

RESEARCH ON ORGANIC CHEMISTRY OF FERROCENE

By

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(I) GENERAL METHODS

(1) Surface-(Thin layer)-Chromatography of Ferrocene-derivatives
(Together with H. Pelousek and A. Mohar (1))

Abstract: Surface-chromatography on Silica-jelly (Kieselgel-G) using benzene-ethanol-mixtures or hexane as solvents has proved to be a very useful analytical method for rapid separation and identification of ferrocene-derivatives.

So far no simple and reliable analytical method has been known for the qualitative separation and rapid identification of ferrocene-derivatives though it is needless to say that such a method would be of great value. Paperchromatography is limited to hydrophilic compounds like ferrocene-carboxylic acids (2) (3); otherwise a rather tedious impregnation-procedure and use of an uncommon solvent (dimethylsulfoxide) are necessary, as has been shown for the case of ferrocene and four of its derivatives (4).

Use has been now made of surface-chromatography (thin-layer-chromatography, Dunnschichtchromatographie (5)), a method already used for the separation of hydrophobic compounds. Chromatography of more than 100 ferrocene-derivatives has proved that we now have a very useful analytical method at hand which in short time (10 - 20 minutes) allows in most cases a clear separation of even complex mixtures. Many examples shown later on in this paper may demonstrate the applicability of this method.

Although its possibilities have not been fully investigated, it has already been of great help for the rapid identification of reaction-mixtures (i.g. Friedel-Crafts acylations) and in checking the purity of products and starting-materials. Moreover many reactions (oxidations with MnO_2 , rearrangements, dehydrations and Friedel-Crafts acylations) may be followed easily by withdrawing samples in certain intervals and analyzing them by the described method. In certain cases surface-chromatography may be extended to a preparative scale thereby allowing the separation of otherwise inseparable isomers. Fractions obtained by chromatography on alumina-columns too can easily be checked for their purity.

No details of the procedure will be given here. In preparing the plates we followed the instructions of Brenner and Niederweiser (6) using "Kieselgel-G Merck" as adsorbent as they did.

The following solvent-systems were the most suitable for ferrocene-derivatives bearing functional groups:

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14. ABSTRACT Surface-chromatography on SUica-jelly (Kieselgel-G) using benzene-ethanol-mixtures or hexane as solvents has proved to be a very useful analytical method for rapid separation and identification of ferrocene-derivatives.			
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A: benzene; B: benzene-ethanol(30:1, v/v); C: benzene-ethanol(15:1).

For ferrocene and alkyl-(aralkyl)-ferrocenes, n-hexane has given the best results.

Ten to 20 minutes are required to develop the chromatogram using these solvents. A good separation, showing distinct spots, is attained along a solvent front 8 cm from the starting point.

As ferrocene-derivatives are coloured, it is a great advantage that no special colour-tests are necessary. In some cases spraying with an oxidizing agent (bromine, NaIO_4 -solution) deepens the original orange colour by production of deeply coloured ferrocenium-compounds thereby increasing the sensitivity of the method.

According to our experience optimal amounts are 50-100 μg for every component present in a mixture. 2-5 μg , however, may still be detected and on the other hand as much as 1 mg gives somewhat big, but nevertheless distinct spots without tailing. Therefore an impurity of 2-5 % may be detected in some cases.

Fig. 1 shows only a few examples out of many so far tested in order to show the range of applicability. Most of them have been chosen because of their interest in connection with our work on ferrocene-acetylenic-compounds (part III of this paper) and bridged ferrocenes (part II). A number of alkyl-ferrocenes are discussed under I-2. The R_F -values of many others are to be found in the original paper (1).

Table 1

Ferrocene-derivatives.

Fc = ferrocenyl = $\text{C}_{10}\text{H}_9\text{Fe}$ and ferrocenylene($\text{C}_{10}\text{H}_8\text{Fe}$)

Number	Compound
1	Ferrocene (Fc.H)
2	1,1'-Trimethylen-ferrocene
3	1,1'-(α -ketotrimethylene)-ferroc.
4	Fc.CHO
5	Fc.COCH ₃
6	Fc(COCH ₃) ₂ (1,1'-)
7	Fc.CH ₂ OH
8	Fc.CHOH.Fc
9	Fc.CH ₂ .Fc
10	Fc(CHOH.CH ₃) ₂ (1,1'-)
11	$\begin{array}{c} \text{CH.CH}_3 \\ \diagup \quad \diagdown \\ \text{Fc} \quad \text{O} \end{array}$
12	Fc.CHOH.C \equiv CH
13	Fc.CO \equiv CH
14	Fc.C ₂ H ₅
15	Fc.CH(CH ₃)C ₂ H ₅

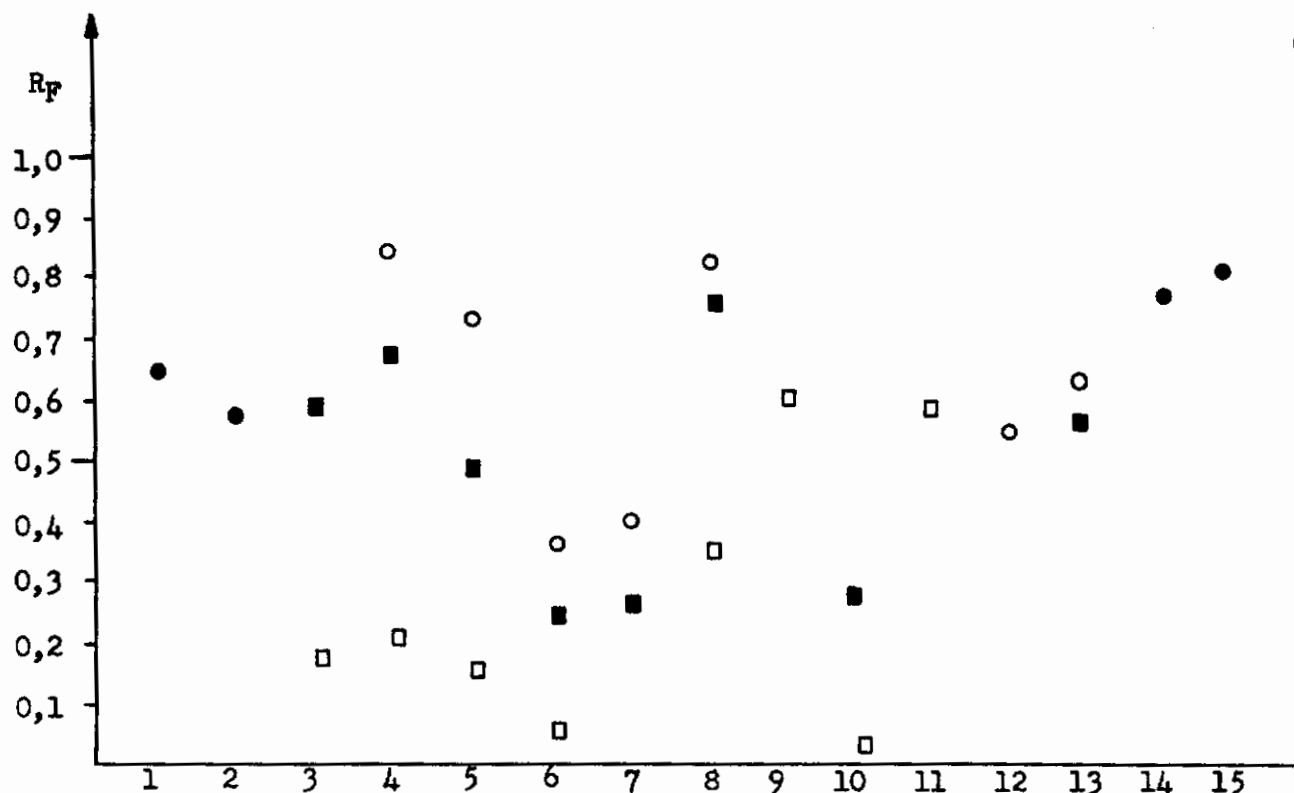


Fig. 1: R_F-values of ferrocene-derivatives
 The numbers refer to the compounds
 of table 1. Solvents A : □ ; B : ■
 C : ○ ; hexane : ●

(2) Preparation of alkylferrocenes from acylferrocenes by reduction with LiAlH₄/AlCl₃ (Together with A. Mohar and M. Peterlik (7)).

Abstract: Acylferrocenes, ferrocenyl-carbinols and ethers of ferrocene, which contain the grouping Fc-C(=O), may smoothly be reduced to the corresponding alkyl-(aralkyl)-ferrocenes by means of LiAlH₄/AlCl₃. This reduction method makes alkyl- and bis-alkyl-ferrocenes easily accessible.

Reduction of ferrocenyl-ketones (Fc.CO.R) to the corresponding alkyl-compounds (Fc.CH₂R) is an important problem in ferrocene-chemistry as it offers the most important possibility of arriving at alkyl- and dialkyl-ferrocenes, the acylferrocenes being easily accessible by Friedel-Crafts-synthesis. This problem has not yet been solved satisfactorily. Both methods applied so far, namely either hydrogenation or Clemmensen-reduction offered some disadvantages being time consuming and/or giving impure products. Na-ethanol reduction may be employed only in certain cases like diferrocenyl-ketone (8), benzoyl-ferrocene (9) or thenoyl-ferrocene (10).

