SovietRxiv

Soviet-era science, translated into English

Academician A. N. NESMEYANOV, E. G. PEREVALOVA, and T. V. NIKITINA

1961

SovietRxiv

View the original and related papers at https://sovietrxiv.org/items/ru-196101.11247

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

SovietRxiv

Abstract

Full Text

Academician A. N. NESMEYANOV, E. G. PEREVALOVA, and T. V. NIKITINA

SYNTHESIS OF AZOFERROCENE, ITS REDUCTION, AND ITS BEHAVIOR UNDER THE CONDITIONS OF THE BENZIDINE REARRANGEMENT

The molecular rearrangements in the ferrocene series known up to the present time are rearrangements in the side chain ([1,2]). Such rearrangements typical of benzene derivatives as the Claisen ([3]), Fries ([4]), and Sommelet ([2]) rearrangements cannot be carried out in the ferrocene series. The named rearrangements of aromatic compounds of the benzene series proceed intramolecularly*, i.e., they are the type of rearrangements most closely associated with the specific electronic interactions within the aromatic ring. In this connection, it is of great interest to expand the number of compounds of the ferrocene series whose behavior under rearrangement conditions characteristic of benzene derivatives has been studied.

In the present work we synthesized azoferrocene, studied its interaction with reagents that convert azobenzene into benzidine, and investigated the behavior of azoferrocene under conditions for obtaining hydrazo compounds and their subsequent rearrangement into benzidine. In no case did we detect a compound of the benzidine type.

Azo derivatives of ferrocene until very recently remained inaccessible. They could not be obtained by the action of diazo compounds on ferrocene ([6–9]). Attempts to diazotize aminoferrocene ([10]) also proved unsuccessful. Recently Nox ([11]) synthesized methyl- and phenylazoferrocene directly from methyl- and phenylazocyclopentadienyllithium and ferric chloride.

We obtained azoferrocene by the action of nitrous oxide on ferrocenyl lithium ([12]). An analogous reaction had previously been described for the example of phenyllithium ([13,14]).

$$C_5H_5FeC_5H_4Li \xrightarrow{N_2O} [C_5H_5FeC_5H_4N{=}NOLi] \xrightarrow{C_5H_5FeC_5H_4Li} C_5H_5FeC_5H_4N{=}NC_5H_4FeC_5H_5$$

We studied the behavior of azoferrocene under the conditions for the formation of benzidine from azobenzene, which occurs upon the action of strong acids

SovietRxiv

on azobenzene in almost all organic solvents ([15]). Under such conditions, azoferrocene does not give compounds of the benzidine type. Upon the action of concentrated hydrochloric or sulfuric acid, azoferrocene is partly converted into ferrocenylamine and is partly destroyed.

The difference in the properties of azoferrocene and azobenzene is apparently explained by the influence of the iron atom. The stability of the ferrocenylmethyl cation $C_5H_5FeC_5H_4\overset{+}{C}H_2$, noted in a number of works ([16]), and the conversion of this carbonium ion into the ion-radical ([17]) $C_5H_5\overset{+}{F}eC_5H_4CH_2\cdot$ convincingly indicate the capacity of the α-ferrocenylmethyl cation for intramolecular oxidation-reduction reactions involving the electrons of the iron atom.

This phenomenon probably has a general character in the series of ferrocene derivatives, and the peculiar behavior of azoferrocene that we found under the action of strong acids can be explained from this point of view. Azoferro-

* The mechanism of the Fries rearrangement has not been clarified. Gernshon ([5]) cites a number of weighty arguments in favor of the intramolecular character of this rearrangement in the case of aromatic esters of aliphatic and fatty-aromatic acids.

in the presence of a strong acid is protonated*, cation I arises, the positive charge of which is quenched by donation of electrons by the iron atom and by formation of ion-radical II, which subsequently, under the action of acid, gives ferrocenylamine and products of cleavage of the ferrocene nucleus

$$C_5H_5FeC_5H_4N{=}NC_5H_4FeC_5H_5 \xrightarrow{H^+} [C_5H_5FeC_5H_4N{=}NC_5H_4FeC_5H_5] \rightarrow$$

$$\rightarrow [C_5H_5\overset{+}{F}eC_5H_4\overset{+}{N}{-}NHC_5H_4FeC_5H_5]Cl^- \xrightarrow[-]{+HCl}$$

$$\rightarrow C_5H_5FeC_5H_4NH_2 + FeCl_2 + [C_5H_6 + C_5H_4NCl].$$

(I) (II)

On the basis of the work of Little and Clark ([19]) on the structure of phenylazo derivatives of ferrocene, to which, from the results of spectroscopic investigation, they ascribe a quinoid structure, it may be assumed that ion-radical II will have structure III.

