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THE ELECTROPHILIC SUBSTITUTION OF FERROCENE BY PROTONATED CARBONYL COMPOUNDS

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Abstract—The α-ferrocenylalkyl carbenium ions are formed from ferrocene and carbonyl compounds in strongly acidic media, in particular mixtures of fluorosulfuric acid and trichloroacetic acid. The α-ferrocenylalkyl carbenium ions are scavenged by nucleophiles or bases. The addition of nucleophiles produces the corresponding α-substituted ferrocenyl alkanes. Proton abstraction by base from the β-position leads to the ferrocenylethene derivatives.

Such electrophilic substitutions of ferrocene by carbonyl compounds, followed by suitable scavengeing of the α-ferrocenylalkyl carbenium ion, form the basis of one-pot syntheses of various ferrocene derivatives.

The chemistry of the α-ferrocenylalkyl carbenium ions and their related compounds has drawn the attention of a large number of investigators in the recent past.

The electronic and geometric structural features of the α-ferrocenylalkyl carbenium ions, as well as their chemical and stereochemical behaviour have been active topics of research for the past two decades.[1] The α-ferrocenyl alkylamines undergo a variety of interesting and unusual reactions, and some of them have a uniquely favorable combination of properties contributing to their ability to induce asymmetrically as chiral templates.[2] These are just a a few of the reasons for developing convenient, economical and widely applicable synthetic methods for the α-ferrocenylalkane derivatives.

In this article we describe the synthesis of α-ferrocenylalkyl carbenium ions from ferrocene and carbonyl compounds, as well as the conversion of the α-ferrocenylalkyl carbenium ions into a variety of desirable ferrocene derivatives.

The reactions of ferrocene with carbonyl compounds has hitherto been studied only under the aspect of generating macromolecules to be used in coating materials.[3] The formation of "oligomeric" products from ferrocene and carbonyl compounds in the presence of Friedel–Crafts catalysts or protic acids has also been reported.[4] Since some "monomeric" one-to-one adducts have also been observed as products of such reactions,[3,5] it is likely that α-ferrocenylalkyl carbenium ions are involved in these reactions.

We succeeded in finding conditions under which the α-ferrocenylalkyl carbenium ions are directly formed, in generally good yield, from ferrocene and carbonyl compounds. These reactions can be studied by NMR-methods, and their products are useful for syntheses.[6] The compounds thus obtained, such as the α-ferrocenyl alkylamines, are valuable intermediates or auxiliarly materials for various syntheses, in particular the syntheses of peptide derivatives by asymmetrically induced four-component condensations.[2b]

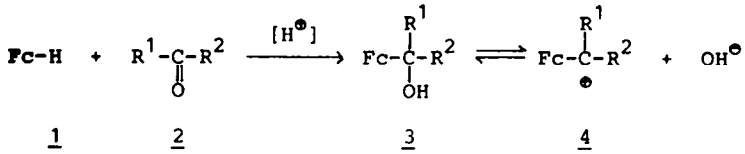
Formation of the α-ferrocenylalkyl carbenium ions

The components and their reactivity. In strongly acidic media ferrocene and carbonyl compounds react to form α-ferrocenylalkyl carbenium ions according to Scheme 1. Trifluoroacetic acid (TFA) and trichloroacetic acid (TCA) are suitable as acidic solvents. The particular solvating properties of TFA have been discussed recently;[7] these and the low basicity/nucleophilicity of TFA are certainly essential for the stabilization of carbenium ions by TFA. At $-20°$ to $+20°$ the presence of fluorosulfuric acid (FSA) is needed to enforce the reaction of ferrocene with ketones in TFA or TCA as the solvent, whereas with the more reactive aldehydes the reaction according to Scheme 1 is also observed in the absence of FSA, although the yield of **4** is generally low.

The sterically hindered ketones react very slowly, and the extent of side reactions is often appreciable, such as oxidative destruction of the ferrocene system by trichloroacetic acid.[8]

It is noteworthy that ferrocene is only monosubstituted by the protonated carbonyl compounds; the α-ferrocenylalkyl carbenium ions seem to be stable against electrophilic substitution under the chosen conditions, since no formation of disubstitution products has been observed.