Brown and White (11) and Nystrom and Berger (12) have recently suggested a reduction method for certain aryl-ketones, using LiAlH₄-AlCl₃ as reducing

agent. As the reduction, however, seems to take its course via an intermediate carbonium-ion and therefore is accelerated by electron-donating groups, only those carbonyl-groups are reducible which are flanked either by two phenyl-groups or at least one bearing electron-donating groups in o- and/or p-position. Simple compounds like acetophenone or benzaldehyde are not at all or only in small yields accessible to $\text{LiAlH}_4/\text{AlCl}_3$ -reduction.

If the ferrocenyl-residue is a stronger electron donor than phenyl(8), then, in contrast to benzene compounds, even simple acylferrocenes should be reducible. Diferrocenyl-ketone(13) and thenoyl-ferrocene(10) have been reduced by $\text{LiAlH}_4/\text{AlCl}_3$, but this was not surprising as these compounds are rather similar to benzophenone which is easily reducible to diphenylmethane.

All the compounds investigated so far, including ferrocene carboxaldehyde ($\text{Fc}\cdot\text{CHO}$), bridged ferrocenes, 1, 1' (α -ketotrimethylene)-ferrocene (Table 2) and mono and diacylferrocenes could be reduced in almost quantitative yields to the corresponding oxygen free derivative by a simple procedure in a very short time - in most cases within a few minutes.

Not only acyl-ferrocenes, but also alcohols and ethers may smoothly be reduced to the corresponding alkyl-(aralkyl) compounds. (Table 3 contains some examples). The only structural requirement being the grouping $\text{Fc}-\text{C}-\text{O}-$.

Therefore the $\text{LiAlH}_4/\text{AlCl}_3$ -reduction represents a method by which alkyl- and aralkyl-ferrocenes are easily accessible, as the Friedel-Crafts-acylation yielding the required starting compounds is one of the best investigated reactions in ferrocene-chemistry(14).

Alkyl-ferrocenes may easily be separated and thereby distinguished from starting materials (ketones, alcohols, ethers) by surface-chromatography (part I-1) using hexane as solvent. Thereby the time may be established after which reduction is complete. Figure 2 shows R_F -values of some mono- and dialkyl-ferrocenes obtained during this investigation.

Table 2 gives the refractive indices of oily alkyl-ferrocenes. It can be observed that the n_D -values decrease regularly with the increasing number of C-atoms in the side-chain(s). Therefore the nature of substitution of an unknown alkyl-ferrocene may be estimated from its refractive-index.

Table 2

n-Alkylferrocenes prepared by $\text{LiAlH}_4/\text{AlCl}_3$ -
reduction of acylferrocenes
All di-substituted products are heteroannular

Acylferrocene	Alkylferrocene			
	Nr.	Formula	mp.	n_D^{20}
Fc.CHO	1	Fc.Me	35°	--
Fc.COMe	2	Fc.Et	--	1.6007
Fc.COEt	3	Fc.C ₃ H ₇	--	1.5900
Fc.COC ₃ H ₇	4	Fc.C ₄ H ₉	--	1.5795
Fc.COC ₄ H ₉	5	Fc.C ₅ H ₁₁	--	1.5711
Fc.COC ₆ H ₅	6	Fc.CH ₂ C ₆ H ₅	74-75°	--

Table 2 (Cont'd)

Acylferrocene	Alkylferrocene			
	Nr.	Formula	mp.	n_D^{20}
Fc(COMe) ₂	7	Fc(Et) ₂	--	1.5807
Fc(COEt) ₂	8	Fc(C ₃ H ₇) ₂	--	1.5603
Fc(COC ₃ H ₇) ₂	9	Fc(C ₄ H ₉) ₂	--	1.5530
Fc(COC ₄ H ₉) ₂	10	Fc(C ₅ H ₁₁) ₂	--	1.5428
Fc(COC ₆ H ₅) ₂	11	Fc(CH ₂ C ₆ H ₅) ₂	103-05°	--
Fc $\begin{matrix} \diagup \text{CO} \\ \diagdown \text{CH}_2 \end{matrix}$	12	Fc $\begin{matrix} \diagup \text{CH}_2 \\ \diagdown \text{CH}_2 \end{matrix}$	105-06°	--

Table 3

Alkylferrocenes from alcohols and ethers by reduction
with LiAlH₄/AlCl₃

Compound reduced	Alkylferrocene obtained	
	Nr.	Formula
Fc.CH ₂ OH	1	Fc.Me
Fc.CHOH.Me	2	Fc.Et
Fc.CHOH.C ₆ H ₅	6	Fc.CH ₂ C ₆ H ₅
Fc(CHOH.C ₆ H ₅) ₂	11	Fc(CH ₂ C ₆ H ₅) ₂
Fc.CHOH.C≡CH	13	Fc.CH ₂ C≡CH
Fc.CH ₂ OCH ₂ .Fc	1	Fc.Me
Fc $\begin{matrix} \diagup \text{CH-Me} \\ \diagdown \text{O} \\ \diagup \text{CH-Me} \end{matrix}$	7	Fc(ET) ₂

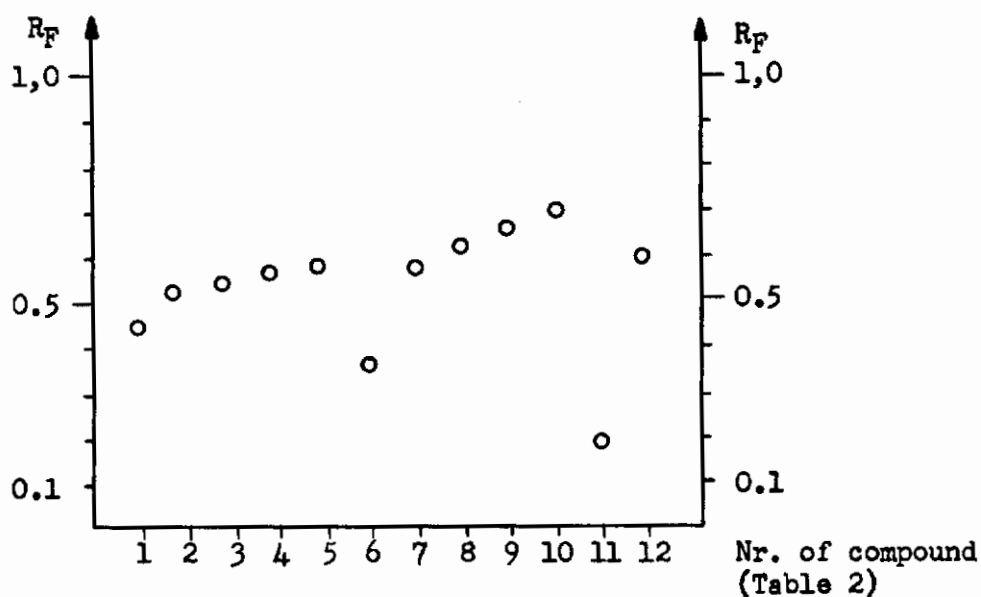


Fig. 2: R_F-values of alkyl- and dialkyl-ferrocenes.
Kieselgel-G "Merck", solvent: n-hexane

(II) BRIDGED FERROCENES

(Together with H. Seiler and M. Peterlik)(3)

Abstract: The following bridged ferrocenes were prepared from the appropriate ferrocene derivatives: bis-(trimethylene)- and diethyl-bis(trimethylene)-ferrocene (twofold bridged) and tris-(trimethylene)-ferrocene (threefold bridged). The ultimate aim was the preparation of a penta-bridged ferrocene and therefore, deca-ethylferrocene was prepared, for comparison purposes, by successive acetylation and reduction. These latter three compounds are the highest known substituted ferrocenes which can be obtained by substitution of the ferrocene-nucleus.

The stereochemistry of bridged ferrocenes has been investigated by acetylation of 1,1'-(trimethylene)-ferrocene and separation of stereoisomeric de-acetyl-derivatives. The diethylcompounds derived therefrom could be synthesized in an independent way.

The stereochemical possibilities of bridged ferrocenes is discussed.

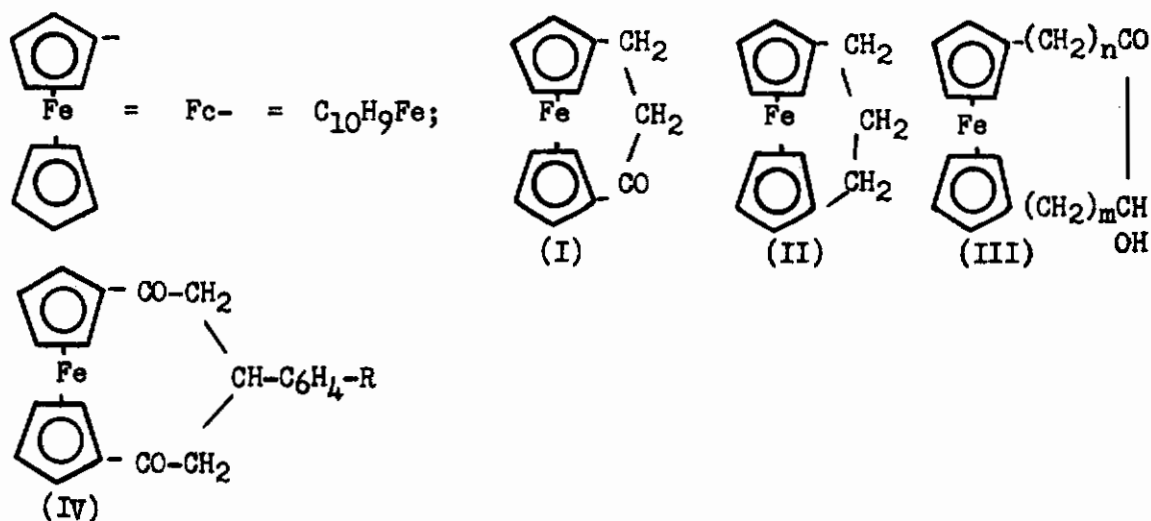
(1) Introduction.