[III

SovietRxiv

Further, we studied the reduction of azoferrocene under conditions in which, from azobenzene, hydrazobenzene is obtained in almost quantitative yield and formation of aniline is not observed. It turned out that azoferrocene does not react with lithium aluminum hydride, with phenylmagnesium bromide, or with lithium in tetrahydrofuran; with hydrazine hydrate and with zinc in an alkaline medium it is reduced to ferrocenylamine (yields 20 and 76%, respectively). Such behavior of azoferrocene has an analogy in the benzene-derivative series, since it has been shown [20] that azobenzenes having electron-donating substituents are reduced to hydrazo compounds with more difficulty than azobenzene itself, but cleavage of the corresponding hydrazo compound to an amine occurs more readily; and it is known that the electron-donating properties of the ferrocenyl group are considerably greater than those of the phenyl group.

In studying the reduction with zinc dust we obtained facts indicating the intermediate formation of hydrazoferrocene. Thus, on stirring and heating the reaction mixture, the violet color characteristic of azoferrocene gradually disappears, and the solution becomes light yellow. However, the color appears again as soon as stirring is stopped and the zinc settles to the bottom. This is repeated several times until, finally, the color disappears irreversibly. Probably the intermediate product in the reduction of azoferrocene is hydrazoferrocene, which is then reduced to the amine; in addition, its disproportionation occurs with formation of azoferrocene and ferrocenylamine.

$$\begin{array}{c} C_5H_5FeC_5H_4NH_2 \\ \uparrow H\cdot \\ C_5H_5FeC_5H_4N{=}NC_5H_4FeC_5H_5 \rightarrow [C_5H_5FeC_5H_4NHNHC_5H_4FeC_5H_5] \\ \downarrow \\ C_5H_5FeC_5H_4N{=}NC_5H_4FeC_5H_5 + C_5H_5FeC_5H_4NH_2 \end{array}$$

In the absence of a reducing agent, only the disproportionation process proceeds, and the concentration of azoferrocene rapidly increases, as is revealed by the appearance of the violet color. If the reduction is stopped at the first disappearance of the violet color and the reaction mixture is then divided into two equal parts, one of which is immediately treated with dilute hydrochloric acid, while the other part is first shaken for some time in air, then in both cases a mixture of azoferro-

* It is unlikely that protonation at the iron atom [18] will play a substantial role in this case.

···cene and ferrocenylamine, but in the second case the amount of azoferrocene is considerably larger, and the amount of ferrocenylamine correspondingly smaller. Evidently, under the action of dilute hydrochloric acid, in the first part the disproportionation* of hydrazoferrocene into the amine and azo compound is

SovietRxiv

rapidly completed, while in the second part the hydrazoferrocene that had not previously disproportionated is oxidized by atmospheric oxygen to azoferrocene.

No other amines, apart from ferrocenylamine, were detected by us in any case, which gives grounds to believe that a rearrangement of the benzidine type does not occur.

Evidently, rearrangements of aromatic compounds of the benzene series that proceed intramolecularly are not realized in the series of ferrocene derivatives. In all those cases where the principal role is played by the general ability of the system to donate electrons, the analogy of ferrocene with benzene or, better, with its derivatives having electron-donor substituents, is quite logical and has proved fruitful, as is shown by the successful study of the properties of ferrocene, which was based on the analogy with aromatic compounds of the benzene series. Rearrangements of benzene derivatives that are intramolecular in character, however, usually proceed through a cyclic transition state including structures of the quinoid type. In the case of ferrocene derivatives, such transition states cannot be of an analogous character, because in structures of this type the specific nature of the electronic interactions within the given system is strongly manifested, and in ferrocene derivatives iron will play the decisive role. Moreover, the "quinoid" structures of the benzene series will correspond, in the ferrocene series, to "fulvenoid" structures of the type of structure III written above. A complete analogy in the transmission of electronic effects for these two types of structures is unlikely.

