Cyclopentadienyl Compounds of Metals and Compounds Related to Them 74-27-1-1/4

structure, as assumed by Pauson, did absolutely not correspond with its physical and chemical properties. The author deals with the magnetic properties of the ferrocene, discusses the results of the radiographic investigations of the known crystals of ferrocene, which confirm their so-called sandwich-structure. Also the method of electron diffraction was confirmed by this structure. Then follows a discussion of the results of the spectroscopic, thermochemical and polarographic investigation of the properties of ferrocene. Moreover the author occupies himself with the electron structure of the dicyclopentadienyl derivatives of the transitional metals. The chemical properties of the ferrocene, its oxidation and the reactions (with the destruction of the compound of iron with cyclopentadienyl rings) are discussed in a very detailed way. A discussion of the acylation of the ferrocene is following. After the interaction took place (ferrocene-acetyl chloride) diacetyl ferrocene was obtained; in a similar way di-β-chloro-propionyl-chloride ferrocene and di-o-carboxy benzoyl ferrocene were obtained. The investigations made it evident that there are acyl groups in all diacyl ferrocenes in several rings of the ferrocene nucleus. The investigations

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Cyclopentadienyl Compounds of Metals and Compounds Related to Them 74-27-1-1/4

with dibenzoyl ferrocene showed similar results. The reactions of the intramolecular acylation of the ferrocene have already been carried out by Nesmeyanov. Vol 'kenau and others. In these reactions 1,1-di-(ω-carboxyl-propionyl)-ferrocene was obtained with a yield of 18%. According to the reduction carried out by Klemmensen di-(ω-carboxy-propyl)-ferrocene was obtained with a yield of 77%. Further descriptions of the synthetization of cyclopentadienyl-ketotetrahydro-indenyl--iron and -ferrocene carried out are following. (References XIII, XIV, XV, formulae p 14). Then a detailed discussion of the possibility of an alkylation of the ferrocene is following. There are 11 tables and 219 references, 39 of which are Soviet.

1. Cyclic compounds--Analysis 2. Cyclic compounds--Synthesis

Card 3/3

PEREVA[illegible]

AUTHORS: [illegible] N., [illegible] N[illegible]

TITLE: [illegible] Mer[illegible] [illegible]fe[illegible]

PERIODICAL: [illegible] SSSR

ABSTRACT: As it [illegible] the fe[illegible] for the first [illegible] by the authors [illegible] the [illegible] synthesis [illegible] interaction [illegible] triphenyl [illegible] oxalic [illegible] nascent [illegible] Diferro[illegible] under [illegible] rig[illegible] tri[illegible]lmethane with [illegible] yie[illegible]

Card 1/4

20- [illegible]9-2-2[illegible]

Diferrocenyl Mercury Reactions

Reaction takes place under greater difficulties with sulfonic acids chloranhydrides. Thus, diferrocenylsulf[illegible] and phenyl ferrocenylsulfone are produced in a yi[illegible] 5-6 % on the heating of diferrocenyl mercury with [illegible] anhydrides of the ferrocene and benzene sulfonic [illegible]. On this occasion 45-38 % of the diferrocenyl mercury are converted into ferrocene. Reaction with acetyl chloride takes place even under greater difficulties. Acetyl ferrocene only forms in a yield of [illegible] % and ferrocene forms in great quantities as described above. Diferrocenyl mercury does not react at all with benzoyl chloride. Reactions take place more easily with sulfo iodides. In the reaction with iodine anhydride of the benzene [illegible] in a yield [illegible] ferrocenyl sulfone forms [illegible] mercury forms a complex with thiocyanogen [illegible] latter is processed by means of a watery s[illegible] sodium thiosulfate diferrocenyl also [illegible] of 15 % calculated with reference [illegible] which entered reaction. 12 % of the [illegible] remain unchanged. Probably the or[illegible]

Card 2/4

20-119-2-27/60

Diferrocenyl Mercury Reactions

thiocyanogen ferrocene is reduced into disulfide by the action of thiosulfate; moreover, 25 % of the diferrocenyl mercury which entered the reaction are converted into ferrocene. With $SeBr_4$ the mentioned compound forms diferrocenyl selenium in a yield of 21 %. On this occasion selenium is reduced to bivalence. In all cases the reaction product is precipitated either totally or partly in an oxidized (ferricinium) form and is then reduced by sodium thiosulfate. Thus, the important nucleophilic activity of the C-atoms in ferrocene (easy electrophilic subsitutution of the H atoms of the cyclopentadienyl rings) is expressed also in the properties of the mercury derivatives of ferrocene: diferrocenyl mercury reacts with sulfohalides under slighter conditions than diphenyl mercury (refs 3,4). The occurrence of ferrocene in all reactions investigated (except for $SeBr_4$) as by-product is possibly due to the forming of the ferrocenyl radical which carries along the hydrogen from the solvent or from other ferrocenyl groups. An experimental part with the usual data follows.

Card 3/4

[illegible]0-119-2-[illegible].60

Diferrocenyl Mercury Reactions

There are 4 references, 2 of which are Soviet

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova (Moscow State University imeni M. V. Lomonosov)

SUBMITTED: [illegible], 1957

[illegible]: [illegible]

Card 4/4

AUTHORS: Nesmeyanov, A. N., Member, Academy of Sciences, USSR, Perevalova, E. G., Churanov, S. S., Nesmeyanova, O. A. 20-119-5-30/59

TITLE: The Reactions of Ferrocene Sulfonic Acids (Reaktsii ferrotsensul'fokislot)

PERIODICAL: Doklady Akademii Nauk SSSR, 1958, Vol. 119, Nr 5, pp. 949-952 (USSR)