Bridged ferrocenes, in which two cyclopentadiene-moieties are heteroannularly linked by a suitable chain, seem to be fitting compounds for studying stereochemical problems in the ferrocene-field. Moreover from the preparation of such bridged compounds some interesting contributions to the chemistry of ferrocene could be expected.

At the start of the present investigation only ferrocenes with one bridge in the molecule were known:

- (a) 1,1'-(α -ketotrimethylene)-ferrocene (I) has been obtained by intramolecular acetylation of ferrocene-propionic acid (15). This ketone (I) could be reduced to the oxygen free 1,1'-(trimethylene)-ferrocene(II). (2,7).
- (b) II and similar compounds with a four or five-membered bridge have been obtained in small yields (0,02 - 2,5 %) from α, ω -bis-cyclopentadienyl-alkanes(16).
- (c) 1,1'-(tetramethylethylene)-ferrocene, a compound bridged by an unusual two carbon-bridge has been reported recently(17).
- (d) Ferrocene-acyloins (III), containing bridges from 4 to 10 C atoms in length, have been obtained by intramolecular condensation of appropriate ferrocene-1,1'-diesters.(2)
- (e) Cyclic ethers, such as 1,1'-(dimethyleneoxy) ferrocene (17) and derivatives thereof, as described in part III of this paper, can be obtained from heteroannular glycols by dehydration (8).
- (f) Furdik et al. recently described a new class of bridged ferrocenes (IV) derived from diacetyl-ferrocene by alkalicatalyzed condensation with aldehydes (benzaldehyde and derivatives) (18).

Contrails



(2) Discussion.

A. Two- (3) and threefold bridged ferrocenes. Starting from β -ferrocenylmethylpropionate(V), from ferrocene-1,1'-dipropionic-acid (VI), the preparation of which could much be improved(2), or from the above mentioned monobridged compound(II) we could synthesize the two- and threefold bridged compounds: bis- or tris (trimethylene)-ferrocene (XVIII, XXIII) arriving in every case at the same intermediate, the bridged ketone (XVII). The best way, however, is to cyclize VI by intramolecular Friedel-Crafts-reaction to the diketone (XVI). Both ketones (XVI and XVII) on reduction gave the bis-bridged ferrocene XVIII. In the latter case (via the dibridged diketone XVI) the overall yield based on ferrocene being 15%. From bis-trimethylene-ferrocene(XVIII) a simple route led to the threefold bridged ferrocene: tris-trimethyleneferrocene (XXIII).

In all cases investigated so far, four types of reactions proved to be useful:

- (a) Formylation with N-methyl-formanilide and POCl_3 (Vielsmeyer-reaction).
- (b) Knoevenagel-condensation of the aldehydes, obtained by the above method, with malonic acid and hydrogenation of the acrylic acids to the corresponding propionic acids.
- (c) Ringclosure of the propionicacids with trifluoroacetic-anhydride (TFAA) or intramolecular Friedel-Crafts-cyclization.
- (d) Catalytic hydrogenation over PtO_2 or reduction with $\text{LiAlH}_4/\text{AlCl}_3$ of the ketones, obtained according to (c), yielded the desired trimethylene-compounds (XIII, XVIII, XXIII).

Formylation of monosubstituted ferrocenes (as electrophilic substitution process) occurs at the ring which is activated by a substituent and thus leads to homoannular disubstituted aldehydes (e.g. VII). This compound exhibits in the IR spectrum a rather strong absorption band at 1105 cm^{-1} and a somewhat weaker band at 1000 cm^{-1} proving homoannular disubstitution in accordance with the so called 9, 10 μ rule(19). Similar behavior is exhibited by formyl-ethylferrocene, obtained by the formylation of ethylferrocene and its reduction product ethyl-hydroxymethyl ferrocene. A further proof for this type of substitution is that the dipropionic acid (X) obtained from the monopropionate (V) differs in many respects from the heteroannular dipropionic acid (VI)(2).

Ring closure of VI or X with TFAA gave only the monoacylated products (XIV, XV) in accordance with the deactivating effects of the CO-group towards a second (heteroannular) acylation. After hydrogenation to the bridged ferrocene propionic acid (XIII), a second ring closure could be achieved yielding the ring ketone (XVII). (XVII) could also be obtained from trimethylene-ferrocene via the aldehyde (XI). The ketone (XVII) could be hydrogenated over PtO_2 or preferably by $\text{LiAlH}_4/\text{AlCl}_3$ (Part I-2) and smoothly converted into the desired bis-bridged ferrocene (VIII).

Friedel-Crafts cyclization of the dipropionic-acid (VI) (after conversion into the dichloride with PCl_3) in high dilution gave in a single step the diketone (XVI) in good yields. Reduction of this diketone provides a convenient route to the compound XVIII.

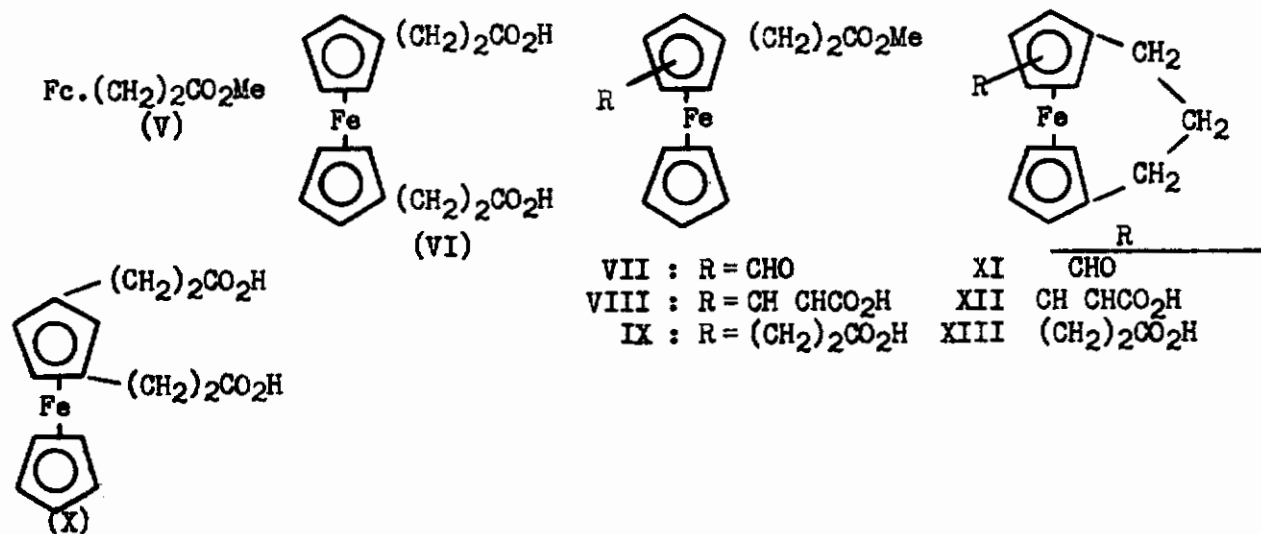
Further formylation (XIX), Knoevenagel-condensation (XX), hydrogenation (XXI), cyclization (TFAA, XXII) and final reduction of the three bridged mono-ketone (XXII) led to the tris-trimethylene-ferrocene (XXIII). This can be used as a precursor for the synthesis of higher bridged ferrocenes and, as a first step towards this goal, the aldehyde XXIV has been obtained in good yields.

Most of the intermediates have been purified by chromatography on alumina and checked for their purity on thin-layer-chromatograms. Some of the aldehydes could be characterized as semicarbazones and the acids have been identified by paperchromatography.

For R_f -values see table 4.

Most of the bridged compounds are crystalline and can easily be purified by chromatography and/or sublimation.

The relative positions of the bridges (very probably 1,3 for XVIII and 1,2,4 for XXIII) will be discussed under (3). The formulae have been formulated according to this assumption, although sometimes a mixture of isomeric 1,2- and 1,3- compounds may be possible.



