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REARRANGEMENTS AND HYDROGEN—DEUTERIUM EXCHANGE IN FERROCENYLCARBENIUM IONS

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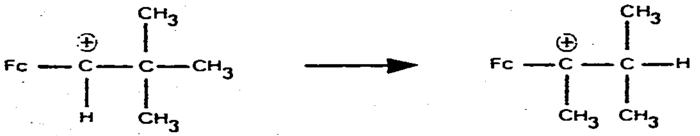
Summary

The rearrangement of the t-butyl group in t-butylferrocenyl carbenium ions (VI) and the hydrogen—deuterium exchange in the methyl group of methylferrocenyl carbenium ions (XVI) has been studied. The reaction rates depend on the size of the substituents at the carbenium ion center, an increase in the size of the substituents causing an increase in the rate. This effect is attributed, on the basis of the Gleiter and Cais models of ferrocenyl substituted carbenium ions, to increased steric hindrance between the substituents and the unsubstituted cyclopentadienyl ring.

Introduction

Ferrocenylcarbenium ions are quite stable in acidic solution. This has been explained by several models [1—3] in which the iron atom participates directly in the stabilization of the carbenium ion. The secondary ferrocenylcarbenium ion (I), however, was found [4] to rearrange quantitatively to the tertiary carbenium ion (II) in trifluoroacetic acid in 2 h at 70°C. When the isomerization was performed in deuterotrifluoroacetic acid, no hydrogen—deuterium (H—D) exchange was found in the migrating hydrogen atom.



$$\mathrm{Fc{-}\overset{\oplus}{C}H{-}C(CH_3)_3} \longrightarrow \mathrm{Fc{-}\overset{\oplus}{C}(CH_3){-}CH(CH_3)_2}$$

I II

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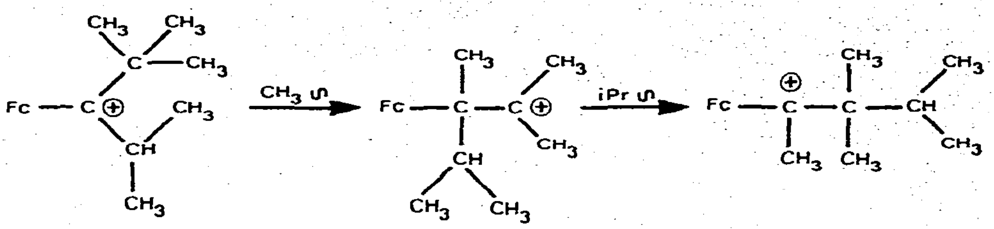
We found that the tertiary carbenium ion (III) rearranged quite rapidly to V in trifluoroacetic acid at room temperature. The reaction involves a sequential 1,2-methyl and 1,2-isopropylshift (III → V) *.



III IV V

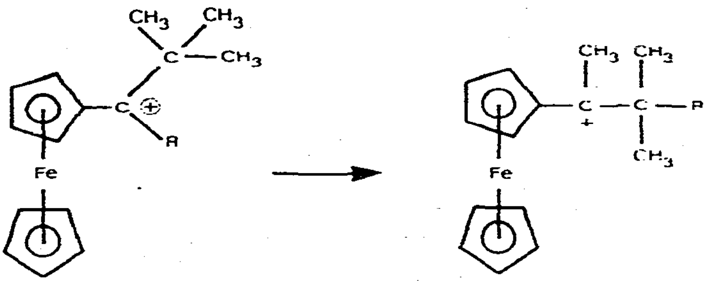
When the rearrangement of III was performed in deuterotrifluoroacetic acid, the methyl groups originating from the t-butyl group showed a rather fast H—D exchange, especially the methyl group directly bound to the carbenium ion center.

The fast rearrangement and the observed H—D exchange of III prompted us to investigate these reactions in some greater detail, especially in respect of the influence of the alkyl substituents at the carbenium ion center.