ABSTRACT: After having described ferrocene by various sulfonating reagents and some derivatives of ferrocene sulfonic acids in an earlier paper (reference 1) the authors in the present paper deal with a number of further sulfurous substituted ferrocenes which they obtained. Further an attempt was made to realize the exchange reaction of the sulfo group. By interaction of the lead salt of ferrocene disulfonic acid $Fe(C_5H_4SO_3)_2Pb.4H_2O$ with phosphorus trichloride they obtained monochlor anhydride $ClSO_2C_5H_4FeC_5H_4SO_3H$. Phosphorus oxychloride with the lead salt of the di-acid forms the acid dichloride of ferrocene disulfonic acid. The lead salt of monosulfonic acid is

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oxidized by phosphorus oxychloride to ferricinium-cation, on which occasion an intensive dark green color is produced. It is neither possible to obtain acid chlorides nor mono or disulfonic acid from barium salts. By heating of ferrocene disulfochloride with diethylamine the bis (diethylamide) of ferrocene disulfonic acid $Fe[C_5H_4SO_2H(C_2H_5)_2]_2$ was produced. From ferrocene monosulfochloride they produced diethylamide, the sodium salt of sulfinic acid, diferrocenyldisulfide and thioferrocenol, the latter as 2 derivatives: benzoate and S-ferrocenyl-thioglycolic acid. Thioferrocenol is in the air rapidly converted to a disulfide. In the infrared spectra of the obtained mono-substituted sulfurous compounds of ferrocene in the domain of 1000-1110 cm^{-1} (taken by L. A. Kazitsyna and B. V. Lokshin) characteristic maxima exist which indicate the presence of a free cyclopentadienyl ring. They are absent in all di-substituted ferrocene derivatives of this type. This confirms the authors' opinion expressed earlier (ref 1) that the sulfo groups are in different cyclopentadiene rings. The authors did not succeed in regaining the su

Card 2/4

The Reactions of Ferrocene Sulfonic Acids [illegible]

group by a hydroxy, (by melting together with alkali), by cyanogen (by means of the influence of potassium ferricyanide) or by a formyl group (by means of heating with sodium formiate); all these attempts led to a complete destruction of the ferrocene nucleus, where either ferric hydroxide or iron salt were liberated. The hydrolysis of sulfonic acids under formation of ferrocene also failed. The stability of the linkages of iron with the cyclopentadienyl rings is apparently highly reduced under the influence of the sulfo groups, as compared with ferrocene. The introduction of a sulfo group reduces the susceptibility to further substitution to a high degree in the same cyclopentadienyl ring and to a much lower degree in the other ring (ref [illegible]). The influence exerted by the sulfo group upon the reactivity of the ferrocene nucleus is similar to that of the acetyl group (reference 5). An experimental part with the usual data follows. There are 5 references, 4 of which are Soviet.

Card 3/4

The Reactions of Ferrocene Sulfonic Acids [illegible]

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova
(Moscow State University imeni M. V. Lomonosov)

SUBMITTED: January 16, 1958

Card 4/4

SOV/20-120-6-27/59

AUTHORS: Nesmeyanov, A. N., Member, Academy of Sciences, USSR, Perevalova, E. G., Beynoravichute, Z. A., Malygina, I. L.

TITLE: Reactions of 1,1'-Dimethyl Ferrocene (Reaktsii 1,1'-dimetilferrotsena)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol. 120, Nr 6, pp. 1263-1266 (USSR)

ABSTRACT: Reports were made already earlier on the influence of the substituents on the reactivity of the ferrocene nucleus. In the present paper the metallization- and acylation reactions of the substance mentioned in the title were investigated. n-amyl sodium was used as metallizing agent. In this connection two directions of reaction are possible: A substitution of a) the hydrogen of the methyl group, and b) of the hydrogen of the cyclopentadienyl cycle. The metallization into the methyl groups expected from the analogy with toluene (Ref 8) did not take place; on the contrary, it takes place into the cyclopentadienyl cycles. The main product (yield of 52 %) is dimethyl ferrocene dicarboxylic acid

Card 1/3

with a decomposition point at from 196 - 200°. Two acids were isolated in small quantities. All 3 acids yield solid dimethyl ethers and, hence, none of it is di-(carboxy-methyl)-ferrocene which forms liquid ether (Ref 9). The mutual position of the methyl- and carboxylic groups has not yet been determined. The acylation of the substance mentioned in the title was carried out by means of acetyl chloride under the presence of $AlCl_3$. The acylated products could not be separated. After protracted storing of the mixture diacetyl dimethyl ferrocene crystallized out. Two isomers could be separated from it by means of fractionated crystallization. On the basis of a comparison with Ref 10 it there is reason to believe that they contain stereoisomeric 1,1'-diacetyl ferrocenes. The monoacylated dimethyl ferrocene was isolated chromatographically from the residual liquid mixture. Due to the oxidation of this mixture with sodium hypochlorite, dimethyl ferrocene carboxylic acid was obtained as trimethyl ether. After the reduction of the same mixture by means of $LiAlH_4$ dimethyl triethyl ferrocene was isolated. Thus, in contradistinction to ferrocene a triacylated product is formed. The ferrocene nucleus is thus considerably activated in the reactions of the electrophilic substituents under the