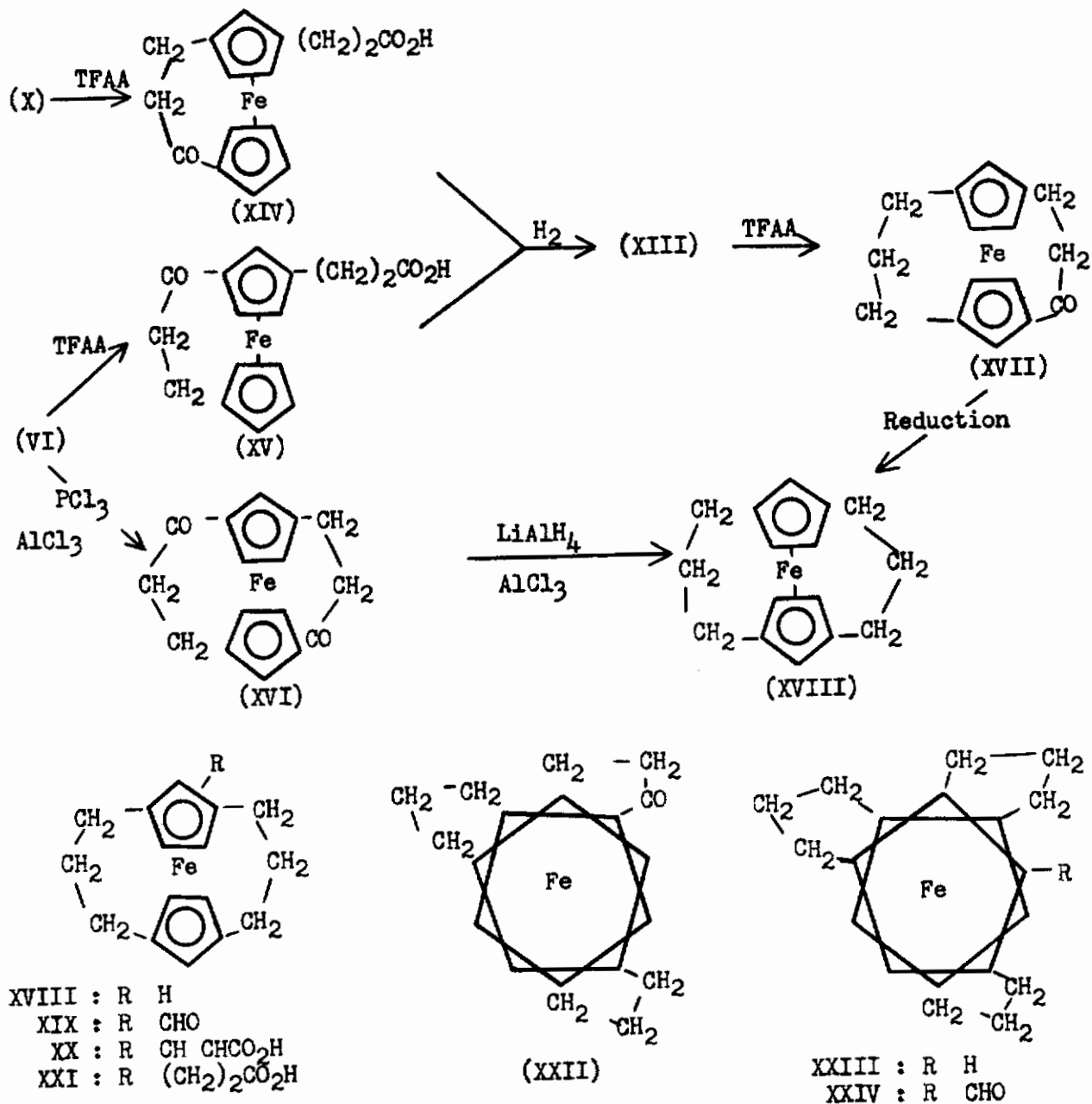


Table 4

R_F-values of ferrocene-carboxylic acids. Descending technique. Solvent: n-butanol-ethanol-aqu.ammonia-water: 4:4:1:1. Paper: Schleicher & Schull 2043 a.

Compound Nr.	R _F	Compound Nr.	R _F
VI	0.38	XXVIII	0.71
VII (corresp. acid)	0.62	XXVIII (corresp. malonic-acid)	0.28
VIII(" diacid)	0.35	XXIX	0.60
X	0.38	XXIX " "	0.25
XII	0.71		

Table 4 (Cont'd)

Compound Nr.	R _F	Compound Nr.	R _F
XIII	0.70	XXXI (corr. acid)	0.53
XIV	0.56	XXXII (corr. mal. acid)	0.18
XV	0.56	XXXIII	0.55
		XXXIII (corr. mal. acid)	0.21

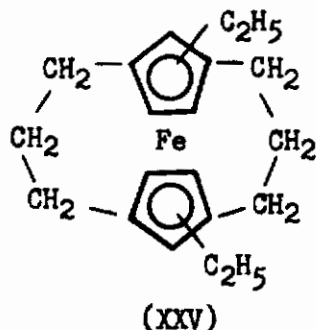
B. Diethyl-bis (trimethylene) ferrocene. In connection with the work on manifoldbridged ferrocenes, also a diethyl-bisbridged compound (XXV) has been prepared.

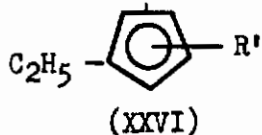
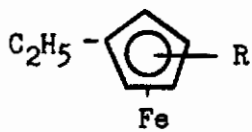
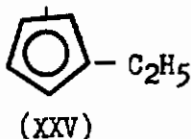
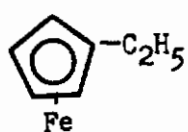
The synthesis has been accomplished making use of the same reactions as mentioned above under A. (Reactions a-d) Starting from 1,1'-diethylferrocene (XXVI), via the aldehyde (XXVII) and the acrylic-acid (XXVIII) the propionic acid (XXIX) has been obtained in good overall yield. After conversion into its methylester (XXX), it could be formylated to give the aldehyde (XXXI). Knoevenagel-condensation (and simultaneous saponification) led to the acrylic acid (XXXII), which over Pd/C could be hydrogenated to the diethyl-dipropionic-acid (XXXIII). In this and other cases the crude Knoevenagel-condensation-products according to paperchromatograms are mixtures of the desired acrylic acids and corresponding malonicacids (i.g. Fc-CH=C(COOH)₂). Accordingly the propionicacids too are mixtures, which, however, after distillation in vacuo are pure, as during the distillation malonic-acids are decarboxylated. In table 4 the malonic-acids in question are included.

In analogy to the above mentioned di-propionicacids (VI, X), the diethyl-ferrocene-dipropionic acid (XXXIII) after twofold ringclosure with TFAA (and subsequent hydrogenation after each cyclization) yielded the desired twofold bridged compound XXV.

It has not been established whether the formyl group enters the mono- or disubstituted cyclopentadiene-ring of diethylferrocenyl- methylpropionate (XXX) to give a "symmetrically" or unsymmetrically substituted compound. In the formula (below), XXXI tentatively has been assigned a sym. bis-heteroannular structure. In regard to the final bisbridged compound, however, the course of substitution is of no significance, as each of the two possible isomers (sym. or unsym.) will give the same final product XXV.

The relative positions of the three substituents in each cyclopentadiene-moiety will be discussed under (3).





	R	R'
XXVII :	CHO	H
XXVIII:	CH=CHCO ₂ H	H
XXIX :	(CH ₂) ₂ CO ₂ H	H
XXX :	(CH ₂) ₂ CO ₂ Me	H
XXXI :	(CH ₂) ₂ CO ₂ Me	CHO
XXXII :	(CH ₂) ₂ CO ₂ H	CH=CH.CO ₂ H
XXXIII:	(CH ₂) ₂ CO ₂ H	(CH ₂) ₂ CO ₂ H

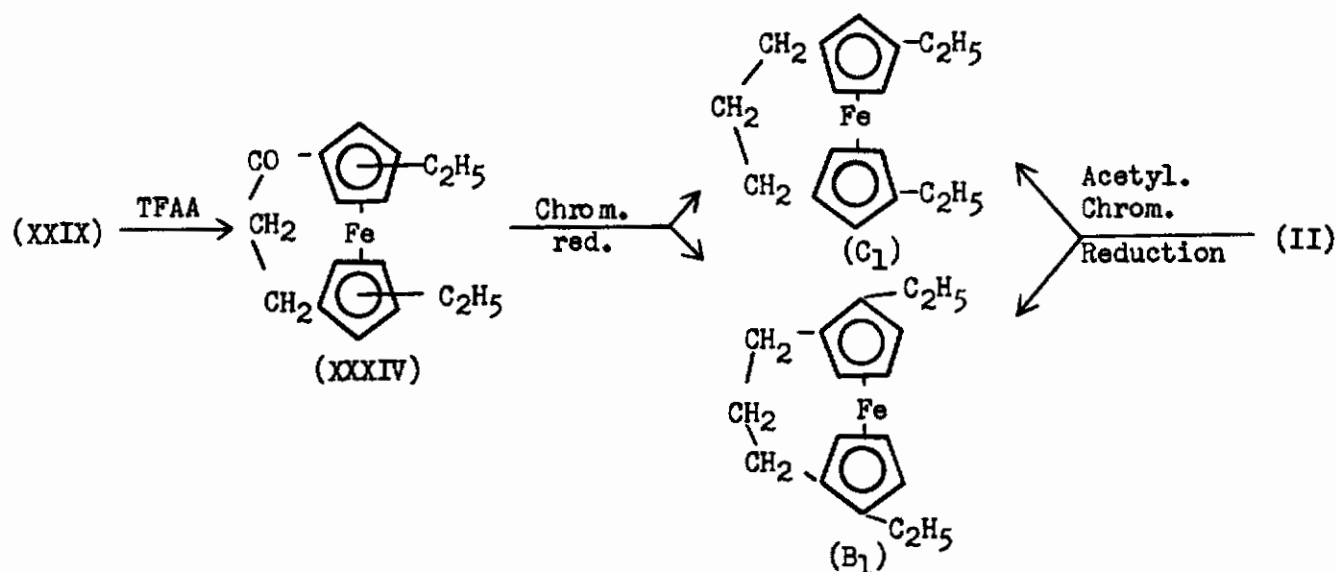
(3) Stereochemistry of bridged ferrocenes.

A. Isomeric diacetyl-1,1'-(trimethylene)-ferrocenes. Rinehart et al. have carried out systematic studies on the acetylation of alkylferrocenes in regard to the steric possibilities(20) and they were able to isolate isomeric diacetyl-dimethyl-ferrocenes (21). For similar work on phenyl-ferrocene see Rosenblum (22).

