Chemistry

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Abstract

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ON PENTAETHANODIFERROCENE

In studying the alkylation of ferrocene by the Friedel—Crafts reaction (1–4), we found (5) that, under the action of aluminum chloride on a solution of ferrocene in dichloroethane, along with a small amount of 1,2-diferrocenylethane (6) obtained in 10% yield, a substance is formed which, according to analysis and molecular weight, corresponds to the formula $C_{30}H_{30}Fe_2$ and which we provisionally accepted as pentaethanodiferrocene. Further investigation confirmed us in this opinion. The infrared spectrum revealed the presence of free cyclopentadienyl rings. Acetylation by Friedel—Crafts (6) gave mono- and diacetyl products. Formation of the latter confirmed the presence of two acetylatable cyclopentadienyls. The proton magnetic resonance spectrum,* the data for which we present here, has the following appearance: it consists of two peaks: a narrow one, with a shift $\sigma = +31 \cdot 10^{-7}$ from benzene, and a broad one, shifted from benzene by $+51 \cdot 10^{-7}$ (Fig. 1). Comparison with the p.m.r. spectra of alkyl-substituted ferrocenes makes it possible to assign the narrow peak with certainty to the protons of the cyclopentadienyl rings. The broad peak is shifted by $5 \cdot 10^{-7}$ toward higher frequencies relative to the protons of the CH_2-groups in diethylferrocene. The ratio of the area of the broad peak to the area of the narrow peak (Fig. 1), measured at minimal power, is equal to 1.3 ± 0.3.

Such a picture seemed not to contradict the accepted structure of pentaethanodiferrocene, including two types of hydrogen atoms—cyclopentadienyl and mutually identical methylene atoms. However, the greater width of the line of the second peak, the noticeable difference of its chemical shift from $\sigma(CH_2)$ in ethyl-substituted ferrocenes, and also the magnitude of the ratio of the areas of these peaks deserved discussion.

In a brief communication by Goldberg (8) it was published that he had obtained a substance with the same properties and an identical infrared spectrum and Debyegram as “pentaethanoferrocene,” in the absence of dichloroethane, directly under the action of aluminum chloride on ferrocene in benzene solution. This, naturally, made impossible the structure of pentaethanodiferrocene proposed by us. We repeated Goldberg’ s experiments and became convinced that the substances obtained under the action of aluminum chloride on ferrocene both in the absence of dichloroethane and in its presence are identical in analysis, molecular weight, infrared spectrum, and proton magnetic resonance spectrum.

Fig. 1. NMR spectrum of the "dimer" of cyclopentenylferrocene

Figure 1: Fig. 1. NMR spectrum of the "dimer" of cyclopentenylferrocene

Fig. 2. NMR spectrum of cyclopentenylferrocene

Figure 2: Fig. 2. NMR spectrum of cyclopentenylferrocene

In both cases there is also obtained a series of substances, identical in analysis, with higher molecular weights. The formula of pentaethanodiferrocene (and structures similar to it for the more high-molecular substances) must be rejected. What, then, actually is pentaethanodiferrocene?

By the time Goldberg' s article appeared we had already observed that ferrocene is partially decomposed under the action of aluminum chloride. When ferrocene is treated with $AlCl_3$ in a medium of aromatic hydrocarbons, as described in the work of A. N. Nesmeyanov, N. A. Vol' kenau, and I. Bolesova (9), one cyclopentadienyl is split off and replaced by an aromatic ring,

so that a cation of the type

[cyclopentadienyl ring]
$Fe^{\oplus}$
[cyclopentadienyl ring]

is obtained.

Long ago Weinmayr (10) observed the cleavage of cyclopentadienyl from ferrocene under the action of anhydrous hydrogen fluoride; the cyclopentadiene thereby formed alkylated the ferrocene that remained undecomposed, with formation of cyclopentenylferrocene.

It became clear that both acids, HF and $HAlCl_4$, could act on ferrocene in a similar manner. However, in Weinmayr' s experiment the reaction stopped at the cyclopentenylferrocene stage, whereas our product corresponded to a doubled molecular weight. Thus, under the action of aluminum chloride, dimerization of Weinmayr' s undefined substance occurred. To test this assumption, we synthesized Δ'-cyclopentenylferrocene. From ferrocenyl lithium and cyclopentanone, cyclopentenylferrocenylcarbinol was obtained, which, upon chromatography on alumina, dehydrated to cyclopentenylferrocene, evidently with the double bond in the position conjugated with the cyclopentadienyl nucleus.

Fig. 1. N.m.r. spectrum of the "dimer" of cyclopentenylferrocene

Fig. 2. N.m.r. spectrum of cyclopentenylferrocene

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* The proton magnetic resonance (p.m.r.) spectra were investigated on a KYS-25 "Trüb—Täuber" spectrometer.

structural formula

Figure 3: structural formula

[ferrocene bearing a cyclopentenyl substituent]
Fe (I)

Found, %: C 71.01, 71.26; H 6.72, 6.76; Fe 21.90, 21.68
$C_{15}H_{16}Fe$. Calculated, %: C 71.58; H 6.42; Fe 22.02

Molecular weight (benzene, cryoscopy) found 260, calculated 252; IR spectrum –1000, 1100, 1640 cm^{-1}. M.p. 65°.