Steric factors. In comparing the substitution of ferrocene by protonated carbonyl compounds with the Friedel–Crafts acylation by acid chlorides, one is led to



Scheme 1.

expect that the relative free energies of the transition states **5** will significantly depend on the steric bulk of the carbonyl components **2**. The aldehydes (**2**, $R^1 = H$, R^2 = Alkyl, Aryl) are sterically less bulky than the acid chlorides (**2**, $R^1 = Cl$, R^2 = Alkyl, Aryl) and the relative reactivity of the protonated aldehydes towards ferrocene is only weakly dependent upon the steric bulk of R^2, while the reactivity of the protonated ketones decreases significantly with increasing size of R^1 and R^2. The acylic alkanals, including pivalic aldehyde (2,2-dimethylpropanal), react smoothly with ferrocene in acidic media. Among the alkanones, only those of the general type

$$R^1\text{–}CH_2\text{–}CO\text{–}CH_2\text{–}R^2$$

(R^1, R^2 = H, Alkyl, Aryl)

react in a satisfactory manner; 1-cyclohexylethanone and 3-methylbutanone-(2) are already too bulky to react. The diaryl ketones, e.g. benzophenone, do not react with ferrocene in acidic media. The behaviour of the aryl alkyl ketones vs ferrocene is shown in Table 1. Apparently, minor structural changes in the alkyl aryl ketones have drastic effects upon their reactivity.

In cyclic ketones the ability to react with ferrocene in acidic media does not follow a simple pattern, except that cyclohexanone derivatives seem to be more reactive than other cyclic ketones, presumably for conformational reasons ("I-strain").[9]

The results are summarized in Table 2.

Electronic influences. From the ^{13}C-NMR spectra of the carbenium ion **4**[10]

Fc—CH—R
⊕
4

4a R = H
4b R = CH_3
4c R = C_6H_5

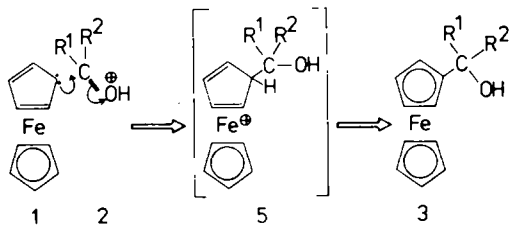
it is known that the density of the positive charge at the carbenium C increases as a function of R in the direction

4a < 4b < 4c.

Thus, the α-aryl-α-ferrocenyl carbenium ions, in particular those with electron withdrawing substituents, are less stable than the α-alkyl-α-ferrocenyl carbenium ions. Accordingly, benzaldehydes with electron withdrawing substituents only form oligomeric products, while the amount of monomeric product formed in the reaction increases if electron donating substituents are present in the benzene ring. This is due to the fact that the carbenium ions are stabilized by a benzene ring with electron donating substituents, and are thus less prone to side reactions. Table 3 shows the results obtained with a variety of substituted benzaldehydes.

Side reactions by other functional groups. Nitro and polyhalogenated carbonyl compounds (with the exception of the fluorinated compounds), e.g. chloral or hexachloroacetone, act as oxidizing agents and destroy the ferrocene system. Hexafluoroacetone is unreactive under the chosen conditions.

Unsaturated carbonyl compounds and carbonyl compounds with hydroxyl groups that are capable of being



Scheme 2

Table 1. Reactivity of the alkyl aryl ketones $R^1\text{–}\underset{\underset{O}{\|}}{C}\text{–}R^2$ vs ferrocene in acidic media (+ = reaction, – = no reaction)

R^1	R^2		R^1	R^2	
C_6H_5	CH_3	+	C_6H_5	C_2H_5	+
C_6H_5	CF_3	–	C_6H_5	$CH_2C_6H_5$	+
CH_3	2-naphthyl	–	CH_3	3-methoxy-	+
CH_3	ferrocenyl	–		phenyl	
CH_3	2-chlorophenyl	+	CH_3	4-chlorophenyl	+
CH_3	2-bromophenyl	–	CH_3	4-bromophenyl	+