By exhaustive Friedel-Crafts-acetylation of the monobridged compound II and after careful chromatography on alumina using benzene-ether(4:1) as eluant, we could separate three isomeric diacetyl-1,1'-(trimethylene)-ferrocenes: (A) mp.139-146°, (B) mp.111-115° and (C) mp.132-136°, A being the fastest, C the slowest moving compound. The same three derivatives (and a trace of a fourth isomer) could be detected on thin-layer-chromatograms, moving in the same order. The approximate amounts of the three isomers were A : B : C (1:40:60). For IR-identification purposes and in order to obtain compounds which could be independently synthesized, B and C were reduced to the corresponding diethyl-trimethylene-ferrocenes B₁ and C₁ resp.

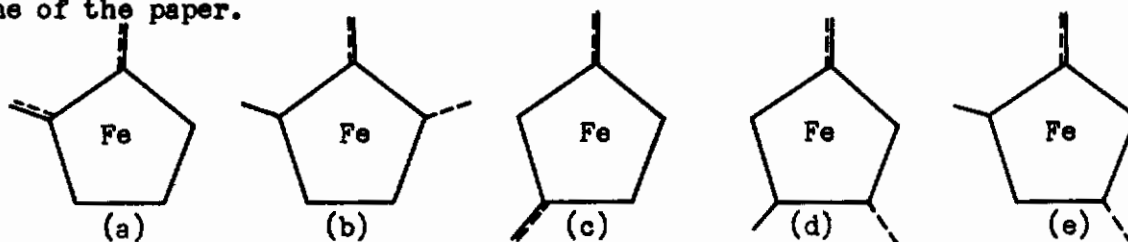
The synthesis of these diethyl-(trimethylene) ferrocenes could be accomplished as follows: the above mentioned 1,1'-diethylferrocene-propionicacid (XXIX) which represents doubtlessly a mixture of isomers has been cyclized with TFAA to get (a mixture of isomeric) ring-ketones (XXIV). This mixture by chromatography on alumina could be separated in two isomers (amounts appr. 1:7). One of these ketones (the main product) on reduction (either catalytically or with LiAlH₄/AlCl₃) gave a diethyl-derivative, which, according to its IR-absorption-spectrum is identical with C₁. The second isomer (obtained in lower yields) on reduction gave a product identical with B₁.

IR-data (absorption in the 900-1000 cm⁻¹ region; for previous discussions of relation between IR-data and substitution cf. inter alia 20, 21, 22, 23) as well as steric considerations seem strongly to indicate, that C₁ (and therefore C) represents the 1,3-(β-)disubstitution-type, whilst B₁ (and B) belong to 1,2-(α-) disubstituted ferrocene-compounds. Cf. the formulation below.



B. Discussion of steric possibilities. To count the number of possible stereoisomers of a given, especially higher substituted ferrocene-derivative, ball and stick-models proved to be very useful.

Of a tetrasubstituted ferrocene with two pairs of equal substituents (diacetyl-dialkylferrocenes, diacetyl-monobridged and diethyl-monobridged ferrocene) five isomers (a-e) are possible, which are shown below. A full line represents a substituent (or half of a bridge) above the plane of the paper, a dotted line a substituent (half a bridge) below the plane. Iron lies in the plane of the paper.



α, α' (2,2')- (a): cis- ; (b) : trans- ; (a) and (c) are mesoforms
 β, β' (3,3')- (c): cis- ; (d) : trans- ; (b), (d) and (e) racemic
 α, β' (2,3')- equal to α', β (2',3) = (e) (DL)

As already mentioned, Rinehart and Motz (21) could isolate four stereoisomeric diacetyl-dimethyl-ferrocenes, to which - mainly according to IR-data - they assigned configurations a - d.

As further shown by models, a dibridged ferrocene (i.g. XVIII) can only exist in two stereoisomeric forms (a) and (c), as in (b), (d) and (e) the distances are too far to allow a second three-carbon-bridge.

Of a dibridged-diethyl-ferrocene (XXV) eight positional isomers are possible, four of which are mesoforms and four being racemates.

previous page), for steric as well for reasons given above (IR-data !) we assume the two bridges to be in 1,3 (β -). (Configuration c).

(b) Similar considerations in the case of the threefold bridged ferrocenes (XXII-XXIV) make it very probable that the three bridges are in the positions 1,2,4 (configuration $g = k$) where a more equal distribution is possible than in the highly crowded configurations $f = j$. The same consideration is valid for the diethyl-dibridged compound (XXV). Here, of course, (g) and (k) are not identical and both isomers may be possible.

(c) Of the three isomeric diacetyl-trimethylene-ferrocenes A, B and C (mentioned above: II-3-A), the main product (C) which on reduction gave the diethyl-bridged ferrocene C_1 (which on the other hand could be obtained on an independent way), very probably corresponds to the 1,3-substitution-type (c and/or d). Consequently B (and B_1) will be a 1,2-disubstituted product (a and/or b). In most cases (20) β -disubstituted products are obtained in larger amounts than the corresponding 1,2-isomers. A, finally which has been obtained in very small amounts could be the 2,3'-isomer (e).

Confirmation of these assumptions has been obtained from IR-absorptions-spectra, as already has been mentioned in some cases. All spectra were in good agreement with previous observations (20-23).

(4) The stepwise ethylation of ferrocene: Deca(?)ethyl-ferrocene.

Although scale-models show that from a steric point of view a fivefold-bridged ferrocene should be possible, it seemed to be advisable to prepare first a fully alkylated ferrocene. So far only an unidentified polyethylferrocene has been described, obtained from ferrocene by reaction with ethylene and $AlCl_3$ (24). We have now obtained a highly ethylated (decaethyl-?) ferrocene by step-wise acetylation and subsequent reduction starting from 1,1'-diethylferrocene.

After four Friedel-Crafts acetylations (acetylchloride/ $AlCl_3$ in CH_2Cl_2) and subsequent reductions with $AlCl_3/LiAlH_4$ (cf. part I-2 of this paper) a liquid polyethylferrocene was obtained. After two further acetylation and reduction steps we arrived at a compound melting from 40-50° (10% overall yield) which according to analysis, however, still was not fully ethylated (octaethyl !). Moreover, after a continuous decrease from diethylferrocene, our product in the IR-absorption-spectrum exhibited a weak band at $3080cm^{-1}$, characteristic for nuclear bonded hydrogen (Fc-H), while in the aliphatic C-H region ($2800-2900cm^{-1}$) an increase from diethyl to the octaethylferrocene was observed. As we had not achieved full ethylation, two further acetylation and reduction steps were carried out. Thus, a product was obtained which had a melting range from 50 to 230°. It was "purified" by spreading it on a porous plate kept at 180° for five minutes. This product melted from 200-230° after sintering at 180°.

Analysis cannot be used to distinguish between a nona and decaethylferrocene ($C_{28}H_{46}Fe$, Calcd. C 76.7, H 10.5; $C_{30}H_{50}Fe$, Calcd. C 77.2, H 10.7). However, our product represents at least a nona-ethylferrocene (Found, C 76.9, H 10.5).

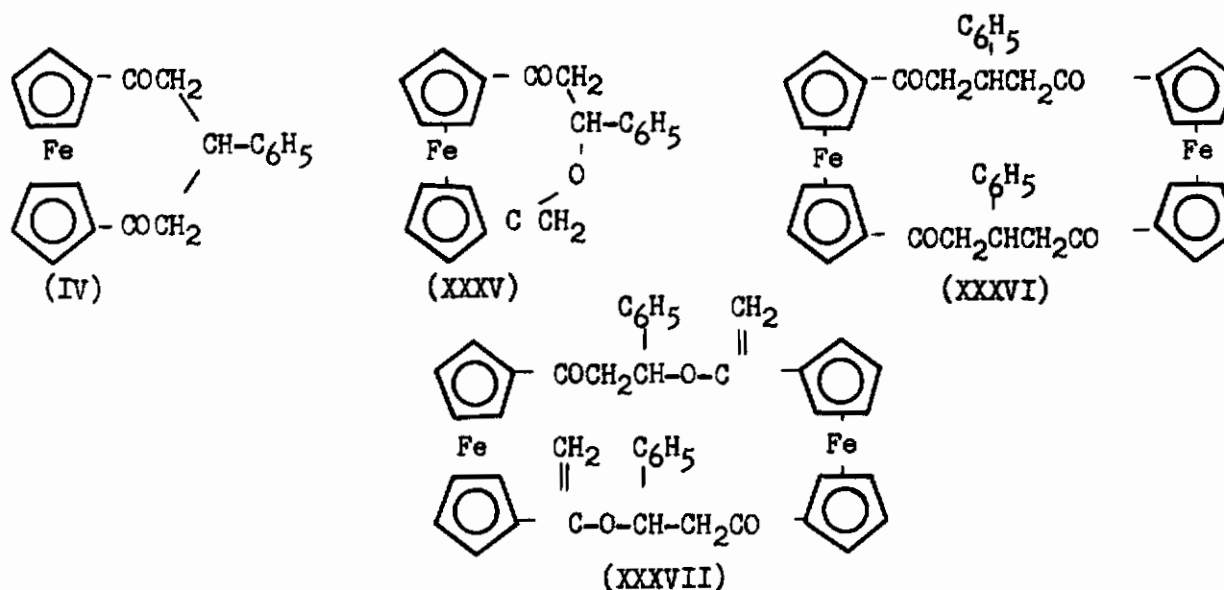
Furthermore, the weak Fc-H band had almost completely disappeared. Final proof may be gained by NMR. We may assume that we have achieved practically complete ethylation and the product is the highest substituted ferrocene derivative

known.