The NMR spectrum of cyclopentenylferrocene contains three peaks ($\sigma_1 = 23 \cdot 10^{-7}$, $\sigma_2 = 34 \cdot 10^{-7}$, $\sigma_3 = 52 \cdot 10^{-7}$) with an area ratio satisfactorily

corresponding to structure I (Fig. 2). The peak of the CH_2 protons of cyclopentenyl is noticeably broadened; its chemical shift agrees well with the position of the broad peak in "pentaethanodiferrocene." This fact clarifies the nature of the peak with a width of $\sigma = 51 \cdot 10^{-7}$ in pentaethanodiferrocene. It is known that the NMR lines of cyclopentane and its derivatives are noticeably broadened even at a frequency of 60 MHz ([16]). This is caused by rapid transitions between different conformations of the ring, as well as by incomplete resolution of the superhyperfine spin-spin interaction. Thus, assigning the peak with $\sigma = 51 \cdot 10^{-7}$ to some modification of cyclopentane corresponds best to the observed picture.

On interaction of cyclopentenylferrocene with aluminum chloride in a heptane solution, from the heptane solution washed free of $AlCl_3$, along with higher-molecular-weight products there was obtained a dimer which, in its properties, analysis, molecular weight (cryoscopy in benzene), IR spectrum, and NMR spectrum, was indistinguishable from "pentaethanoferrocene."

It cannot be regarded as excluded that "pentaethanoferrocene" is a dimer with the single double bond remaining as a result of dimerization in the joined cyclopentane rings, for example, of the following structure:

Such a compound has the molecular formula $C_{30}H_{32}Fe_2$ and, of course, on the basis of analytical figures and molecular-weight determination is indistinguishable from $C_{30}H_{30}Fe_2$.

Found, %:	C 70.96, 71.55; H 6.49, 6.41; Fe 21.42, 21.21
$C_{30}H_{32}Fe_2$. Calculated, %:	C 71.58; H 6.42; Fe 22.02
$C_{30}H_{30}Fe_2$. Calculated, %:	C 71.68; H 6.02; Fe 22.30

However, in the NMR spectrum of a compound of this structure a special hydrogen in the CH group of the cyclopentene ring should have been detectable, reaction scheme

Figure 4: reaction scheme

Reaction scheme showing protonation and coupling of a ferrocenylcyclopentenyl system, followed by reduction with $+2e$, giving structure II.

Figure 5: Reaction scheme showing protonation and coupling of a ferrocenylcyclopentenyl system, followed by reduction with $+2e$, giving structure II.

as is the case for cyclopentenylferrocene (cf. Fig. 1 and Fig. 2). Our previous attempts to hydrogenate "pentaethanodiferrocene" over platinum and nickel catalysts in cyclohexane solution did not lead to absorption of hydrogen. Thus, the presence of a double bond in the substance does not reveal itself. If one recalls that carbonium cations attached to the ferrocene nucleus behave according to the scheme ($^{11-14}$):

with reduction at the last stage, possibly at the expense of an excess of ferrocene, it is natural to suppose that cyclopentenylferrocene, having attached a hydrogen ion, for example at the expense of an impurity of $H^+(AlCl_4)^-$ in chloroform-

aluminum is capable of a similar dimerization reaction in the sense of the scheme:

This structure II already corresponds to the formula $C_{30}H_{34}Fe_2$ and lies within the limits of the experimental molecular weight and analysis; however, it corresponds more closely to the NMR data, since it contains only 2 types of hydrogen atoms: 18 ferrocenyl and 16 methylene. Within the accuracy of the spectroscopic method, it is not excluded that, along with substance II, other isomers may also be present in some amount:

In the event that structure II, bis-1,1′-diferrocenyl-di-1,1′-dicyclopentyl, correctly expresses the structure of the substance previously described as pentaethanodiferrocene, the structure of the diacetyl derivative isolated by us in low yield should most probably be expressed by the formula:

since its IR spectrum did not have frequencies 1000—1107; the structures of the substances with molecular weights of about 1000 and 2000 described in our works (5^{-7}) must represent higher polymers of cyclopentenylferrocene.

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Displayed structural formula of a possible dimeric isomer, with the whole fragment in parentheses and subscript 2.

Figure 6: Displayed structural formula of a possible dimeric isomer, with the whole fragment in parentheses and subscript 2.

Displayed structural formula of the diacetyl derivative, with CH_3OC on the left and $COCH_3$ on the right.

Figure 7: Displayed structural formula of the diacetyl derivative, with CH_3OC on the left and $COCH_3$ on the right.

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