Table 2. Reactivity of some cyclic ketones vs ferrocene in acidic media (+ = reaction; – = no reaction or very slow reaction)

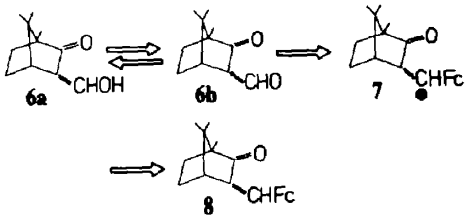
Ketone		Ketone	
cyclopentanone	–	cyclohexanone	+
cycloheptanone	–	cyclododecanone	–
2-methylcyclohexanone	+	2,6-dimethylcyclo-	–
1-tetralone	–	hexanone	
bicyclo[2.2.1]heptan-	–	3-cholestanone	+
2- one			

Table 3. The effect of substituents (R^1–R^5) on the reactivity of benzaldehydes (+ = prevailent formation of monomeric products; (+) = monomeric products isolated in low yields; – = formation of oligomeric products only)

R^1	R^2	R^3	R^4	R^5	
H	H	H	H	H	(+)
Cl	H	H	H	H	–
H	NO_2	H	H	H	–
H	H	CN	H	H	–
H	H	CH_3	H	H	(+)
H	H	OCH_3	H	H	+
H	H	OH	H	H	+
CH_3	H	CH_3	H	H	(+)
CH_3	H	CH_3	H	CH_3	+
H	OCH_3	OCH_3	OCH_3	H	+

eliminated under the reaction conditions lead to oligomeric or polymeric products (e.g. 2-butenal, 4-methyl-3-pentenone-(2), dihydrotestosterone, glucose).

The dicarbonyl compounds and the ketocarboxylic acids and their derivatives are either totally inert or react to form hard-to-separate mixtures of products (e.g. 2-oxopropanoic acid, 2,3-butane-dione, 2,4-pentane-dione, 2,5-hexane-dione, 1,3-diphenyl-1,3-propane-dione etc.). If however, a carbonyl group is sterically too hindered to react with ferrocene, its presence will not influence the reactivity of other carbonyl groups. Such is the case in 3-(hydroxymethylene-1,7,7-trimethylbicyclo[2.2.1]-heptanone-(2), which reacts like a "normal" aldehyde, probably via the aldehyde form **6b**:



Scheme 3

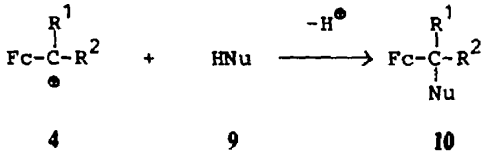
The resulting carbenium ion **7** has a high tendency to deprotonate to form a double bond which is in conjugation with the CO group.

Secondary reactions of the α-ferrocenyl carbenium ions

Deprotonation. Those α-ferrocenylalkyl carbenium ions with β-protons are deprotonated by bases to form the corresponding α-ferrocenyl alkenes (Table 4).

In all cases the "Saytzeff" product is formed preferentially. This occurs because the resonance stabilized α-ferrocenylalkyl carbenium ions are too low in free energy to form the thermodynamically less stable "Hoffmann" products.[11] The reaction of 2-methylcyclohexanone with ferrocene leads to a carbenium ion whose deprotonation leads to both the "Saytzeff" and the "Hoffmann" products in the proportion 1.2:1, according to ^{1}H-NMR.

Scavengeing of the α-ferrocenyl alkyl carbenium ions by nucleophiles. The α-ferrocenylalkyl carbenium ions react with a variety of nucleophiles according to Scheme 4 to form ferrocenyl alkane derivatives.



4 **9** **10**

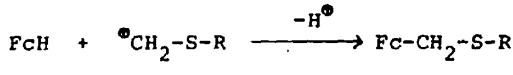
Scheme 4.

Among the nucleophiles whose reactions with the α-ferrocynyl alkyl carbenium ions have been studied (ammonia, prim. and sec. amines, hydroxylamine, hydrazine and derivatives, cyanide, acids, water, alcohols, phenols), mercaptans, ammonia and the amines have received most attention.