Reactions of 1,1'-Dimethyl Ferrocene

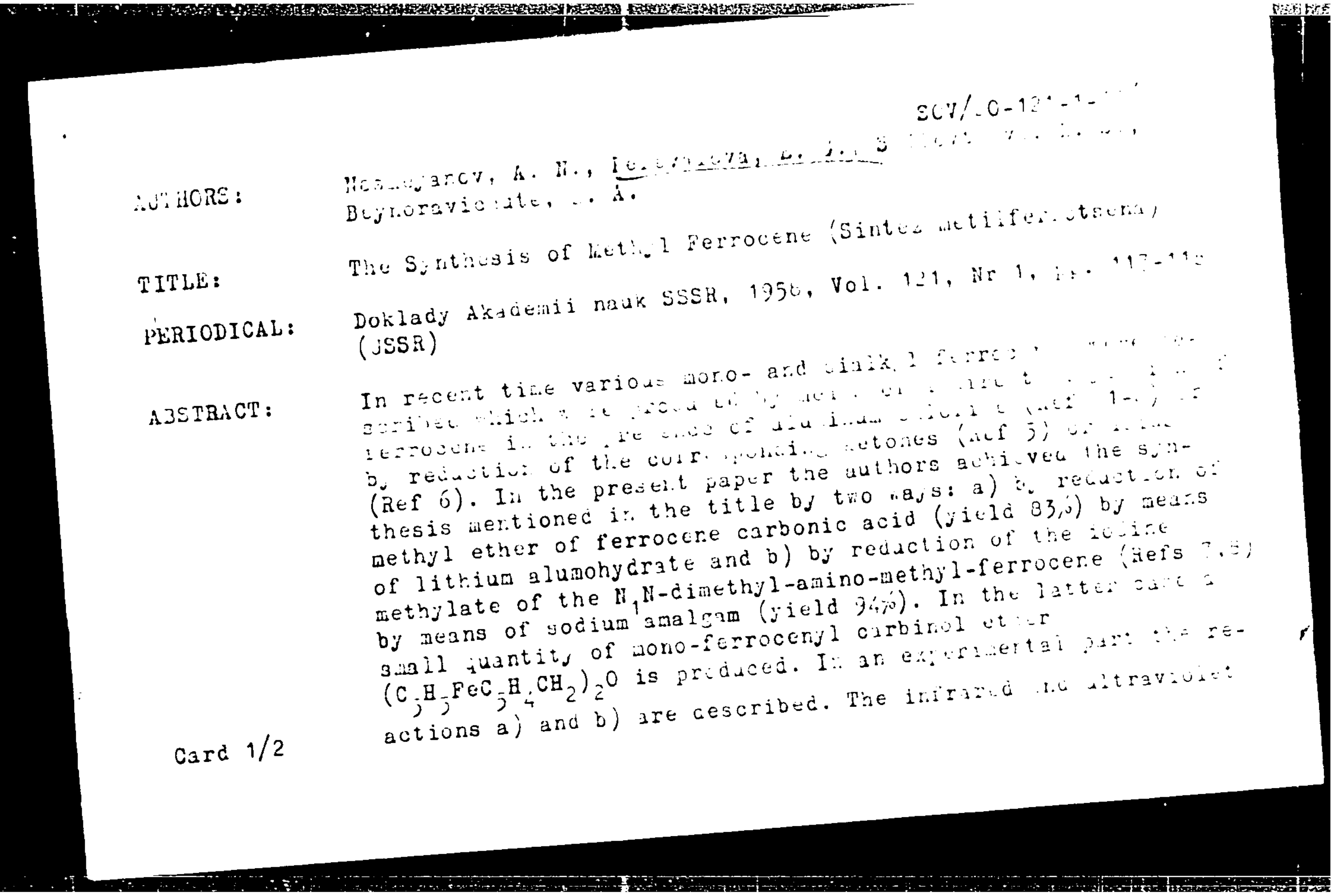
SOV/ 20-120-6-27

influence of the methyl groups. Moreover, the initial mixture was hydrogenized under pressure in the presence of skeleton nickel. Thereby, dialkyl cyclopentanes were isolated by means of distillation. There are 15 references, 7 of which are Soviet.

SUBMITTED: March [illegible], 1958

1. Ferrocenes--Chemical reactions

Card 3/3



SOV/20-121-1-[illegible]

AUTHORS: Nesmeyanov, A. N., Perevalova, E. G., S[illegible],
Beynoravichute, [illegible] A.

TITLE: The Synthesis of Methyl Ferrocene (Sintez metilferrotsena)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol. 121, Nr 1, pp. 117-119
(USSR)

ABSTRACT: In recent time various mono- and dialkyl ferrocenes [illegible] de-
scribed which were produced by [illegible] (Refs 1-4) of
ferrocene in the presence of aluminum chloride [illegible]
by reduction of the corresponding ketones (Ref 5) or also
(Ref 6). In the present paper the authors achieved the syn-
thesis mentioned in the title by two ways: a) by reduction of
methyl ether of ferrocene carbonic acid (yield 83%) by means
of lithium alumohydrate and b) by reduction of the iodine
methylate of the N,N-dimethyl-amino-methyl-ferrocene (Refs 7,8)
by means of sodium amalgam (yield 94%). In the latter case a
small quantity of mono-ferrocenyl carbinol ether
$(C_5H_5FeC_5H_4CH_2)_2O$ is produced. In an experimental part the re-
actions a) and b) are described. The infrared and ultraviolet

Card 1/2

The Synthesis of Methyl Ferrocene

SOV/20-121-1-32/[illegible]

spectra of the methyl ferrocene which was produced according to the reactions a) and b) are correspondingly identical. They were taken in the laboratoriya molekulyarnoy spektroskopii kafedry organicheskoy khimii (Laboratory of Molecular Spectroscopy of the Faculty of Organic Chemistry of the Moscow State University). In a paper on ferrocene alkylation (Ref 2) methyl ferrocene with a melting point of 118 - 119° was described. The produced product has a melting temperature of [illegible]. These last data are undoubted. The reasons for the [illegible] divergence are explained later. There are 9 references, [illegible] of which are Soviet.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova (Moscow State University imeni M. V. Lomonosov)

SUBMITTED: March 12, 1958

1. Methyl ferrocene--Synthesis 2. Methyl ethers--Reduction 3. Lithium aluminum hydrates--Chemical reactions 4. Methyl iodide--Reduction 5. Sodium--Chemical reactions

5(3)

AUTHORS: Nesmeyanov, A. N., Perevalova, E. G., Shilovtseva, L. S., Ustynyuk, Yu. A. SOV/20-124-2-25/71

TITLE: Synthesis of Ferrocene Derivatives by Means of the N,N-Dimethyl-Aminomethyl Ferrocene Methiodide (Sintez proizvodnykh ferrotsena s pomoshch'yu yodmetilata N,N-dimetilaminometilferrotsena)

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 124, Nr 2, pp 331-334 (USSR)

ABSTRACT: The compound last mentioned in the title was earlier used by the authors (Ref 5) for the synthesis of methyl ferrocene. It proved to be a suitable reagent for the introduction of the ferrocenyl-methyl group (Refs 2 - 8). In the present paper some substitution reactions of the dimethyl-amino group were carried out, furthermore methyl ferrocene was aminomethylated and ferrocene aminoethylated. It was thus possible to obtain the sodium salt of ferrocenyl-methane sulfonic acid by the interaction between the compound mentioned in the title and sodium sulfite. By the influence of potassium thiocyanate ferrocenyl-methyl thiocyanate was formed. Sodium phenolate and -β-naphtholate yielded the phenyl- and β naphthyl ether of the ferrocene carbinol.