Results

The rearrangement

The rearrangement of the t-butyl group (VI → VII) was studied for a number of t-butyl ferrocenylcarbenium ions (VI) with R = H, Me, Et, i-Pr, t-Bu, cyclopropyl (cyclo-Pr), cyclobutyl (cyclo-Bu) and for the corresponding [3]-ferrocenophane carbenium ion (VIII). The reaction was followed most easily by NMR-spectroscopy. The signal of the t-butyl group disappears and three new signals of the α- and the two β-methyl groups appear. The signals of the two β-methyl groups are observed separately because these groups are diastereotopic due to chirality of the carbenium ion [5—7].



VI VII

With R = H or i-Pr the reaction proceeded quantitatively to VII, but with R = Et an equilibrium mixture was formed containing about 5% of the starting

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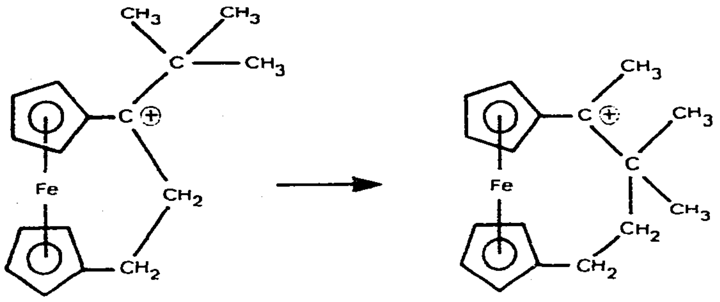
* The possibility of a 1,2-ferrocenyl shift in IV followed by a 1,2-methyl shift cannot be ruled out, and would lead to the same end-product, V. ^{13}C labeling and ^{13}C-NMR might distinguish between these two pathways.

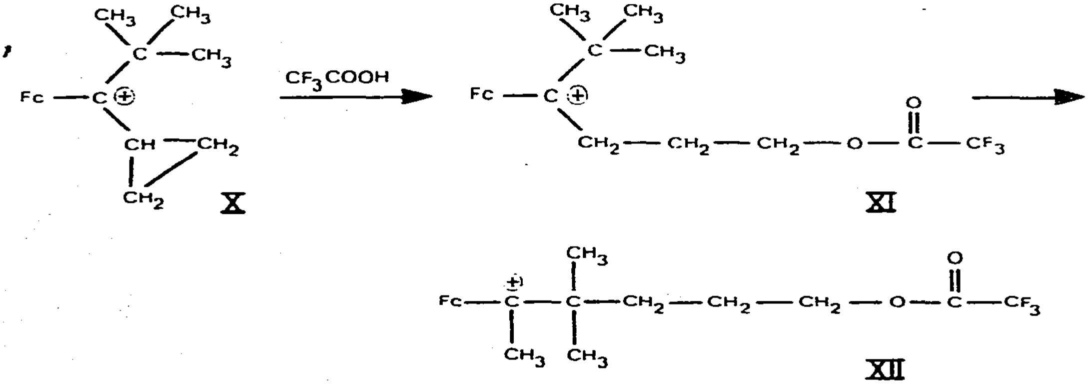
component. With R = t-Bu the carbenium ion VI could not be observed owing to a fast rearrangement to VII, followed by a rapid decomposition. The nature of the decomposition products and the mechanism for their formation, was described recently by Abram and Watts [8].

The reaction rate depended markedly on the steric bulk of R. With R = H or Et the reaction took several days at room temperature, but could be forced to completion by heating on a water bath for 1 h. With R = i-Pr the reaction was complete within 2 h at 35°C and could be followed by NMR spectroscopy. The signals from the unsubstituted cyclopentadienyl rings of III and V were separated by 4 Hz, and afforded the possibility of measuring the ratio of III and V by determining the peak heights. First order reaction kinetics were found up to 80% reaction, with a rate constant $k = 1.3 \times 10^{-3}$ sec^{-1}. With R = t-Bu the reaction was complete within 1 min, so the half-life of the reaction must be less than 15 sec, and consequently the rate constant $k > 4 \times 10^{-2}$ sec^{-1}. The rearrangement was found to be very fast also with the 6-t-butyl-[3]-ferrocenophan-6-carbenium ion VIII, because the 6,7,7-trimethyl-[4]-ferrocenophan-6-carbenium ion IX was detected only by NMR-spectroscopy after dissolving the corresponding alcohol in trifluoroacetic acid.