Mercaptans as nucleophiles. Thioglycolic acid seems to have some particular affinity towards the α-ferrocenylalkyl carbenium ions. In contrast to other nucleophiles, it reacts with those ions in media that are sufficiently acidic to suppress deprotonation, the most prevalent side reactions of the scavengeing reaction by nucleophiles. The reactions of the α-ferrocenylalkyl carbenium ions with thiogylcolic acid have been studied extensively, in particular because this reaction has been shown to be synthetically useful.[13]

Table 5 contains a survey of the reactions involving the condensation of ferrocene with carbonyl compounds and subsequent scavengeing of the formed α-ferrocenylalkyl carbenium ions by mercaptans.

Recently Ratajczak and Misterkiewicz reported the formation of ferrocenylmethylsulfane derivatives from ferrocene, formaldehyde and mercaptans.[15] These authors proposed a mechanism according to Scheme 5 for this reaction, a mechanism which is similar to the aminomethylation of ferrocene.[16]



1 **12** **11**

Scheme 5.

The authors introduced the term "thiomethylation" for this reaction, a term which would be justified if the reaction took place as indicated in Scheme 5. However, the above reaction is more likely to begin with an electrophilic substitution of the ferrocene by a protonated carbonyl compound to form the ferrocenylmethyl carbenium ion which is scavenged by the mercaptan, in analogy to our results.

Our investigations have not produced any evidence that the mercapto carbenium ions **12** are capable of attacking ferrocene as electrophiles. For instance, a TFA solution of ferrocene and **13** does not undergo a significant reaction at room temperature, despite the protonation of **13**.

$$Me_2C{=}CH{-}S{-}CH_2{-}CO_2H$$

13

Table 4. The synthesis of ferrocenyl alkenes by condensing a carbonyl compound with ferrocene and subsequent deprotonation

carbonyl compound	compound no.	alkene	yield (%)	mp. (C°)	reference
3-(hydroxymethylene)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one	8	3-(ferrocenylmethylene)-1,7,7-trimethylbicyclo-[2.2.1]heptan-2-one [a]	66	109-111	-
2-methylpropanal	16	1-ferrocenyl-2-methyl-1-propene	81	-	12
(methoxymethylene)-cyclopentane	17	(ferrocenylmethylene)-cyclopentane	52	-	-
bicyclo[2.2.2]octane-2-carbaldehyde	18	2-(ferrocenylmethylene)-bicyclo[2.2.2]octane	73	77-78	-
1-phenylpropan-2-one	19	(E)-1-phenyl-2-ferrocenyl-1-propene	66	69-68.5	-
4-methylpentan-2-one	20	(E)-2-ferrocenyl-4-methylpentene-(2)	65	28.5-30	-
1-phenylpropan-1-one	21	1-phenyl-1-ferrocenyl-1-propene	64	-	5a
1,2-diphenylethanone	22	1-ferrocenyl-1,2-diphenylethene	63	117-118	-
cyclohexanone	23	1-ferrocenylcyclohexene	95	67-68	5a
2-methylcyclohexanone	24a	1-ferrocenyl-2-methylcyclohexene	30 [c]	-	-
	24b	2-ferrocenyl-3-methylcyclohexene	25 [c]	-	-
3-cholestanone	25	3-ferrocenylcholestene-(2) [b]	60	176-178	-

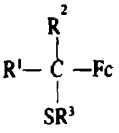
[a] $[\alpha]_D^{23} = -120.8^\circ$ (c = 1.0; benzene)

Racemic product: mp. 129-131°C

[b] For purification, the crude product is dissolved in benzene and precipitated with methanol; $[\alpha]_D^{22} = +21.6^\circ$ (c = 1.6; benzene)

[c] 24a and 24b were not separated.