Card 1/3

Synthesis of Ferrocene Derivatives
by Means of the N,N-Dimethyl-Aminomethyl Ferrocene Methiodide

SOV/20-124-2-25/71

By ferrocenyl methylation of the p-oxy-azo benzene an azo compound was formed containing a ferrocenyl group. This had hitherto not been possible. On the aminomethylation of the methyl ferrocene (Ref 5) with a mixture of N,N,N^1,N^1-tetramethyl-diamino methane and paraform a homoannular (N,N, dimethyl-amino methyl) methyl ferrocene was obtained in a 60% yield. The aminomethylation of the methyl ferrocene was carried out in the substituted cyclopentadiene ring in a yield which was somewhat higher than for ferrocene (51%, Ref 2). The addition of phosphoric acid increased the yield up to 80%. Besides, diaminomethylated methyl ferrocene is formed (10% yield). Thus the methyl group in the methyl ferrocene considerably activates the ferrocene nucleus against electrophilic attacks. The formation of the homoannular compound suggests that the ring to which the methyl group is bound, is activated to a more considerable degree. The successful production of the diamino-methylated methyl ferrocene further proves that the influence exerted by the substituents is transferred from one cyclopentadienyl ring to the other one by means of the iron atom (Ref 9). From the compound mentioned in the title the authors

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Synthesis of Ferrocene Derivatives SOV/20-124-2-25/71
by Means of the N,N-Dimethyl-Aminomethyl Ferrocene Methiodide

synthesized the homoannular dimethyl ferrocene. It may be assumed from the comparison of infrared spectra that the alkyl groups are in a 1.3-position. There are 12 references, 2 of which are Soviet.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova (Moscow State University imeni M. V. Lomonosov)

SUBMITTED: October 14, 1958

Card 3/3

5 (2,3)

AUTHORS: Nesmeyanova, O. A., Perevalova, E. G. SOV/20-126-5-26/69

TITLE: Diferrocenyl (Diferrotsenil)

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 126, Nr 5, pp 1007 - 1008 (USSR)

ABSTRACT: In order to produce diferrocenyl the authors have investigated the decomposition of diferrocenyl-mercury in the presence of palladium black. When heating mercury-organic compounds with metal powders without solvents, a radical doubling occurs (Ref 1). Thus, in the case of diphenyl-mercury, a satisfactory yield of diphenyl is obtained. In the present case, however, diferrocenyl is formed, but the yield is small. The main reaction product was ferrocene (Refs 2,3). Further in organic solvents insoluble substances, probably ferrocene-polymers were formed. The formation of ferrocene can apparently only be explained by the disproportioning of the ferrocenyl radicals formed as intermediate products. From these radicals ferrocene is formed, as well as its polymer or diferrocenylene. Yields are shown by table 1. The separation of ferrocene and diferrocenyl is described. Besides, the existence of the said polymers among the reaction products is proved. Diferrocenyl is an orange-colored

Diferrocenyl

SOV/20-126-5-26/69

crystalline substance, easily soluble in benzene, but less easily soluble in petroleum ether, ether, and alcohol. It crystallizes from alcohol. Diferrocenyl is thermally less stable than ferrocene. It becomes dark at 205°, and melts at 230° under partial decomposition. In this manner no ferrocene is formed. Consequently, the ferrocene forming in the catalytical splitting of the diferrocenyl-mercury is not a product of the chemical decomposition of diferrocenyl. There are 1 table and 3 Soviet references.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova (Moscow State University imeni M. V. Lomonosov)

PRESENTED: April 14, 1959, by A. N. Nesmeyanov, Academician

SUBMITTED: April 10, 1959

Card 2/2

PEREVALOVA, E.G.; NESMEYANOVA, O.A.; LUK'YANOVA, I.G.

Ferrocenesulfinic acids. Dokl.AN SSSR 132 no.4:853-856 Je '60. (MIRA 13:5)

1. Moskovskiy gosudarstvennyy universitet im. M.V.Lomonosova. Predstavleno akademikom A.N.Nesmeyanovym.
(Sulfinic acids)

S/020/60/132/04/33/064
B011/B003

5.3700(B)

AUTHORS: Perevalova, E. G., Nesmeyanova, O. A., Luk'yanova, I. G.

TITLE: Ferrocenesulfinic Acids

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 132, No. 4, pp. 853-856

TEXT: In a previous paper the authors described the production of ferrocenesulfinic acid (Ref. 1). In the article under review, they synthesized ferrocenedisulfinic acid and examined the properties of both acids. Ferrocenedisulfinic acid was obtained by reduction of the acid chloride of ferrocenedisulfonic acid with zinc dust. It is difficultly soluble in water and organic solvents. Its solutions are rapidly decomposed, and its disodium salt is much more stable. Both mono- and diferrocenesulfinic acid react with sublimates in a similar way as benzosulfinic acid and yield large quantities of mono- and di-(chloromercury)-ferrocene. The authors tried to obtain in a similar way a ferrocene derivative of tin by action of tinchloride on the sodium salt of sulfinic acid. They found, however, that a reduction 4

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Ferrocenesulfinic Acids

S/020/60/132/04/33/064
B011/B003

11

PRESENTED: January 12, 1960, by A. N. Nesmeyanov, Academician

SUBMITTED: January 3, 1960

PEREVALOVA, E.G.; NESMEYANOVA, O.A.