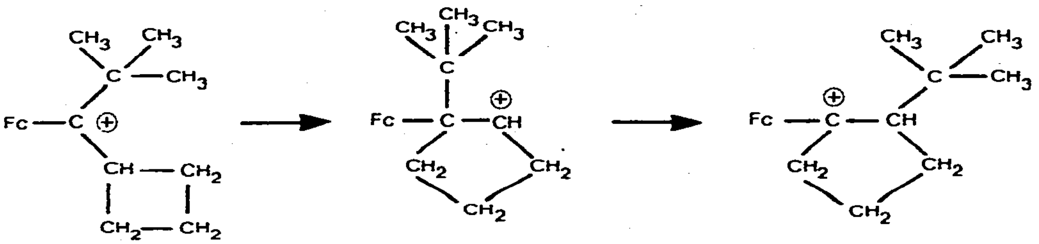


VIII IX

With R = cyclo-Pr or cyclo-Bu, ring opening and ring enlargement was the first observed reaction. It appeared that the cyclopropyl group was opened by addition of trifluoroacetic acid [9], yielding a trifluoroacetyl ester (XI). On ring opening an upfield shift of 3 Hz for the t-Bu signal and a downfield shift of 5 Hz for the ubsubstituted cyclopentadienyl ring was observed, while a signal at 4.50 ppm (triplet) of the ester methylene group appeared. IR spectros-



copy of the product after quenching in water, indicated the presence of an ester carbonyl function. A half-life of 10 min was found, which corresponds to $k = 1.1 \times 10^{-3}$ sec^{-1} for a psuedo first order reaction.
The rearrangement of the t-Bu-group (XI → XII) was very slow, and only 25% reaction was observed after 50 h at room temperature. ($k = 1.2 \times 10^{-6}$ sec^{-1}). When the carbenium ion VI with R = cyclo-Bu was prepared it was observed that the NMR spectrum was unchanged even after several days at room temperature, whereas we expected rearrangement of the t-butyl group at about the same rate as for R = i-Pr. Closer observation of the spectrum however revealed that the position of the t-butyl signal differed from signals of t-butyl groups bound to a carbenium ion center, viz. 1.00 and 1.47—1.57 ppm resp. From this we conclude that the t-butyl group was not bound to the carbenium ion center, and that ring enlargement of the cyclobutyl group had occured (XIII → XV). This enlargement is apparently extremely fast and complete on dissolving the alcohol in trifluoroacetic acid. ($k > 4 \times 10^{-2}$ sec^{-1}). This ring enlargement has been observed in a number of other cyclobutyl substituted carbenium ions [10].

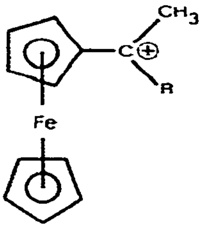


XIII XIV XV

The rearrangement rates of VI are summarized in Table 1.

Hydrogen—deuterium exchange

When rearrangement of III was performed in deuterotrifluoroacetic acid, the methyl groups originating from the t-butyl group showed a rather fast H—D exchange, especially the methyl group directly bound to the carbenium ion center. We therefore investigated the H—D exchange rates of the methyl group in a number of ferrocenyl carbenium ions XVI.



XVI

TABLE 1

R	H	Me	Et	i-Pr	t-Bu	cyclo-Bu	XI	VII
k[a]	$\sim 10^{-6}$	—	$\sim 10^{-5}$	1.3×10^{-3}	$>4 \times 10^{-2}$	—	$\sim 10^{-6}$	$>4 \times 10^{-2}$

[a] k in sec^{-1} at 35°C.