Table 5. The synthesis of α-ferrocenylalkylsulfanes **11**



11

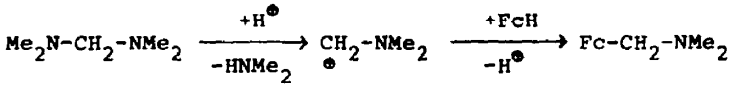
compound no.	R^1	R^2	R^3	yield (%)	mp. (°C)	reference
26	H	iPr	$-CH_2CO_2H$	71	82-84	13b; 13c
27	H	cHex	$-CH_2CO_2H$	66	92.5-94	14
28	H	H	$-CH_2CO_2H$	15 [a]	123-125	13c
29	$-(CH_2)_5-$		$-CH_2CO_2H$	62 [b]	123-125	-
30	H	cHex	$-CH_2C_6H_5$	42	84-85	-
31	H	4-methoxy-phenyl	$-(CH_2)_2OH$	35	-	-
32	H	3,4,5-tri-methoxy-phenyl	$-(CH_2)_2OH$	37	-	-
33	H	tBu	2-benzothia-zolyl	75	116-118	-
55	CH_3	2-chloro-phenyl	$-CH_2CO_2H$	55	128-130	-
56	H	tBu	$-CH_2CO_2CH_3$	74	62-64	-
57	H	tBu	$-CH_2CO_2C_2H_5$	70	51-53	-
58	CH_3	C_2H_5	$-C_6H_4-2-CO_2H$	51	80-82	-

[a] Preparation of the carbenium ion: Only 0,5 ml of fluorosulfuric acid were used (see exp. part.); reaction time: 15 minutes at -20°C.

[b] In addition to 13% 1-ferrocenylcyclohexene.

Ammonia and amines as nucleophiles. Dimethylamino methylferrocene can be prepared by condensation of ferrocene with bis-(dimethylamino)methane **14** in a suitable acidic medium (Scheme 6).[16]

An electrophilic substitution of ferrocene by the iminium ion **15**, a characteristic intermediate of the Mannich reactions, is here the essential step. According to a recent study of the present authors, no iminium ions

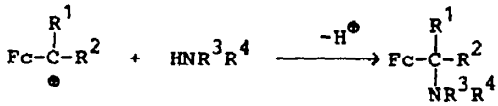


14 **15**

Scheme 6

which are less reactive than **15** are capable of electrophilically substituting ferrocene. Accordingly, it seems unlikely that general methods for the synthesis of he α-ferrocenylalkylamines will be found which are based on Mannich-type condensations. As we have found recently, the α-ferrocenylalkylamines can generally be synthesized from the α-ferrocenylalkyl carbenium ions by the addition of ammonia or suitable amines according to Scheme 7 (see Table 6).[6b]

Since the α-ferrocenylalkyl carbenium ions are formed from ferrocene and carbonyl compounds, this synthesis



Scheme 7

Table 6. The synthesis of α-ferrocenylalkylamines from ferrocene, carbonyl compounds and amines, via the α-ferrocenylalkyl carbenium ions

compound no.	R^1	R^2	R^3	R^4	[a]	yield (%)	mp. (°C)	reference
34	H	Me	H	Me	15	31	-	17
35	H	Me	Me	Me	13	62	-	18
36	H	Me	H	iPr	30	42	-	6b
37	H	iPr	H	H	25	32	-	13b
38	H	iPr	H	Me	15	37	51.5-52	6b
39	H	iPr	Me	Me	13	50	-	13b
40	H	iPr	H	iPr	30	40	79-80	6b
41	H	iPr	$-(CH_2)_5-$		30	51(*)	64-66	-
42	H	iPr	$-(CH_2)_2-O-(CH_2)_2-$		30	59(*)	75.5-76.5	6b
43	H	tBu	H	H	25	57	67-68	14
44	H	tBu	H	Me	15	74	114-115	6b
45	H	tBu	Me	Me	13	80	41-42	6b
46	H	tBu	H	Phe	40	36(*)	74.5-75.5	6b
47	H	tBu	H	tBu	35	36	53-54	6b
48	H	tBu	$-(CH_2)_5-$		30	68(*)	103-104	6b
49	H	tBu	$-(CH_2)_2-O-(CH_2)_2-$		30	59(*)	79.5-80	6b
50	H	tBu	1-imidazolyl	H	[b]	33(*)	136-139	-
51	H	cHex	H	H	25	40	88.5-89	14
52	H	cHex	H	Me	15	37	98.5-99	6b
53	H	cHex	CH_2Phe	H	30	60(*)	94-95	6b
54	H	2,6,6-trimethyl-3-bicyclo [3.1.1] heptyl	H	H	25	29(*)	73-75	-

(*) See experimental procedure.