Synthesis of diferrocenyl by the Ullmann reaction. Dokl.AN SSSR 132 no.5:1093-1094 Je '60. (MIRA 13:6)

1. Moskovskiy gosudarstvennyy universitet im. M.V.Lomonosova. Predstavleno akademikom A.N. Nesmeyanovym.
(Iron)

83136

S/020/60/133/005/014/019
B016/B060

1312
5.3700(B)

AUTHORS: Nesmeyanov, A. N., Academician, Perevalova, E. G., Ustynyuk, Yu. A.

TITLE: Ferrocenyl Methyl Lithium

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 133, No. 5, pp. 1105-1107

TEXT: The authors previously described the production of ethers of ferrocenyl carbinol (Ref. 1). In the present study they used lithium to cleave ferrocenyl carbinol methyl ether dissolved in tetrahydrofuran. The resulting ferrocenyl methyl lithium was used to produce ferrocene derivatives. The authors proved furthermore that ferrocenyl carbinol ethers can be readily obtained by heating ferrocenyl carbinol with the respective alcohols in the presence of acetic acid. In this way, the authors obtained methyl-, ethyl-, and benzyl ethers of ferrocenyl carbinol in yields of 73, 80, and 72%. The ready formation of these ethers is explained by the stability of the ferrocenyl methyl

Card 1/2

NESMEYANOV, A.N., akad.; PEREVALOVA, E.G.; SIMUKOVA, N.A.; SHEYNKER,
Yu.N.; RESHETOVA, M.D.

Formation of the 1,2,3-oxadiazine ring in the reaction of
1,1'-diacetylferrocene with aryldiazonium compounds. Dokl.AN
SSSR 133 no.4:851-854 Ag '60. (MIRA 13:7)

1. Moskovskiy gosudarstvennyy universitet imeni M.V.Lomonosova.
(Oxadiazine) (Ferrocene) (Diazonium compounds)

87406

S/020/60/135/006/022/0[illegible]
B016/B060

53700

AUTHORS: Perevalova, E. G., Yur'yeva, L. P., and Baukov, Yu. I.

TITLE: Direct Cyanation of Ferricinium Salts

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 135, No. 6, pp. 1402-1405

TEXT: The authors report on the substitution of hydrogen atoms in ferricinium ferrichloride and ferricinium ferribromide. As had been expected, the ferricinium cation was passive in the electrophilic substitution, since the positive charge, no matter whether localized on the iron atom or distributed over the whole molecule, prevents electrophilic attacks. Thus the authors did not succeed in performing any electrophilic substitution in ferricinium. They therefore attempted nucleophilic substitution. Notable yields (over 50%) of nitrile of the ferrocene carboxylic acid were obtained when using the solution of liquid HCN in anhydrous tetrahydrofuran. A yield over 80% was obtained when ferricinium salt was replaced by a mixture of ferrocene and anhydrous $FeCl_3$. By this method one may also obtain the hitherto undescribed nitriles of substituted

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Direct Cyanation of Ferricinium Salts S/020/60/135/006/022/0
B016/B060

(methyl- and ethyl-) ferrocene carboxylic acids. It was observed from the infrared spectra of these nitriles that they contain a nonsubstituted cyclopentadienyl ring. It was concluded that the nitrile group enters such a ring as contains an electron donor substituent. A nonsubstituted cyclopentadienyl ring was missing in the other two compounds produced by the authors: in nitrile of heteroannular chloro ferrocene carboxylic acid and in dinitrile of heteroannular ferrocene dicarboxylic acid. This was spectroscopically confirmed (Ref. 14). Electron acceptor substituents (Cl, CN) are therefore believed to render the cyanation of the cyclopentadienyl ring with which they are linked more difficult; the CN group enters the free ring. The authors doubt their original assumption of the ferricinium cation being capable of a nucleophilic substitution, since the effect of electron donor and electron acceptor substituents was found to be as strong as in the electrophilic substitution. The material yielded by their experiments is regarded as being insufficient to establish the reaction mechanism. The only certain fact is that the reaction does not begin by an attack of the CN anion against one of the carbon atoms of the cyclopentadienyl rings. Two assumptions are put forth concerning the reaction mechanism: 1) a bond is formed first between the CN anion and the iron

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Direct Cyanation of Ferricinium Salts

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B016/B060

atom of the ferricinium cation, and the proton then attacks one of the hydrogen atoms of the cyclopentadienyl rings. This hydrogen is split off as a hydride compound and may be used up for the reduction of the ferricinium cation, while CN binds with the carbon atom of the cyclopentadienyl ring. Possibly, all these stages take place simultaneously within one single reaction complex (or a cyclic transitional stage). 2) There occurs a specific electrophilic (or homolytic) substitution, and ferrocene and CN^+ cation (or CN• radical) are involved in the reaction. In this case, the role of the ferricinium cation (or of $FeCl_3$) would consist in the transformation of the CN anion into a cation (or into a radical). L. A. Kazitsyna is thanked for having taken the spectra. A paper by Ye. M. Shustorovich and M. Ye. Dyatkina is mentioned (Ref. 8). There are 17 references: 10 Soviet, 4 US, 1 German, and 2 British.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova (Moscow State University imeni M. V. Lomonosov)

Card 3/4

Direct Cyanation of Ferricinium Salts

87406

S/020/60/135/006/022/037
B016/B060

PRESENTED: July 12, 1960, by A. N. Nesmeyanov, Academician

SUBMITTED: June 22, 1960

Card 4/4

89402
S/062/61/000/001/007/016
B101/B220

5 3700 2209, 1274, 1273

AUTHORS: Perevalova, E. G., Simukova, N. A., Nikitina, T. V., Reshetov, P. D., and Nesmeyanov, A. N.