The H—D exchange in the methyl group was followed by NMR spectroscopy and it was found that the H—D exchange rate of the methyl group increased with increasing size of R.

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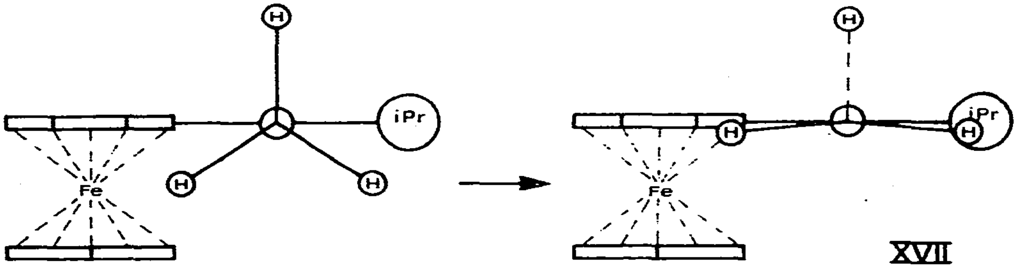
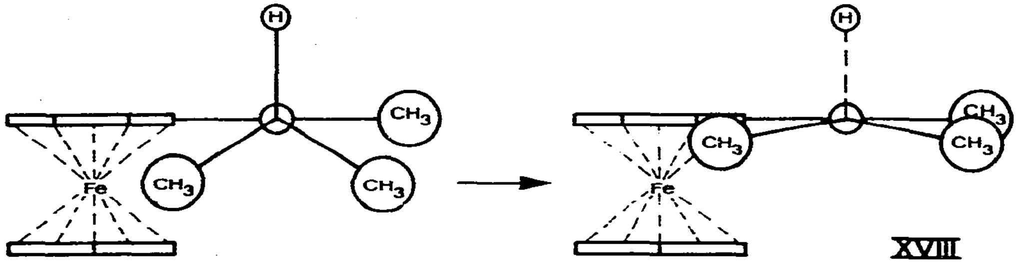
With R = Me or Et about 50% H—D exchange was found after 72 h at 35°C while with R = i-Pr or t-Bu the exchange could be followed by NMR spectroscopy. The reaction was followed by measuring the peak height of the methyl group, or by comparing the intensities of the methyl signal and the signal of the unsubstituted cyclopentadienyl ring. First order reaction kinetics were found up to about 60% reaction; beyond this the peak height was influenced too much by the H—D coupling in the methyl signal. The results are summarized in Table 2. With R = i-Pr not only H—D exchange was found with the methyl group, but also with the isopropyl methine proton, although the latter reaction proceeded considerably slower. This observation can be explained by assuming that the H—D exchange proceeds via a rate determinating elimination of a proton to an alkene, followed by a rapid reprotonation *. On formation of an alkene from the carbenium ion the proton will leave in exo-direction, to obtain a maximum overlap of the sp^3-orbital of the carbon—hydrogen bond and the empty p-orbital of the carbenium ion. This will result in the transition states XVII and XVIII for elimination into the CH_3 and i-Pr group, respectively.



XVII



XVIII

TABLE 2

R	H	Me	Et	i-Pr	t-Bu
k	—[a]	2.7×10^{-6}	3.1×10^{-6}	2.7×10^{-4}	1.9×10^{-3}

[a] It was found that this carbenium ion formed a green precipitate on standing in trifluoroacetic acid after ½—2 h.

