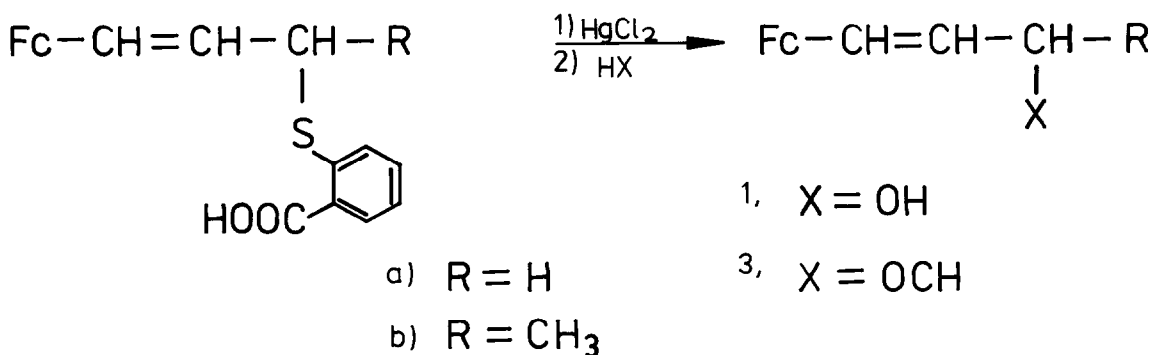
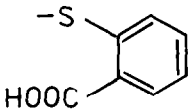
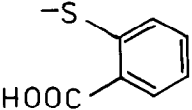


Table II. The physicochemical data of the investigated compounds

Compound <u>A</u>	-X	D a t a ^x
<u>1a</u>	-OH	PMR/ δ , ppm/: 1.85/s, 1H, OH/, 3.55/d, 2H, CH ₂ /, 4.05/s, 5H, C ₅ H ₅ Fe/, 4.15-4.40/m, 4H, C ₅ H ₄ Fe/, 6.20-6.85/m, 2H, CH=CH/, mp. 69-70°C, yield 97%.
<u>1b</u>	-OH	PMR: 1.29/d, 3H, J=6Hz, CH ₃ /, 1.96/s, 1H, OH/, 4.05/m, 6H, C ₅ H ₅ Fe+CH/, 4.15-4.40/m, 4H, C ₅ H ₄ Fe/, 5.62-6.38/m, 2H, CH=CH/, mp. 87-88°C, yield 98%.
<u>3a</u>	-OCH ₃	PMR: 3.32/s, 3H, OCH ₃ /, 4.00/m, 11H, C ₅ H ₄ FeC ₅ H ₅ +CH ₂ /, 5.50-6.40/m, 2H, CH=CH/, mp. 56°C, yield 92%, MS/ m/e, %/: M ⁺ 256/100/, 225/40.9/, 185/18.1/, 121/34.8/.
<u>3b</u>	-OCH ₃	PMR: 1.15/d, 3H, J=6Hz, CH ₃ /, 3.08/s, 3H, OCH ₃ /, 3.55/m, 1H, CH/ 3.85/s, 5H, C ₅ H ₅ Fe/, 3.95-4.10/m, 4H, C ₅ H ₄ Fe/, 5.15-6.10/m, 2H, CH=CH/, mp. 53°C, yield 93%, MS: M ⁺ 270/100/, 239/51.9/, 185/18.6/, 121/33.8/.
<u>4a</u>		PMR: 4.00/m, 9H, C ₅ H ₅ FeC ₅ H ₄ /, 4.15/d, 2H, CH ₂ /, 5.40-6.40/m, 2H, CH=CH/, 7.20/m, 4H, C ₆ H ₄ /, 11.0/s, 1H, COOH/, mp. 188°C, yield 80%, MS: M ⁺ 378/15.7/, 225/100/, 185/15.8/.
<u>4b</u>		PMR: 1.22/d, J=6Hz, 3H, CH ₃ /, 3.90/m, 1H, CH/, 4.00/s, 5H, C ₅ H ₅ Fe/, 4.10-4.20/m, 4H, C ₅ H ₄ Fe/, 5.25-6.20/m, 2H, CH=CH/, 7.15/m, 4H, C ₆ H ₄ /, 10.5/s, 1H, COOH/, mp. 118°C, yield 82%, MS: M ⁺ 392/9.6/, 239/100/, 218/95.0/, 185/15.6/.

^xThe results of the elemental analysis agree with the calculated ones

These reactions yielded alcohols 1a and 1b when water was used and respective methyl ethers 3a and 3b for the case of methanol. The reaction proceeds in a short time, in about 5 min, and at high yields of about 80%. In that case also no rearrangement products were found but slight amounts of dimerization and oxidation products. It was found that the reactions described above are a good method of preparation of δ -ferrocenylallyl derivatives.

The detailed interpretation of the NMR spectra of carbocations as well as their reactions with other nucleophilic reagents will be presented in the paper to be published.

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