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Preliminary communication

CARBON-13 MAGNETIC RESONANCE STUDIES ON THE FORMATION OF SECONDARY α-FERROCENYL CARBOCATIONS FROM TERTIARY CARBINOLS

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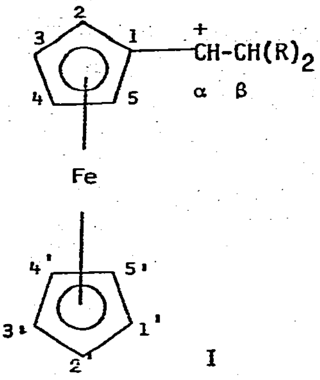
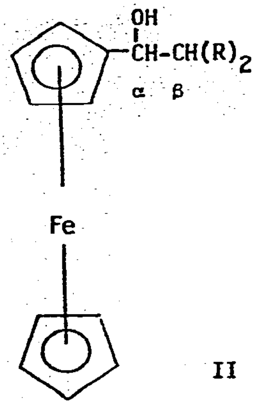
Summary

The same secondary ferrocenylisopropylcarbenium ion was formed from treatment with concentrated H_2SO_4 at 10°C of either ferrocenylisopropylcarbinol or ferrocenylmethyldimethylcarbinol and the same secondary ferrocenyldiphenylmethylcarbenium ion was obtained when either ferrocenyldiphenylmethylcarbinol or ferrocenylmethyldiphenylcarbinol was treated with CF_3COOH at 5°C. The results indicate the occurrence of 1,2-hydride shifts converting tertiary to secondary carbocations, thus providing a novel demonstration of the extraordinary stability of α-ferrocenyl substituted carbocations.

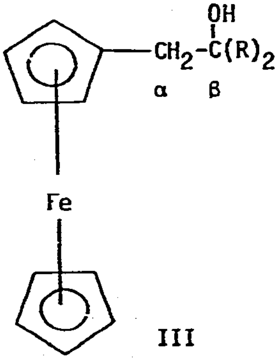
We wish to report the formation of the same secondary ferrocenylisopropylcarbenium ion (Ia) from either the secondary ferrocenylisopropylcarbinol (IIa) or the tertiary ferrocenylmethyldimethylcarbinol (IIIa), and the formation of the same secondary ferrocenyldiphenylmethylcarbenium ion (Ib) from either the secondary ferrocenyldiphenylmethylcarbinol (IIb) or the tertiary ferrocenylmethyldiphenylcarbinol (IIIb).



I



II



III

Ia, IIa, IIIa R = CH_3

Ib, IIb, IIIb R = C_6H_5

Data from the ^1H-decoupled ^{13}C NMR spectra of IIa, IIIa and carbenium ion Ia from treatment of either IIa or IIIa in concentrated H_2SO_4 at 10°C are summarized in Table 1. Braun, Abram and Watts [1] have recently reported the ^{13}C NMR spectrum of Ia generated from IIa in CF_3COOD. The present data for Ia and IIa (Table 1) are essentially identical to those observed by these workers [1]. It has been pointed out that the asymmetric center at C-α in IIa renders the C-2,5 and C-3,4 pairs of carbons diastereotopic, thus giving rise to five signals for the substituted cyclopentadienyl ring of IIa [1]. Similarly, the nonequivalence of the CH_3 groups of IIa is also due to the presence of the asymmetric center, a

TABLE 1

DATA FROM THE ^{1}H-DECOUPLED ^{13}C NMR SPECTRA OF FERROCENYLISOPROPYLCARBINOL (IIa), FERROCENYLMETHYLDIMETHYLCARBINOL (IIIa), AND THE FERROCENYLISOPROPYLCARBENIUM ION (Ia).