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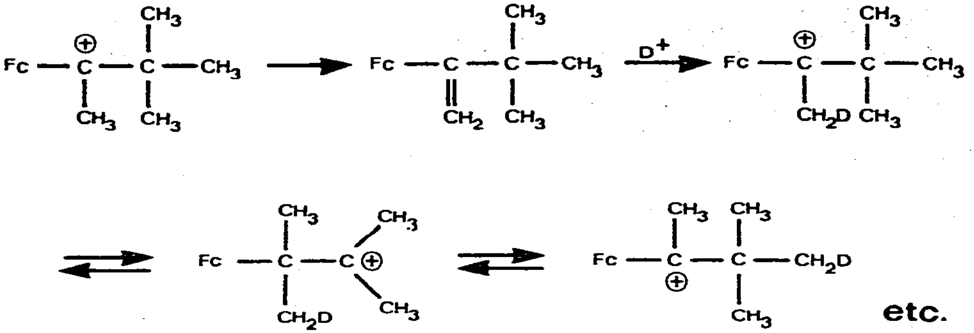
* The formation of ferrocenyl carbenium ions from alkenes is known to proceed quantitatively on dissolving the alkene in trifluoroacetic acid [11].

It appears that on reaching the transition state XVIII, serious steric repulsion between the isopropylmethyl group and H-2 of the cyclopentadienyl ring occurs, while in XVII this interaction is absent. This will raise the energy of XVIII in relation to XVII, and accounts for the difference of the rate in H—D exchange between the methyl group and the isopropyl methine proton *.

With R = t-Bu not only H—D exchange in the methyl group was found, but also in the t-butyl group, which can be explained easily by H—D exchange in the methyl group followed by a rearrangement involving sequential methyl and deuteromethyl shifts as shown in Scheme 1.



Experimental

The carbenium ions were prepared by dissolving the corresponding alcohols in distilled trifluoroacetic acid to a concentration of 0.1 g ml^{-1}. The alcohols were prepared by standard procedures involving Friedel—Crafts acylation of ferrocene and addition of the appropriate Grignard reagent or alkyllithium compound to the carbonyl bond. The [3]-ferrocenophane-1-on was prepared as described by Turbitt and Watts [13]. The general procedure is illustrated by the synthesis of ferrocenyl-cyclopropyl-t-butyl-carbinol.

Ferrocenylcyclopropylketone

To a solution of 28 g (0.15 mol) of ferrocene and 25 g (0.12 mol) of aluminium chloride in 100 ml of dry ether, a solution of 10 g (0.10 mol) of cyclopropanecarbonylchloride in 250 ml of ether was added at 0°C during 1 h. The mixture which was kept under nitrogen, refluxed for 3 h and then added to an icecold solution of ammonium chloride. The organic products were extracted with ether and the combined extracts washed with water, saturated sodium hydrogen carbonate solution, and water again, then dried on magnesium sulfate. After evaporation of the solvent, the residue was chromatographed on a silica column. The unreacted ferrocene was eluted with petrol ether and the ketone with a 1 : 1 mixture of toluene and ether. The product was recrystallized from petrol ether. Yield 4.0 g (16%). M.p. 63—64°C. Mass spectrum $M^{+} = 254$.

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* Kieboom and van Bekkum [12] studied the acid-catalyzed dehydration of 2-aryl-3-methyl-2-butanols and found a kinetic preference for elimination into the methyl group, which was explained similarly. They estimate an energy difference of 1 kcal mol^{-1} between the two transition states.

Ferrocenyl-cyclopropyl-t-butylcarbinol.

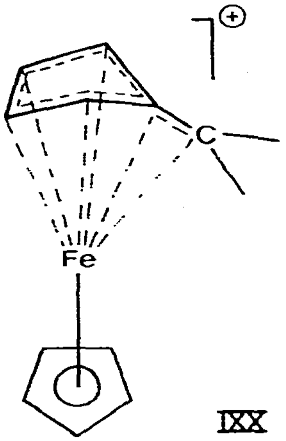
To a stirred solution of 4.0 g (0.02 mol) of ferrocenylcyclopropylketone in 200 ml of n-pentane was added 64 ml of 0.7 *M* t-butyllithium in n-pentane. The mixture was kept at 0°C under nitrogen for 30 min and then added to ice. The organic products were extracted with n-pentane and the extract was washed with 5% $NaHCO_3$, satd. NaCl solution and water. After drying over $MgSO_4$, the solvent was evaporated and the product chromatographed on a silica column with toluene as the eluent. Yield: 1.9 g (39%). M.p. 98—99°C. Mass spectrum $M^{+} = 312$. IR $\nu(OH) = 3560\ cm^{-1}$.