All diacetylated polyethylferrocenes were purified by chromatography on alumina and checked on thin-layer-chromatograms. According to theory (cf. II-3-B) most of them proved to be mixtures of positional isomers. The liquid polyethylferrocenes were purified by distillation in high vacuum. The refractive indices decrease from diethylferrocene ($n_D = 1.5807$) towards a final value: 1.5460. In a similar regular fashion the R_F -values (thin-layer chromatograms, Kieselgel-G, hexane) increased from diethylferrocene (0.60) to decaethyl-ferrocene (0.85).

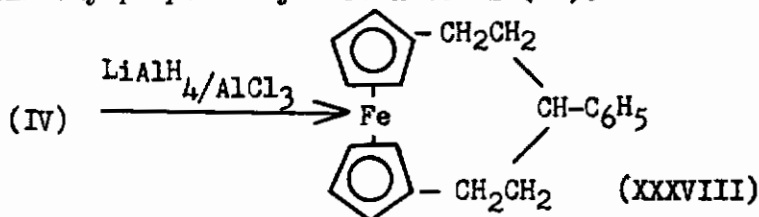
(5) Elucidation of the structure of a bridged ferrocene, obtained from 1,1' diacetylferrocene.

Both C. R. Hauser and coworkers (25) and M. Furdik et al. (18) by alkali-catalyzed reaction of diacetylferrocene with benzaldehyde have obtained a high melting compound (mp. $> 300^\circ$), to which Furdik tentatively assigned the structure (IV) whilst Hauser discusses three further possible structures (XXXV - XXXVII).



On account of some IR-data and formation of a mono-phenylhydrazone Hauser prefers XXXV or XXXVII rather than IV or XXXVI. To clarify this matter and to establish the structure of the compound in question we have reduced it with $\text{LiAlH}_4/\text{AlCl}_3$ to the corresponding O-free ring: $\text{C}_{21}\text{H}_{22}\text{Fe}$, mp. $110-112^\circ$. This compound according to IR-data and hydrogenation - results lacks a $\text{C}=\text{CH}_2$ group and is monomolecular, as has been proved by cryoscopic and ebullioscopic molecular-weight determinations (Calcd. for XXXVIII 330, found 320-326).

It has been established therefore that the bridged-ferrocene in question has the structure IV as already proposed by Furdik et al (18).



(III) FERROCENE ACETYLENIC COMPOUNDS
(Together with A.Mohar) (8,26)

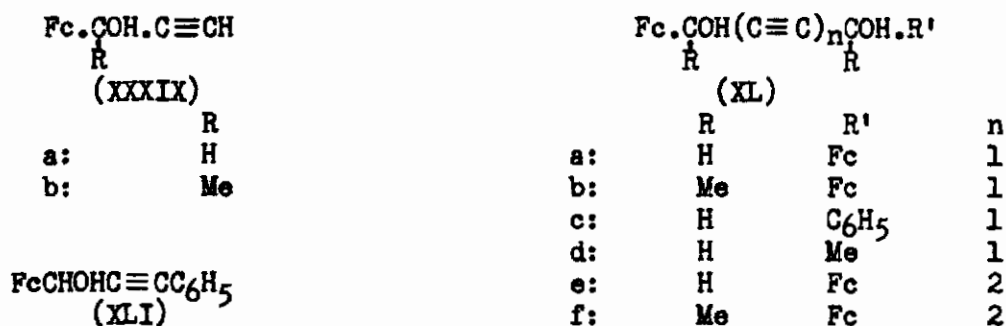
Abstract: Ferrocenyl-ethynyl-carbinols and -acetylenic-glycols were obtained from Fc.CHO (and Fc.COCH₃) by appropriate synthetic methods. Reactions carried out with these novel compounds included:

- (a) Oxidative coupling which led to diacetylenic-glycols.
- (b) Oxidation with MnO₂ yielding acetylenic-mono-and di-ketones, which served as starting materials for heterocyclics containing the ferrocene-nucleus.
- (c) Catalytic hydrogenation of sec. carbinols which gave saturated ferrocenyl-carbinols whilst tert, carbinols underwent simultaneous hydrogenolysis to give ferrocenyl-alkanes.
- (d) Saturated ferrocenyl-carbinols and -glycols can easily be dehydrated with acid alumina thereby yielding ferrocenyl-alkenes. Compounds of suitable structure give ethers.
- (e) Reduction of ferrocenyl-acetylenic-carbinols and -glycols with LiAlH₄/AlCl₃ leading to oxgen-free acetylenic compounds containing the grouping Fc.CH(R)C≡C- (R=H, Me).
- (f) LiAlH₄-treatment of ferrocenyl-acetylenic-glycols (Whiting-reaction) which gave diferrocenyl-butadiene and -hexatriene. Some rearrangements of unsaturated systems were observed.

(1) Introduction.

The manifold preparative possibilities offered by acetylenic compounds prompted us, to introduce acetylenic-groups into suitable ferrocene-derivatives.

For comparison with phenyl-and thienyl-ethynyl-carbinols (28, 29), we have prepared ferrocenyl-ethynyl-carbinols (XXXIX) and acetylenic glycols (XL). These compounds were easily synthesised from ferrocene-carboxaldehyde or acetyl-ferrocene.



(2) Discussion.

A. Synthesis. Synthesis of the simple carbinols XXXIX a and b was achieved by reaction of FcCHO or FcCOCH₃ with Na-acetylide in liquid ammonia and both compounds were obtained in a crystalline form. The ferrocenyl-ethynyl carbinol (XXXIXa) was obtained in a much higher yield, 70%, than its methyl homologue, the tertiary carbinol XXXIXb, 16%. Because of steric factors, the lower yield might be attributed to a higher reactivity of the aldehyde as compared with the ketone. The IR-absorption spectrum of XXXIXa nicely exhibited four different

-H-bands: OH : 3600, $C\equiv C-H$: 3300, Fc-H 3090 and C-H (aliph.) 2880 cm^{-1} . A characteristic band at 1106 cm^{-1} in both cases (XXXIX a and b) proved monosubstituted ferrocenes.

Some difficulties have been encountered during the preparation of simple glycols of type XL ($n=1$), as Fc.CHO neither reacted with acetylene-di-magnesiumbromide nor with XXXIX a (as the Na-salt in liquid ammonia). These reactions should have given XL a. 1,4-diphenyl-but-2-yn-diol-1,4, however, can be obtained from benzaldehyde without difficulty. This is another case of ferrocene-aldehyde reacting more slowly than benzaldehyde, especially in carbonyl-addition-reactions (30), which is in contrast, to the electron-donating behaviour of the ferrocenyl-group, which should make the CO-group in Fc.CHO more strongly polarized than in benzaldehyde, as also shown by IR-data (30).

Ferrocene reacts with substituted acetylenes as well as with acetylene itself. Thus, the phenyl acetylene XLI was obtained in good yields.

According to the literature, Li-salts of acetylenes should give better yields in reactions with carbonyl groups and should be more soluble (31). Therefore, in the preparation of the desired glycols XL ($n=1$), Li-salts instead of Na-salts (again in liquid ammonia) were used. Indeed from methyl-ethynyl-carbinol with Fc.CHO and XXXIXa with benzaldehyde (where Na-salts had given no results) by using Li-salts, the desired glycols XL d and c could be obtained. Equally diferrocenyl-acetylene-glycol (XLa) could be prepared via Li-salts (reaction of Fc.CHO in liquid ammonia with either di-Li-acetylide or the Li-salt of XXXIX a). Di-Li-acetylide is rather easily accessible from phenyl-Li and acetylene. (32)

From the reaction of dilithio-acetylide with FcCHO, the glycol and small amounts of the carbinol XXXIX were obtained and these two products were easily separated.

On the other hand, di-Li-acetylide with Fc.COCH₃ in tetrahydrofuran gave only the carbinol XXXIX b in even better yields than in the reaction of Fc.COCH₃ with Na-acetylide, whilst the expected glycol XL b could not be isolated.

With the unsymmetrical glycols (XL, R' not Fc) two racemates are possible. The symmetrical compounds (R' = Fc) contain two equivalent asymmetric C-atoms and therefore may be present as a mixture of the meso and DL-form. Indeed, all crude glycols had a considerable melting-range whilst on analysis they gave correct values. In some cases separation of the diastereomers could be achieved by crystallization, but not by chromatography. In the case of XL a only the higher melting form could be obtained in a pure state. In analogy to the corresponding diphenyl-compound it may be assumed that this isomer corresponds to the racemate, the lower melting diastereomer would be the meso-form.

B. Reactions.

a) Oxidative coupling. Coupling of ethynyl-compounds with Cu_2Cl_2 in NH_3/NH_4Cl with oxygen (31) which gives diacetylenic-derivatives, in our case (ferrocenyl-compounds) led to extensive oxidation of the ferrocene-moiety. Eglinton's modification (33), however, using Cu-II-acetate in pyridine-ether as coupling-agent, gave the diacetylenic-glycols XLe and f (from the carbinols

XXXIX a and b) in good yields.

b) Oxidation with MnO₂. For oxidation of ferrocenyl-acetylenic-carbinols and -glycols to corresponding ketones, oxidizing agents, as usually applied to acetylenic compounds (chromic acid, (31)) of course were out of question. MnO₂ seemed to be a much more promising oxidant (13,34). Indeed, by treating the following ferrocenyl-carbinols and glycols with MnO₂ in chloroform, the corresponding ketones could be obtained in excellent yields (table 5). The optimal conditions (time and temperature) could be determined easily by analyzing the reaction-mixtures with the aid of thin-layer-chromatography. Thereby the deeply coloured ketones can be distinguished from the yellow to orange starting materials, which are more strongly adsorbed and therefore exhibit lower R_F-values.