	Chemical Shifts, ppm[a]			
	IIa (Acetone-d_6)	IIa[b] ($CDCl_3$)	IIIa (Acetone-d_6)	Ia[b] (H_2SO_4)
C-1	93.7	93.4	85.4	104.7
C-2,5	66.1,68.3	64.9,68.9	68.0	81.4,82.1
C-3,4	67.7	67.6,67.9	70.8	95.1,95.6
C-1'-C-5'	69.1	68.3	69.1	82.1
C-α	75.2	75.1	45.7	133.4
C-β	36.3	34.9	---	35.5
CH_3	18.2,19.0	18.6,18.8	29.4	22.5,28.7

[a] Chemical shifts were measured from external TMS in a capillary tube which also contained some CD_3NO_2 as a locking compound in studies with Ia. [b] Essentially identical results were reported in ref. 1 for IIa in $CDCl_3$ and Ia in CF_3COOD.

finding that was first observed for asymmetric isopropylcarbinols by Roberts et al [2]. The C-2,5 and C-3,4 pairs of carbons and the CH_3 groups are also nonequivalent in carbocation Ia, and the origin of this nonequivalence has been attributed to a restricted rotation about the C-1—C-α bond in the α-ferrocenyl substituted carbocation [1,3]. The fact that tertiary carbinol IIIa also gave rise to Ia indicates the occurrence of a 1,2-hydride shift, converting the tertiary ferrocenylmethyldimethylcarbenium ion to the more stable α-ferrocenyl substituted secondary carbocation Ia.

In similar studies with IIb and IIIb, it was found that treatment of either of these alcohols with concentrated H_2SO_4 gave rise to extensive decomposition. Carbocation Ib, however, was obtained by dissolving IIb in CF_3COOH at 5°C. The data from the ^{13}C NMR spectra of IIb, IIIb and ion Ib are summarized in Table 2. When tertiary alcohol IIIb was treated with neat CF_3COOH, decomposition also

TABLE 2

DATA FROM THE ^1H-DECOUPLED ^{13}C NMR SPECTRA OF FERROCENYLDIPHENYLMETHYLCARBINOL (IIb), FERROCENYLMETHYLDIPHENYLCARBINOL (IIIb) AND THE FERROCENYLDIPHENYLMETHYLCARBENIUM ION (Ib).

	Chemical Shifts, ppm[a]		
	IIb (Acetone-d_6)	IIIb (Acetone-d_6)	Ib (CF_3COOH)
C-1	94.5	83.6	104.9
C-2,5	66.3,68.6	67.8	79.9,81.2
C-3,4	67.7	71.3	94.5,94.7
C-1'-C-5'	69.1	69.1	81.7
C-α	72.9	43.8	140.3
C-β	61.5	78.9	56.0[b]
Aromatic	126.8,128.7 129.7,130.1	127.0,128.3	124.3,127.8,128.2 129,5,130.0,130.5
Aromatic quaternary	143.7,144.3	148.7	----

[a] Chemical shifts were measured from external TMS in a capillary tube which also contained some CD_3NO_2 as a locking compound in studies with 1b. [b] Becomes a doublet in off resonance studies, indicating the presence of 1H at C-β.

occurred. Ion Ib was generated from IIb when CF_3COOH (about 10%) was added to a solution of IIb in $CDCl_3$ at 5°C and the ^{13}C NMR spectrum was recorded after a relatively short contact time (about 4000 scans) in order to minimize decomposition The identification of Ib as the secondary ferrocenyldiphenylmethylcarbenium ion is based on the general similarity of its ^{13}C NMR spectra with that of Ia, the nonequivalence of the C-2,5 and C-3,4 pairs of carbon atoms, and the fact that off resonance gave a doublet for the C-β absorption showing the presence of one H on this carbon. The formation of Ib from IIIb again indicates the occurrence of a 1,2-hydride shift converting the tertiary ferrocenylmethyldiphenylcarbenium ion to the secondary ferrocenyldiphenylmethylcarbenium ion.

The great stability of α-ferrocenyl substituted carbenium ions is well known. The early literature has been reviewed by Cais [4]. More recently, ^{13}C NMR [1,3] and other techniques [5-8] have been applied in studies of stable α-ferrocenylcarbenium ions. The present results show that instead of the usual rearrangement of secondary to tertiary carbocations, a reversal has taken place. Tertiary carbocations, including a diphenyl substituted tertiary cation, could undergo 1,2-shifts to give secondary carbocations containing an α-ferrocenyl substituent. These findings, therefore, constitute another, but rather novel, demonstration of the extraordinary stability of α-ferrocenyl substituted carbocations.

Acknowledgement

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