TITLE: Interaction between ferrocene derivatives and aryl diazonia

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, no. 1, 1961, 77-83

TEXT: The authors have shown in Refs. 1-3 that ferrocene reacts with aryl diazonia to form aryl ferrocenes. The present paper deals with the arylation of p-tolyl, methyl, ethyl ferrocene, as well as acyl and carboxy ferrocenes. It was possible to arylate p-tolyl ferrocene by means of p-tolyl diazonium and this resulted in the formation of heteroannular di-(p-tolyl) ferrocene:

$$C_5H_5FeC_5H_4C_6H_4CH_3\text{-p} \xrightarrow{p\text{-}CH_3C_6H_4N_2Cl} Fe(C_5H_4C_6H_4CH_3\text{-p})_2$$

The yield amounted to only 9% of the theoretical one; this is attributed to the poor stability of the cation of this compound. Reaction between phenyl

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diazonium and methyl ferrocene resulted in a mixture of phenylated methyl ferrocenes from which it was possible to isolate the heteroannular methyl-phenyl ferrocene in a poor yield.

$C_5H_5FeC_5H_4CH_3 \xrightarrow{C_6H_5N_2X} CH_3C_5H_4FeC_5H_4C_6H_5$. The ethyl ferrocene reacted similarly (20% yield). Heteroannular dipropionyl, dibutyryl, and di-benzoyl ferrocene reacted with p-nitro-phenyl diazonium in the same way as observed in the case of diacetyl ferrocene. The bond between the iron and the cyclopentadienyl ring was split, and derivatives of 1,2,3-oxa-diazine were formed. Resinification took place in the reaction between p-nitro-phenyl diazonium and the dimethyl ester of ferrocene dicarboxylic acid. It was proved possible to isolate chromatographically a reduced amount of p-nitro-phenyl-dicarbomethoxy ferrocene, but the ferrocene ring was destructed at the same time (appearance of iron ions). Monosubstituted ferrocenes, such as acetyl ferrocene and carbomethoxy ferrocene, react with p-nitro-phenyl diazonium like ferrocene, but with a lower yield of arylation products. Monoacetyl ferrocene formed both homoannular and heteroannular p-nitro-phenyl acetoferrocene:

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S/062/61/000/001/007/016
B101/B220

Interaction between ferrocene...

$$C_5H_5FeC_5H_4COCH_3 \xrightarrow{p\text{-}NO_2C_6H_4N_2Cl} CH_3COC_5H_4FeC_5H_4C_6H_4NO_2\text{-}p$$

$+ C_5H_5FeC_5H_3(COCH_3)C_6H_4NO_2\text{-}p$. The methyl ester of ferrocene carboxylic acid reacts to form heteroannular p-nitro-phenyl carbomethoxy ferrocene (yield 7%). The presence or absence of the non-substituted cyclopentadienyl ring was always established spectroscopically. The free mono- and dicarboxylic acids of ferrocene as well as their sodium salts together with p-nitro-phenyl diazonium gave mixtures from which the arylation products could not be isolated. L. V. Yershova and M. Kristynyuk assisted in the experiments. There are 14 Soviet-bloc references.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova (Moscow State University imeni M. V. Lomonosov)

SUBMITTED: July 28, 1959

Card 3/3

NESMEYANOV, A.N., akademik; PEREVALOVA, E.G.; GUBIN, S.P.; NIKITINA, T.V.;
PONOMARENKO, A.A.; SHILOVTSEVA, L.S.

Properties of phenylferrocene. Dokl. AN SSSR no.4:888-891 Ag '61.
(MIRA 14:7)

1. Moskovskiy gosudarstvennyy universitet im. M.V. Lomonosova.
(Ferrocene)

NESMEYANOV, A.N.; PEREVALOVA, E.G.; SHILOVTSEVA, L.S.

Reactions between organomagnesium compounds and (Ferrocenylmethyl) trialkylammonium salts. Izv.AN SSSR.Otd.khim.nauk no.11:1982-1985 N '61.
(MIRA 14:11)

1. Moskovskiy gosudarstvennyy universitet im. M.V.Lomonosova.
(Magnesium organic compounds) (Ammonium compounds)

5 3700

25317

S/020/61/138/005/017/025
B103/B215

AUTHORS: Nesmeyanov, A. N., Academician, Perevalova, E. G., and Nikitina, T. V.

TITLE: Synthesis of azoferrocene, its reduction and behavior under the conditions of benzidine rearrangement

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 138, no. 5, 1961, 1118-1121

TEXT: The authors synthesized azoferrocene, examined its interaction with reagents transforming azobenzene into benzidine, and studied the behavior of azoferrocene under the conditions of the production of hydrazo compounds and their subsequent benzidine rearrangement. Azo derivatives of ferrocene were first synthesized by G. R. Knox (Ref. 11: Proc. Chem. Soc., 1959, 56) (methyl- and phenyl azoferrocene). The authors obtained azoferrocene by the action of N_2O upon ferrocenyl lithium (Ref. 12: Tetrahedron Letters, No. 1, 1 (1960)). A similar reaction was described for phenyl lithium (F. M. Beringer, J. A. Farr, S. Sands, Ref. 13: J. Am. Chem. Soc., 75, 3984 (1953); R. Meier, W. Frank, Ref. 14: Ber., 89, 2747 (1956)). There is hardly any organic solvent with which azoferrocene would form

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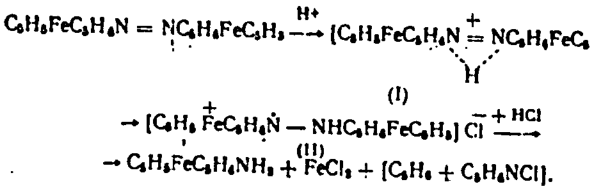
Synthesis of azoferrocene, its..25317