Table 5

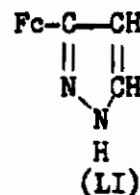
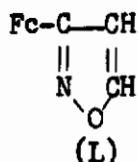
Ferrocenyl-(acetylenic)-mono and diketones.

Hydroxy-compounds		Keto-compounds		
Formula	Nr.	Formula	Nr.	mp.
Fc.CHOH.C≡CH	XXXIX a	Fc.CO.C≡CH	XLII	78-80°
Fc.CHOH.C≡C.C ₆ H ₅	XLI	Fc.CO.C≡C.C ₆ H ₅	XLIII	103-06°
Fc.CHOH.CH=CH.C ₆ H ₅	XLIV	Fc.CO.CH=CH.C ₆ H ₅	XLV	
cis	XLIV a	cis	XLV a	129-30°
trans	XLIV b	trans	XLV b	139-40°
Fc.CHOH.CH ₂ CH ₂ C ₆ H ₅	XLVI	Fc.CO.CH ₂ CH ₂ C ₆ H ₅	XLVII	84-86°
Fc.CHOH.C≡C.CHOH.Fc	XL a	Fc.CO.C≡C.CO.Fc	XLVIII	158-61°
(Fc.CHOH.C≡C-) ₂	XL e	(Fc.CO.C≡C-) ₂	XLIX	charring until 200

XLII: Ferrocenyl-ethynyl-ketone (XLII) on treatment with hydroxylamine or hydrazine gave the heterocyclic compounds 3-ferrocenyl-isoxazole (L) and 3-ferrocenyl-pyrazole (LI). For similar reactions in benzene-chemistry cf. Bowden and Jones (35).

XLIII, XLV: XLI could be smoothly oxidized with MnO₂ to give the ketone XLIII.

The two geometrical isomers a and b of the ketone XLV were obtained on oxidation of the corresponding cis and trans ethylenic carbinols XLIV a and b. These were prepared by stereospecific reduction of the acetylenic compound XLI. See under (c) below. The trans-compound XLV b was identical with a cinnamoyl-ferrocene formerly obtained by Knoevenagel-condensation of benzaldehyde with acetylferrocene (36, 37) or from ferrocene and cinnamoylchloride (38).



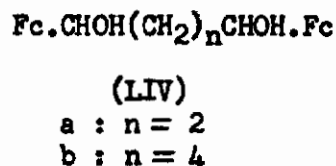
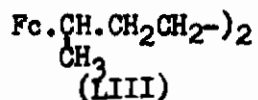
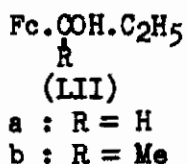
XLVII: The saturated ketone XLVII obtained by MnO₂-oxidation of the corresponding carbinole (XLVI) which, on the other hand was prepared by hydrogenation

of either XLI or XLIV, proved to be identical with a product already obtained formerly (25, 36, 38). The same ketone was accessible by prototropic rearrangement of the unsaturated carbinols XLIV a and b after treatment with alkali in ethanol, albeit in rather poor yields.

XLVIII, XLIX: Containing two asymmetric C-atoms, both (crude) glycols (XL a and XL e) are mixtures of two possible diastereomers (meso- and racemic form), the separation of which sometimes is rather tedious.

As expected, both stereoisomeric forms of XL, a or e, and the crude mixture thereof gave uniform diketones upon oxidation. Product XLVIII, from XL a, was sharp melting while XLIX, from XL e, had no melting point.

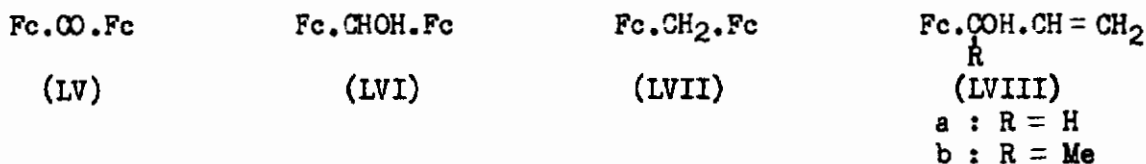
c) Hydrogenation - Hydrogenolysis. Catalytic hydrogenation of ferrocenyl-ethynyl-carbinol (XXXIX a) over Pd/C in ethanol gave the saturated compound ferrocenyl-ethyl-carbinol (LII a) which, on the other hand, could be obtained by a Grignard-reaction of ferrocene-carboxaldehyde with ethylmagnesium bromide, or by LiAlH_4 -reduction of propionyl-ferrocene (Fc.COEt). The methyl-compound (XXXIX b), however, showed a different behaviour. After a rapid uptake of two moles hydrogen a third mole was consumed more sluggishly and a oxygen-free compound could be isolated which proved to be sec. butyl-ferrocene: Fc.CH(Me)Et. This alkyl-ferrocene was also obtained by hydrogenation of ferrocenyl-methyl-ethyl-carbinol (LIIb) which in turn could be prepared from acetyl-ferrocene and ethylmagnesium bromide. Such a hydrogenolytic cleavage of a C-O-bond is well known in benzene-chemistry, where benzylalcohol as well as substituted benzyl-alcohols under similar conditions (Pd-catalysts in alcohol) of hydrogenation give rise to alkyl-benzenes (39). In the ferrocene-field apparently only tertiary carbinols are subject to hydrogenolysis to give O-free compounds and therefore this is a further example of a reaction where a distinct difference in reactivity between benzene- and ferrocene-chemistry exists. As expected, also the tertiary glycol XL f could be hydrogenated to the parent "hydrocarbon" 2,7-diferrocenyl-n-octane (LIII) whilst the secondary glycols XL a and e yielded the saturated glycols LIV a and b.



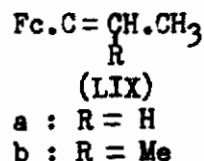
For a further study of hydrogenolysis, diferrocenyl-carbinol (LVI) was prepared from diferrocenyl-ketone (LV) with LiAlH_4 . Hydrogenation of this carbinol using Pd/C in ethanol gave - albeit only in 33% yield - diferrocenyl-methane (LVII) which in turn could be obtained from the ketone (LV) by reduction with $\text{LiAlH}_4/\text{AlCl}_3$ (13). The low yield of LVII in the hydrogenolysis-reaction certainly is due to the bad solubility of the OH-free compound (LVII) in ethanol.

Partial hydrogenation of some of the acetylenic compounds, mentioned in this paper, over Lindlar's catalyst (31) gave the corresponding ethylenic compounds (i.g. LVIII a and b), which undergo rearrangements rather easily. These and similar rearrangements are still under investigation. In the case of the ferrocenyl-phenyl-compound XLI (cf. table 5), by partial catalytic hydrogenation the cis-isomer (XLIV a) was obtained whilst chemical reduction (LiAlH_4) gave the

trans-isomer (XLIV b, table 5).



d) Dehydration. After chromatography of the above mentioned saturated carbinols (LII a and b) on acid alumina ("Woelm", activity grade I) in benzene, products were obtained which according to their IR-spectra had no more OH-groups but possessed a C=C-double-bond (LIX a, b). In both cases on hydrogenation over Pd/C in ethanol one mole hydrogen was consumed rapidly. Thereby from LIX b the same sec. butyl-ferrocene was obtained which has been mentioned above (hydrogenolysis of LII b). The unsaturated compound derived from LIIa (= LIXa) gave n-propyl-ferrocene (cf. part I-2, table 2). LIX a and b represent therefore propenyl-ferrocene (a) and sec. butenyl-ferrocene (b) respectively.



To our knowledge, this mild method of dehydration has no parallel in benzene or even in ferrocene chemistry. Up to now, dehydrations have been run under rather drastic conditions such as with alumina at 200° (40) or by heating with KHSO₄ (41). This new method has been applied to other examples.

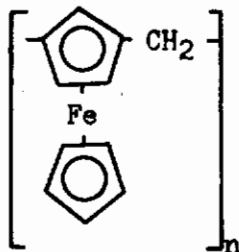
For preparative purposes it is preferable to carry out the dehydration by short shaking (15-30 min.) of a benzene-solution of the appropriate carbinol or glycol together with a five-tenfold amount of acid alumina at room temperature. Short heating is not advisable since sidereactions sometimes occur, as shown below.

Ferrocenyl-methyl-carbinol (Fc.CHOH.Me), easily accessible from acetyl-ferrocene and LiAlH₄, gave vinyl-ferrocene (Fc.CH=CH₂) in 50% yield. Under similar conditions neither phenyl-methyl-carbinol nor phenyl-ethyl-carbinol gave unsaturated products. With regard to preparative simplicity the new synthesis of this interesting vinyl compound certainly is superior to the hitherto described methods: pyrolysis of the carbinol (Fc.CHOH.Me) or its acetate with alumina at 200° (yields 21 and 56% resp. (40) or treatment of FcCH₂CH₂NMe₃⁺ I⁻ with OH⁻ (yield: 3% (42)).

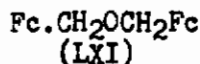
The facility with which ferrocenyl-carbinols can be dehydrated, doubtlessly is in close connection with the stability of ferrocenyl-carbonium-ions of the following type: Fc-C⁺, which has been observed by many authors. According to the E₁-mechanism these ions have to be postulated as intermediates in a dehydration-reaction. A further proof for this assumption was gained by the following reactions: when Fc.CH₂OH (36) was treated with acid alumina in refluxing benzene, polymeric ferrocenes such as LX could be isolated (IR, CH-analysis). Very probably they have been formed by an electrophilic substitution in which the cation Fc.CH₂⁺ took part.