Experimental Part

Preparation of azoferrocene ([12]). A solution of 0.04 mole of ferrocenyl lithium**, prepared from 20 g (0.11 mole) of ferrocene and 0.1 mole of butyllithium, in 300 ml of a mixture (2 : 1) of abs. ether and tetrahydrofuran was saturated for 30 min with nitrous oxide (8 l was passed through) with stirring and cooling (bath temperature −15°). The reaction mixture was then stirred for 1 hour at room temperature and left overnight.

Azoferrocene was separated from the other reaction products chromatographically on Al_2O_3 and recrystallized from benzene. Yield 2 g (25% of theory). M.p. 256–258° (with decomp.) in a sealed capillary.

Found, %: C 59.91; 60.10; H 4.88; 4.79; Fe 28.14; 28.11; N 7.27
$C_{20}H_{18}N_2$. Calculated, %: C 60.34; H 4.55; Fe 28.06; N 7.03

UV spectrum (in isooctane): λ_{max} 315, 375, 510 mμ ($\lg \xi_{max}$ 2.55; 1.88; 1.91).

Action on azoferrocene of conc. H_2SO_4. 0.5 g (0.00125 mole) of azoferrocene was thoroughly ground with a mixture of 0.2 g (0.0020 mole) of 98% H_2SO_4 and 8 ml of benzyl alcohol. The reaction mixture was then shaken for 8 hours at room temperature and left overnight. After this, 100 ml of water and 100 ml of benzene were added. The organic layer was separated, washed with

SovietRxiv

2N HCl and water, dried over Na_2SO_4, and chromatographed on Al_2O_3. 0.32 g (63% of the amount taken into the reaction) of azoferrocene was isolated.

The sulfuric-acid solution, combined with the hydrochloric-acid extracts, after alkalization with 2N NaOH was extracted with ether. The ether extracts

* Disproportionation of hydrazobenzene occurs only on heating above 100°, while under the action of acids a benzidine rearrangement takes place; disproportionation also occurs in this case, but to an insignificant extent. Introduction of electron-donor substituents noticeably facilitates the disproportionation process ([21]).

** The yield of ferrocenyl lithium was determined from the amount of ferrocenecarboxylic acid formed after carboxylation of a separate sample of the solution.

washed with water and dried over K_2CO_3. The ether was evaporated in vacuo under N_2. This gave 0.05 g (10% of theoretical) of ferrocenylamine, which was sublimed in vacuo. M.p. 150–154° in a capillary sealed under N_2; a mixed sample with an authentic specimen melted without depression.

The iron hydroxide precipitated on alkalization of the acidic solution was filtered off, reprecipitated with ammonia, and ignited in a muffle furnace. This gave 0.05 g of Fe_2O_3, corresponding to 0.13 g (26%) of decomposed azoferrocene.

Action of conc. HCl on azoferrocene. 0.1 g of azoferrocene was dissolved in 4 ml of conc. HCl. After alkalization, the hydrochloric acid solution was extracted with ether. Ferrocenylamine and Fe_2O_3 were isolated as described in the preceding experiment. This gave 0.44 g (44% yield) of ferrocenylamine and 0.02 g of Fe_2O_3, corresponding to 0.05 g (50%) of decomposed azoferrocene.

Reduction with zinc dust in alkaline medium.

Experiment No. 1. A mixture of 0.1 g of azoferrocene, 25 ml of alcohol, 10 ml of benzene, 0.5 ml of 20% NaOH, and 20 g of zinc dust was heated with vigorous stirring in an atmosphere of pure nitrogen until the violet coloration disappeared (15 min), then diluted with 200 ml of benzene and filtered under nitrogen into a separatory funnel. The solution, which again turned violet, was divided into two equal portions. One portion was immediately extracted with 3% HCl*. From the organic layer, 0.020 g (20%) of the starting azoferrocene was isolated, and from the acidic extracts, after alkalization, 0.023 g (23%) of ferrocenylamine was obtained.