The purity and the identity of the compounds was checked by thin-layer chromatography and NMR, mass spectrum and IR spectroscopy.

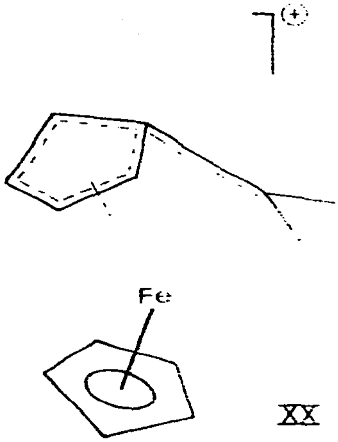
Discussion

The rearrangement and the H—D exchange have in common that the rate increases with increasing steric bulk of the substituents at the carbenium ion center. In other words there is a decrease of the stability of the carbenium ion with increase of the bulk of the substituents.

This influence can be rationalized on the basis of the Cais (IXX) [2] or Gleiter (XX) [3] model for the ferrocenyl carbenium ion. In both models the main factor influencing the stability of the carbenium ion is the bending of the carbenium ion center towards the iron atom. The amount of this movement is not known for the different ferrocenylcarbenium ions. Gleiter calculated an angle of 40° between the plane of the cyclopentadienyl ring and the plane of the carbenium ion center for the ferrocenylmethylcarbenium ion. In two X ray crystallographic studies [14,15] angles of 14.6° and 19.9° were found. In both carbenium ions, however, extra stabilizing effects can be expected, making an angle of 40° more realistic for ferrocenylalkylium ions.



IXX



XX

When the bulk of the substituents of the carbenium ion increases, this will result in an increasing interaction of the substituents and the unsubstituted cyclopentadienyl ring. Evidence for an interaction between a substituent of the carbenium ion and a substituent on the second cyclopentadienyl ring has been found by Turbitt and Watts [16,17] in the NMR spectrum of the 1′-methyl-t-butyl-ferrocenylethylium ion. This interaction will result in a smaller movement of the carbenium ion towards the iron atom and in a decreased stabilization of the carbenium ion by the decreased overlap of the empty *p*-orbital and the iron *d*-orbitals. As a result the positive charge of the carbenium ion center will increase with increasing alkyl substitution. The positive charge on a carbon atom can be correlated with the ^{13}C chemical shift and we measured therefore a number of ^{13}C NMR spectra [18] of different ferrocenylcarbenium ions and found an increase in the ^{13}C chemical shift of the C atom of the carbenium ion center with increasing steric demands of the alkyl substituents. The same observation was made in a number of recent determinations of ^{13}C NMR spectra of ferrocenylcarbenium ions [19,20].

It is therefore concluded that the driving force for the rearrangement reaction is a decrease in the steric repulsion between the alkyl substituents of the carbenium ion center and the unsubstituted cyclopentadienyl ring, which will result in a stabilization of the rearranged carbenium ion. In this respect it is interesting to note that calorimetric measurements of the heat of formation of some ferrocenylcarbenium ions indicate that methyl substitution destabilizes the cation [21].

The very rapid rearrangement of VIII can be explained by the bad overlap of the empty *p*-orbital and the iron-*d*-orbitals due to internal strain, which results in a low stability of the carbenium ion. This low stability of the [3]-ferrocenophane-6-carbenium ion is evident also from its lower pK_{R^+} in comparison to that of the unbridged ferrocenyl carbenium ions [22,23].

Acknowledgement

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