At room-temperature, however, intermolecular attack of this cation on an oxygen-atom of unchanged carbinol (Fc.CH₂OH) takes place, thereby yielding diferrocenyl-di-methylether (LXI) which could be isolated in high yields. This

ether formerly has been prepared under conditions where also formation of $\text{Fc}\cdot\text{CH}_2^+$ might be expected (36).



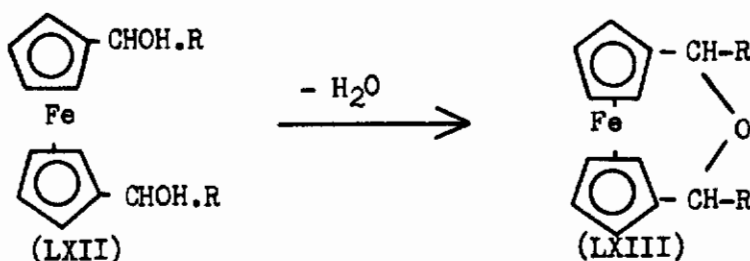
(LX)



Similar results were observed when the glycols LXII a and b (LiAlH_4 -reduction-products of 1,1'-diacetyl and dibenzoylferrocene) were subjected to dehydration with acid alumina in benzene. At room-temperature the intermediate carbonium-ion attacks a neighbouring OH-group and cyclic (bridged) ethers LXIII a and b are formed. Recently a simple compound of this type: 1,1'-(dimethylenoxy) ferrocene has been obtained by Rinehart et al. (17) by treatment of 1,1'-di-hydroxy-methylferrocene with p-toluenesulfochloride in refluxing benzene. LXII a on treatment with acid alumina in refluxing benzene gave appreciable amounts of instable 1,1'-divinylferrocene which, after hydrogenation, has been identified

as 1,1'-diethyl-ferrocene. Is it obvious therefor that at more drastic conditions bis-dehydration had occurred to a larger extend.

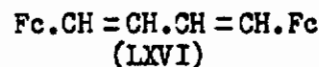
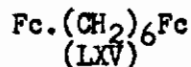
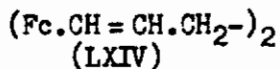
LXIII a and b contain two asymmetric C-atoms and therefor have to occur as racem- and meso-forms. Thin-layer-chromatograms showed indeed, that at least in the case of the dimethyl-compound (LXIIIa) two spots were present which both corresponded to compounds of similar melting point and gave the same analytic values.



a : R = Me
b : R = phenyl

a : R = Me
b : R = phenyl

The glycol LIV b could be dehydrated to give a hexadiene (LXIV) which after hydrogenation afforded 1,6-diferrocenyl-n-hexane (LXV). Dehydration of LIV a should have given 1,4-diferrocenyl-butadiene (LXVI) but no distinct product could be isolated. LXVI, however, could be prepared by the Whiting-reaction from XL a (cf. discussion below, under (f)).



e) Reduction with $\text{LiAlH}_4/\text{AlCl}_3$. Rather surprisingly, the new reduction-method (part I-2 of this paper) offered a convenient possibility for the preparation of oxygen free ferrocenyl-acetylenic compounds containing the structural element $\text{Fc}\text{-CH-C}\equiv\text{C-}$.

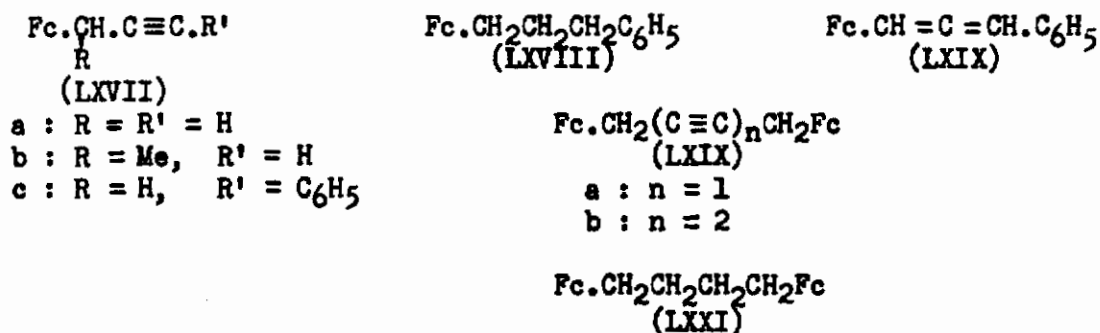
Both ferrocenyl-ethynyl-ketone (XLII) and its precursor, the easily accessible ferrocenyl-ethynyl-carbinol (XXXIX a) on reduction with the complex hydride

gave propargyl-ferrocene (LXVII a), identified by its IR-absorption-spectrum, its Hg-compound (mp. 175-178°), its R_F-value (thin-layer-chromatography), and by hydrogenation which gave n-propyl-ferrocene. Similarly, the tert, carbinol XXXIX b yielded secondary butynyl ferrocene (LXVII b), which was characterized in the same way as the propargyl-compound (Hg-compound, mp. 169-172°).

Both alkynes are distillable liquids and are rather unstable. After some time, even when kept at 0°, insoluble products are deposited from the liquid. Propargyl ferrocene turns red and by chromatographing the tar, a ketone could be separated which in every respect was identical with ferrocenyl ethynyl ketone (XLII). Since the carbinol XXXIX a is quite stable, it can be excluded as an intermediate in this autoxidation reaction.

From Fc.CHOH.C≡C.C₆H₅ (XLI) and its corresponding ketone (XLIII) with LiAlH₄/AlCl₃ 1-ferrocenyl-3-phenyl-propyn-2 (LXVII c) was obtained which could be hydrogenated (Pd/C) to give 1-ferrocenyl-3-phenyl-n-propane (LXVIII). The propyne again was susceptible to oxidation and by MnO₂ could be easily converted into the ketone XLIII. In this reaction, as a by-product, a yellow oil could be isolated which could be catalytically reduced to the above mentioned ferrocenyl-phenyl-propane (LXVIII). For this substance, rather tentatively, the preliminary structure of an allene (LXIX) is proposed.

The glycols XL a and e, as well as their corresponding di-ketones (XLVIII and XLIX, table 5) could be reduced to the desired acetylenic "hydrocarbons" LXX a and b, which in turn could be hydrogenated to give the corresponding saturated compounds diferrocenyl-butane (LXXI) and -hexane (LXV) respectively. LXX b containing the diacetylenic-moiety, is very unstable and after short time is contaminated with the di-ketone XLIX and therefore its purification is rather difficult.



f) LiAlH₄-treatment of acetylenic-glycols: diferrocenyl-polyenes. As previously mentioned (under d), the so-called Whiting-reaction (treating alkyn-diols with LiAlH₄ to obtain butadienes (43) offered the possibility of preparing 1,4-diferrocenyl-butadiene (LXVI) from the corresponding glycol (XLa). Thereby the higher melting (DL-) form yielded a product which decomposed at appr. 230°, whilst the lower melting isomer (meso-) gave a diferrocenyl-butadiene, melting range 130-230°. Both products analyzed correctly for C₂₄H₂₂Fe₂ (LXVI), could not be distinguished on thin-layer chromatograms and on hydrogenation gave the same diferrocenyl-butane (LXXI). It had to be assumed, that they might represent geometrical isomers: namely trans-trans from the DL- and a possible mixture of cis-cis and trans-cis from the meso-form.

Contrails

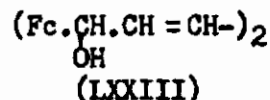
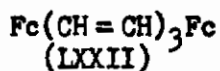
To settle this question, both racemic (mp. 140°) and meso-(mp. 104°) diphenylbutyn-diol ($C_6H_5CHOH.C\equiv C.CHOH.C_6H_5$) were treated with $LiAlH_4$, thereby giving pure trans-trans (mp. 148) and a crude diphenyl-butadiene (mp. 40-120°). Pure cis-cis should melt at 70°; cis-trans is an oil. After a few recrystallizations, the melting point reached 140° indicating that a rearrangement to the stable trans-trans isomer had taken place.

It may be concluded that in both cases (diferrocenyl and diphenyl) the DL glycols give the trans-trans butadienes, while the lower melting meso forms yield a mixture of geometrical isomers; possible, the cis-cis compounds form under the controlled conditions.

The UV-absorption-spectra of diphenyl-, phenyl-ferrocenyl and diferrocenyl-butadiene (LXVI) have been compared and the following results been obtained: (the "mixed" phenyl-ferrocenyl-butadiene was prepared from XL c and $LiAlH_4$).

In hexane- CH_2Cl_2 the three butadienes exhibited peaks at 330m μ . Besides this main-band, in the diphenyl-compound two weaker maxima could be observed at 316 and 345 m μ , respectively. In the ferrocenyl-phenyl derivative the 345m μ was present as a shoulder whilst diferrocenyl-butadiene only had one broad maximum at 330 m μ . Therefore it is obvious that with increasing number of electron-donating ferrocene-moieties at the ends of the conjugated system the fine structure of the spectra disappears.

Finally, the diacetylenic glycol XL e was treated with $LiAlH_4$ and 1,6-diferrocenyl-hexatriene (LXXII) was obtained in good yields. Only traces of the dihydroxy-diene (LXXIII) could be detected, whilst in the case of the corresponding diphenyl-compound the triene as well as the dihydroxy-diene are obtained. (Yields 30% and 27% respectively (44). The triene (LXXII) which is more stable than the diyne (LXXb) after hydrogenation have the already mentioned 1,6-diferrocenyl-hexane (LXV).



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