S/020/61/138/005/017/025
B103/B215

benzidine-type compounds under the action of strong acids (conditions of benzidine formation from azobenzene). The action of concentrated HCl or H_2CO_4 partly causes its decomposition, and partly its transformation into ferrocenyl amine. The authors explain this peculiar behavior of azoferrocene which differs from that of azobenzene as follows: azoferrocene is protonized in the presence of a strong acid, and cation I forms whose positive charge is neutralized due to electrons supplied by the iron atom, and due to the formation of ion radical II. Ferroacenyl amine and fission products of the ferrocene ring were obtained from II by acid action:



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

(I)

$$\rightarrow [C_5H_5\overset{+}{Fe}C_5H_4\dot{N} - NHC_5H_4FeC_5H_5]\overset{-}{Cl} \xrightarrow{+HCl}$$

(II)

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

No. 1

The authors assume that the ion of II has a III structure:

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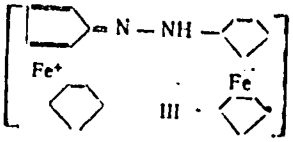

No.2

(W. F. Little, A. K. Clark, Ref. 19: J. Org. Chem., 25, 1979 (1960)). Furthermore, the authors studied the reduction of azoferrocene under conditions under which hydrazo benzene is formed from azobenzene with almost quantitative yield, while almost no aniline is formed. Azoferrocene proved to react neither with lithium aluminum hydride, nor with phenyl magnesium bromide, nor with lithium in tetrahydrofuran medium. In alkaline medium it is reduced to ferrocenyl amine (yields: 20 %, and 76 %, respectively) by hydrazine hydrate and zinc. This behavior of azoferrocene is similar to that of benzene derivatives; azobenzenes with donor substituents cannot be reduced to hydrazo compounds as easily as azobenzene itself, whereas the corresponding hydrazo compound can more easily be reduced to amine. It is known that the donor properties of the ferrocenyl group are much stronger than those of the phenyl group. Hydrazo ferrocene probably formed as an intermediate in the reduction with

Synthesis of azoferrocene, its... 25317 S/020/61/138/005/017/025
B103/B215

zinc dust. Stirring and heating of the reaction mixture makes the violet color of azoferrocene disappear gradually. However, it appears again as soon as stirring has stopped, and zinc has dropped to the bottom. This is repeated until the color disappeared irreversibly. The authors assume a further reduction of hydrazo ferrocene to amine, and also its disproportionation into azoferrocene and ferrocenyl amine. Without a reducing agent, only disproportionation takes place and causes a rapid increase in the azoferrocene concentration and violet coloring. If the reduction is interrupted at the first disappearance of the violet color, and if the reaction mixture is divided into two equal parts one of which is treated with diluted HCl whereas the other one is shaken in the air, a mixture of azoferrocene and ferrocenyl amine is formed in both cases. In the second case, however, the amount of azoferrocene is much higher than that of ferrocenyl amine. In the first case, the disproportionation of hydrazo ferrocene into amine and azo compound is much faster under the action of HCl. In the second half, the hydrazo ferrocene which so far has not been disproportionated, is oxidized into azoferrocene by atmospheric oxygen. Since no other amine besides ferrocenyl amine has been found, the authors conclude that a benzidine-type rearrangement does

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Synthesis of azoferrocene, its... 25317 S/020/61/138/005/017/025
B103/B215

not take place. They hold the opinion that ferrocene derivatives do not undergo intramolecular rearrangement characteristic of the benzene series. An analogy of ferrocene and benzene proved successful in those cases where the general ability of electron supply of the system played the main part. Intramolecular rearrangement of benzene derivatives is usually characterized by a cyclic transition stage including quinoide-type structures. In the case of ferrocene derivatives, similar transition states cannot be of the same character. The specifity of electron interactions within the system is very distinct in such structures, and iron plays a decisive role in ferrocene derivatives. Furthermore, "fulvenoid" structures (see III in scheme no. 2) will correspond to the "quinoide" structure of the benzene series. A complete analogy in the conveyance of electron influences in these two structures is very unlikely. G. I. Gershzon is mentioned. There are 21 references: 7 Soviet-bloc and 14 non-Soviet-bloc. The four references to English-language publications are given in the body of the abstract.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova (Moscow State University imeni M. V. Lomonosov)

Card 5/6

25856
S/020/61/139/004/016/025
B 103/B206

5 3750

AUTHORS: Nesmeyanov, A. N., Academician, Perevalova, E. G., Gubin, S. P., Nikitina, T. V., Ponomarenko, A. A., and Shilovtseva, L. S.

TITLE: Properties of phenyl ferrocene

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 139, No. 4, 1961, 868-89

TEXT: The authors investigated: 1) the amino methylation, 2) sulfonation, 3) concurrent (with ferrocene) acetylation, and 4) nitration of phenyl ferrocene. They established that the alkyl group, if linked with the ferrocene ring, facilitates the subsequent electrophilic substitution In this case, the cyclopentadienyl ring to which the alkyl group is bonded, is more strongly activated. In relation to the ferrocenyl group, the phenyl group is an electron-acceptor group (A. N. Nesmeyanov et al. Ref. 5: DAN, 103, 81 (1955)). These data by the authors were confirmed by M. Rosenblum (J. Am. Chem. Soc., 81, 4530 (1959)): The electrophilic substitution of the hydrogen atoms in the ferrocene ring is deactivated by the phenyl group. 1) Amino methylation. To a mixture of 70 ml of glacial