[a] Amount of amine (g); (see experimental procedure).

[b] The solution of the carbenium ion is introduced dropwise into a vigorously stirred solution of 4.0 g imidazole in 20 ml 2-propanol and 12 g trietylamine at -78°C.

Table 7. Analytical data of new compounds

compound no.	formula	calculated [%]			found [%]		
		C	H	N	C	H	N
8	$C_{21}H_{24}FeO$	72.42	6.95	-	72.40	6.97	-
17	$C_{16}H_{18}Fe$	72.20	6.82	-	71.79	7.08	-
18	$C_{19}H_{22}Fe$	74.52	7.24	-	74.73	7.46	-
19	$C_{19}H_{18}Fe$	75.52	6.00	-	75.66	6.15	-
20	$C_{16}H_{20}Fe$	71.66	7.52	-	71.05	7.85	-
22	$C_{24}H_{20}Fe$	79.14	5.53	-	79.15	5.60	-
25	$C_{37}H_{54}Fe$	80.12	9.81	-	80.05	9.86	-
27	$C_{19}H_{24}FeO_2S$	61.30	6.50	-	61.05	6.32	-
29	$C_{18}H_{22}FeO_2S$	60.43	6.19	-	60.12	6.27	-
30	$C_{24}H_{28}FeS$	71.28	6.98	-	71.22	6.84	-
31	$C_{20}H_{22}FeO_2S$	62.84	5.80	-	62.10	5.53	-
32	$C_{22}H_{26}FeO_4S$	59.73	5.92	-	59.21	5.61	-
33	$C_{22}H_{23}NFeS_2$	62.71	5.50	3.32	62.65	5.55	3.36
36	$C_{15}H_{21}FeN$	66.44	7.81	5.16	66.19	8.15	5.16
38	$C_{15}H_{21}FeN$	66.44	7.81	5.16	66.31	8.09	5.17
40	$C_{17}H_{25}FeN$	68.24	8.42	4.68	68.45	8.59	4.63
41	$C_{19}H_{27}FeN$	70.16	8.37	4.31	69.98	8.40	4.19
42	$C_{18}H_{25}FeNO$	66.07	7.70	4.28	66.16	8.08	4.05
43	$C_{15}H_{21}FeN$	66.44	7.81	5.16	66.56	7.87	4.98
44	$C_{16}H_{23}FeN$	67.38	8.13	4.91	67.37	8.09	4.97
45	$C_{17}H_{25}FeN$	68.24	8.42	4.68	68.41	8.47	4.73
46	$C_{21}H_{25}FeN$	72.63	7.26	4.03	72.65	7.54	3.92
47	$C_{19}H_{29}FeN$	69.73	8.93	4.28	69.77	8.93	4.17
48	$C_{20}H_{29}FeN$	70.80	8.61	4.13	70.79	8.85	4.25
49	$C_{19}H_{27}FeNO$	66.87	7.97	4.10	67.03	8.10	3.82
50	$C_{18}H_{22}FeN_2$	67.09	6.88	8.69	66.85	7.08	8.41
51	$C_{17}H_{23}FeN$	68.70	7.80	4.71	68.53	7.68	4.62
52	$C_{18}H_{25}FeN$	69.46	8.10	4.50	69.70	8.36	4.47
53	$C_{24}H_{29}FeN$	74.42	7.55	3.62	74.44	7.57	3.73
54	$C_{21}H_{29}FeN$	71.80	8.32	3.99	71.58	8.60	4.11
55	$C_{20}H_{19}ClFeO_2S$	57.92	4.62	-	58.04	4.67	-
56	$C_{18}H_{24}FeO_2S$	60.01	6.71	-	59.79	6.74	-
57	$C_{19}H_{26}FeO_2S$	60.97	7.00	-	60.69	7.07	-
58	$C_{21}H_{22}FeO_2S$	63.97	5.62	-	63.61	5.51	-

of the α-ferrocenylalkylamines corresponds overall to the Mannich condensation. Note that here the mechanistic roles of the amine and the ferrocene are reversed vs the Mannich condensation.[19]