The second portion was first shaken for 20 min with air. From the organic layer, 0.040 g (40%) of azoferrocene was isolated, and from the acidic extracts, after alkalization, 0.013 g (13%) of ferrocenylamine was obtained.

Experiment No. 2. This was carried out analogously to the preceding experiment, but stirring and heating were continued until the coloration had irreversibly disappeared (1 hour). After saturation with air, the solution filtered

SovietRxiv

from zinc was extracted with 3% HCl. From the acidic extracts, after alkalization, 0.076 g of ferrocenylamine was isolated. Yield 76% of theoretical. No azoferrocene was detected in the benzene layer.

Moscow State University
named after M. V. Lomonosov

Received
3 February 1961

CITED LITERATURE

1. K. Schlögl, H. Seiler, *Naturwiss.*, **45**, 337 (1958); A. Berger, J. Kleinberg, W. E. McEwen, *Chem. and Ind.*, **1960**, 204.

2. C. R. Hauser et al., *J. Org. Chem.*, **23**, 358 (1958).

3. A. N. Nesmeyanov, V. A. Sazonova, V. N. Drozd, L. A. Nikonova, *DAN*, **133**, 126 (1960).

4. R. E. Benson, R. V. Lindsay, *J. Am. Chem. Soc.*, **79**, 5471 (1957).

5. G. I. Geriizon, *ZhOKh*, **13**, 84 (1943).

6. A. N. Nesmeyanov, É. G. Perevalova, R. V. Golovnya, O. A. Nesmeyanova, *DAN*, **97**, 459 (1954).

7. A. N. Nesmeyanov, É. G. Perevalova, R. V. Golovnya, *DAN*, **99**, 539 (1954).

8. G. D. Broadhead, P. L. Pauson, *J. Chem. Soc.*, **1955**, 367.

9. V. Weinmayr, *J. Am. Chem. Soc.*, **77**, 3012 (1955).

10. A. N. Nesmeyanov, É. G. Perevalova, R. V. Golovnya, L. S. Shilovtseva, *DAN*, **102**, 535 (1955).

11. G. R. Knox, *Proc. Chem. Soc.*, **1959**, 56.

12. A. N. Nesmeyanov, É. G. Perevalova, T. V. Nikitina, *Tetrahedron Letters*, No. 1, 1 (1960).

13. F. M. Beringer, J. A. Farr, S. Sands, *J. Am. Chem. Soc.*, **75**, 3984 (1953).

14. R. Meier, W. Frank, *Ber.*, **89**, 2747 (1956).

SovietRxiv

15. A. N. Nesmeyanov, R. V. Golovnya, *DAN*, **133**, 1337 (1960).

16. L. H. Richards, E. A. Hill, *J. Am. Chem. Soc.*, **81**, 3484 (1959); D. S. Trifan, R. Bacskai, *Tetrahedron Letters*, No. 13, 1 (1960); M. F. Hawthorne, *J. Org. Chem.*, **21**, 363 (1956); C. Jutz, *Tetrahedron Letters*, No. 2, 1 (1959); G. R. Buell, W. E. McEwen, J. Kleinberg, *Tetrahedron Letters*, No. 5, 16 (1959).

17. A. Berger, J. K. Kleinberg, W. E. McEwen, *Chem. and Ind.*, **1960**, 1245.

18. T. J. Curphey, J. O. Santer et al., *J. Am. Chem. Soc.*, **82**, 5249 (1960).

19. W. F. Little, A. K. Clark, *J. Org. Chem.*, **25**, 1979 (1960).

20. M. Khalifa, *J. Chem. Soc.*, **1960**, 1854; M. Khalifa, W. H. Linnell, *J. Org. Chem.*, **24**, 853 (1959); G. P. Warwick, *J. Soc. Dyers and Colourists*, **75**, 291 (1959); *RZhKhim*, **1960**, 26490.

21. V. O. Lukashevich, L. G. Krolik, *DAN*, **120**, 316 (1958).

* Azoferrocene does not react with dilute HCl.

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.