EXPERIMENTAL

Synthesis of the α-ferrocenylalkyl carbenium ions from ferrocene and carbonyl compounds

General procedure. 1.86 g (10 mmol) ferrocene and 20 mmol carbonyl compound (or its enol ether or acetal) were dissolved by stirring into a mixture of 10.0 g TCA and 1.5 ml AcOH under N_2. At −10°, 1.5 ml fluorosulfuric acid were added. The mixture was allowed to react at −10 to 0° for 20 to 45 min, the time depending on the reactivity of the carbonyl compound.

Preparation of the ferrocenylethene derivatives (*Table* 4). The soln of the carbenium ion was made alkaline by 30% NaOH aq and diluted with 100 ml water and 100 ml CH_2Cl_2. The organic layer was dried with Na_2SO_4. After removal of the solvent, the residue was purified by recrystallisation from hexane or by chromatography.

Preparation of the α-ferrocenylalkylsulfane derivatives (*Table* 5). To the soln of the carbenium ion 40 mmol of the mercaptan was added. Stirring was continued for 15 min at 0°. Then the mixture was slowly neutralized with satd Na_2CO_3 aq. 200 ml CH_2Cl_2 was added, and the organic layer separated. Products containing carboxylic groups were purified by extracting the organic layer with 10% NaOH aq and treating the extracts with H_2SO_4 until the product separated. This was dissolved in CH_2Cl_2, dried with Na_2SO_4 and, after removal of the solvent, recrystallized from

Table 8. ^{1}H-NMR-data of new compounds (spectra recorded at 60 MHz, δ-values (ppm) given. Internal standard: TMS. compounds **8**, **55**, **56**, **57**, **58** in $CDCl_3$, other compounds in CCl_4)

compound no.	δ(intensity; multiplicity)
8	0.80(3;s) 0.93(3;s) 0.97(3;s) 1.31-1.78(4;m) 2.92(1;d) 4.05(5;s) 4.27(2;m) 4.32(2;m) 6.90(1;s)
17	1.77(4;m) 2.38(4;m) 4.04(5;s) 4.19(4;m) 6.05(1;m)
18	1.63(8;m) 1.85(1;m) 2.14(1;m) 2.43(2;m) 4.03(5;s) 4.11(2;m) 4.28(2;m) 5.88(1;m)
19	2.07(3;d) 3.97(5;s) 4.07(2;m) 4.30(2;m) 6.58(1;m) 7.15(5;m)
20	0.97(6;d) 1.90(3;d) 2.25-2.75(1;m) 3.94(5;s) 4.04(2;m) 4.21(2;m) 5.39(1;m)
22	4.07(5;s) 4.18(4;m) 5.10(1;s) 7.00-7.20(10;m)
25	0.50-2.20(44;m) 3.86(5;s) 3.94(2;m) 4.12(2;m) 5.65(1;m)
27	0.89-2.07(10;m) 3.20(1;m) 3.28(2;s) 3.83(1;d) 4.07(4;m) 4.20(5;m) 10.40(1;s)
29	1.40-2.12(10;m) 2.57(2;s) 4.05(9;m) 11.50(1;s)
30	0.80-1.95(11;m) 3.35(1;d) 3.81(2;s) 4.00(9;m) 7.35(5;m)
31	2.08(1;s) 2.62(2;tr) 3.70(2;tr) 4.00(3;s) 4.23(9;m) 4.98(1;s) 7.00(2;d) 7.53(2;d)
32	2.01(1;s) 2.45(2;tr) 3.55(2;tr) 3.75(3;s) 3.82(6;s) 4.04(9;m) 4.73(1;s) 6.60(2;s)
33	0.88(9;s) 3.93(5;s) 4.09(4;m) 5.08(1;s) 7.23(2;m) 7.75(2;m)
36	1.04(6;dd) 1.38(3;d) 1.45(1;s) 2.87(1;sept.) 3.58(1;qua) 4.09(4;m) 4.12(5;s)
38	0.66(6;dd) 1.47(1;s) 1.82(1;m) 2,48(3;s) 2.96(1;d) 3.96(5;s) 4.07(4;m)
40	0.70(6;dd) 1.13(6;dd) 1.20(1;s) 1.85(1;m) 2.97(1;sept.) 3.31(1;d) 4.02(9;m)
41	1.04(6;dd) 1.24-1.52(6;m) 1.60-2.62(4;m) 3.04(1;d) 3.96(9;m)
42	1.05(6;dd) 2.23(5;m) 3.08(1;d) 3.53(4;m) 4.10(9;m)
43	0.71(9;s) 1.73(2;s) 3.36(1;s) 4.13(9;m)
44	0.73(9;s) 1.73(1;s) 2.60(1;s) 2.72(3;s) 4.10(4;m) 4.20(5;s)
45	1.05(9;s) 2.35(6;s) 3.12(1;s) 4.12(9;m)
46	1.05(9;s) 4.04(5;s) 4.18(5;m) 4.26(1;s) 6.88(3;m) 7.33(2;m)

Table 8 (*Contd.*)

compound no.	δ (intensity; multiplicity)
47	1.00(9;s) 1.03(1;s) 1.10(9;s) 2.98(1;s) 4.08(9;m)
48	1.09(),s) 1.43(6;m) 2.41(4;m) 3.13(1;s) 4.16(9;m)
49	0.97(9;s) 2.50(4;m) 3.00(1;s) 3.55(4;m) 4.10(9;m)
50	0.80(9;s) 3.65(5;s) 3.95(4;m) 4.22(1;s) 6.85(1;m) 6.94(1;m) 7.42(1;m)
51	0.88-1.76(13;m) 3.37(1;m) 4.04(10;m)
52	0.87-1.92(12;m) 2.58(3;s) 2.98(1;m) 4.13(9;m)
53	0.80-1.90(12;m) 3.22(1;d) 4.00(11;m) 7.36(5;m)
54	0.82(3;m) 0.95-1.33(6;m) 1.60-2.10(9;m) 2.23(1;m) 3.55(1;m) 4.05(9;m)
55	2.12(3;s) 3.00(2;s) 4.14(9;m) 7.43(4;qua) 9.95(1;s)
56	0.86(9;s) 3.35(1;s) 3.38(2;s) 3.75(3;s) 4.03(4;m) 4.12(5;s)
57	0.85(9;s) 1.30(3;tr) 3.38(3;s) 4.03(4;m) 4.13(7;m)
58	1.19(3;tr 1.69(3;s) 1.81-2.33(2;m) 3.89(2;m) 4.17(7;m) 7.46(3;m) 8.37(1;m) 10.40(1;s)

hexane. Products not containing acidic groups were directly recrystallized from hexane after drying the organic layer and removal of the solvent or purification by chromatography.

Preparation of the α-ferrocenylalkylamines (*Table* 6). A soln of the carbenium ion was diluted with 15 ml CH_2Cl_2 and added dropwise to a vigorously stirred mixture of 2-propanol (20 ml) and the amine (quantities given in Table 6) at −78°. After slow warming to room temp, 100 ml CH_2Cl_2 was added, and the mixture washed three times with water. In the cases indicated by (*) in Table 6, the CH_2Cl_2 solution was dried with Na_2SO_4 and, after removal of the solvent, the residue was recrystallized from hexane. In all other cases, the CH_2Cl_2 soln was extracted twice with 100 ml 8% phosphoric acid, and the acid extracts washed with 100 ml CH_2Cl_2 and neutralized with conc NaOH. The separated amine was dissolved in CH_2Cl_2 and, after drying with Na_2SO_4 and removal of the solvent, it was recrystallized from hexane or distilled in vacuum.

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