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B103/B206

Properties of phenyl ferrocene

acetic acid and 4 g of H_3PO_4, cooled to 10°C, 2.25 g (0.019 mole) of tetramethyldiaminoethane is gradually added, and then 4 g (0.015 mole) of phenyl ferrocene. The reaction mass was stirred for 1 hr at room temperature and for 10 hr at 110 - 115°C in a nitrogen current and subsequently diluted with water to the double amount. The ferrocene (1.5 g) which had not entered into reaction was extracted with benzene. 40% NaOH solution was added to the acidic solution, and the formed (N, N-dimethylaminomethyl)-phenyl ferrocene was extracted with ether. After distilling off the ether, 2.6 g of the above-mentioned compound was obtained as a viscous, dark, reddish-brown oil. The yield amounted to 54% of the theoretical one (related to phenyl, ferrocene) and to 86% of the phenyl ferrocene reacted. The final product was distilled in vacuo its boiling point was 150-160°C/3 mm Hg; n_D^{20} 1.6315. In the infrared spectrum of the final product, weak absorption bands existed in the range 1000 and 1100 cm^{-1}. From this, the authors assume the formation of a mixture from the hetero- and homoannular isomers. The latter seems to form in small quantities The methiodide of the final product was produced by addition of CH_3I to

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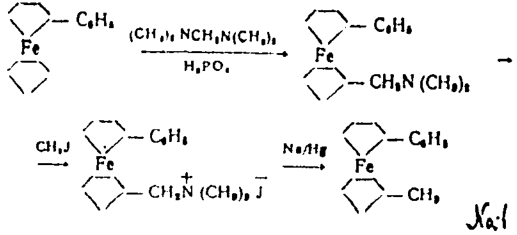
a solution of 3.2 g in absolute Ch_3OH (or in benzene) with precipitation after 15 min by a great amount of anhydrous ether. An almost quantitative (4.3 g) amount of methiodide was produced. It is a yellow, crystalline substance with the decomposition point 70 - 75°C. Since in the infrared spectrum of the methiodide which was produced from the distilled final product, absorption at 1000 and 1100 cm^{-1} is missing, the authors conclude that the substituting groups are in various cyclopentadienyl rings. Through reduction of the methiodide by sodium amalgam, the heteroannular 1, 1-methyl-phenyl ferrocene was obtained (see reaction no. 1).



Card 3/6

25636

Properties of phenyl ferrocene

S/020/61/139/004/016/025
B103/B206

The yield was 1.8 g (71% of the theoretical one). Absorption at 1000 and 1100 cm^{-1} was missing in its infrared spectrum. A free cyclopentadienyl ring can only be proved spectroscopically in the substance which was isolated from the mother liquor. The authors came to the conclusion that the heteroannular isomer was the main component of the mixture produced by amino methylation. Therefore, this reaction mainly occurs in the free cyclopentadienyl ring. 2) To a solution of 10 g (0.038 mole) of phenyl ferrocene in 100 ml of dichloroethane, 10 g (0.060 mole) of freshly prepared dioxane sulfotrioxide was added while cooling with ice. Under the conditions of formation of ferrocene monosulfonic acid, 1', 1 phenyl ferrocene sulfonic acid was obtained.

$C_6H_5C_5H_4FeC_5H_5 \xrightarrow{SO_3\text{-dioxane}} C_6H_5C_5H_4FeC_5H_4SO_3H$. This acid was isolated as lead salt, which crystallizes with 4 water molecules. Absorption at 1000 and 1100 cm^{-1} was here also missing: the phenyl and sulfo groups are therefore in different cyclopentadienyl rings. The formation of heteroannular sulfonic acid is also proof of a lower reactivity of the ring

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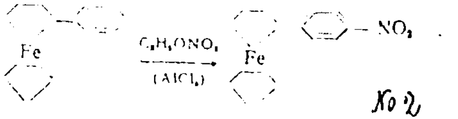
linked with phenol. 3) The deactivating effect of the phenyl group on the ferrocenyl ring is specially marked during the Friedel-Crafts reaction. A solution of 1.4 ml of acetyl chloride and 2.66 g of $AlCl_3$ in 10 ml of absolute ether was added in the course of 20 min to a solution of ferrocene (3.72 g) and phenyl ferrocene (5.42 g) in 100 ml of CS_2. All components were used at a molar ratio of 1:1:1:1. The authors obtained acetyl ferrocene only with a yield of 25% of the theoretical one, and a mixture of acetyl phenyl ferrocenes of only 5%, 64% of phenyl ferrocene and 30% of ferrocene being recovered unchanged. From this, the authors conclude that ferrocene may be acetylated more easily than phenyl ferrocene. 4) Phenyl ferrocene was nitrated by means of ethyl nitrate in CS_2 in the presence of $AlCl_3$. The authors obtained a 13% yield (of the theoretical one) of p-nitro-phenyl ferrocene (see reaction no. 2).



No 2

Properties of phenyl ferrocene

S/020/61/139/004/016/025
B103/B206

The main quantity of this final product is isolated together with part of the nonreacted phenyl ferrocene in nonoxidized state (and not as a cation). The authors presume that nitration does not take place with the phenyl ferrocene cation but with phenyl ferrocene. The continuance of the ferrocenyl ring under these conditions is noticeable, probably as a consequence of a reduced capability of being oxidized to a cation as compared with ferrocene. Ferrocene itself cannot be nitrated under these conditions. Attempts of the authors to nitrate ferrocene with various other reagents (e. g., nitronium borofluoride) also failed. Only oxidation of ferrocene to the cation which is inert in reactions of the electrophilic substitution, was brought about. There are 9 references: 7 Soviet-bloc and 3 non-Soviet-bloc. One reference to English-language publications is given in the body of the abstract, the another one reads: M. Rosenblum, R. B. Woodward, J. Am. Chem. Soc., 80, 5443 (1958).

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova (Moscow State University imeni M. V. Lomonosov)

SUBMITTED: April 19, 1961

Card 6/6

PEREVALOVA, E. G.

Dissertation defended for the degree of Doctor of Chemical Sciences at the Institute of Elemento-organic Compounds in 1962:

"Ferrocene as an Aromatic System."

Vest. Akad. Nauk SSSR. No. 4, Moscow, 1963, pages 119-145

ACCESSION NR: AP4010040 S/0062/64/000/001/0062/0069

AUTHORS: Usty*nyuk, Yu. A.; Perevalova, E. G.

TITLE: Reactivity of compounds containing the ferrocenylmethyl group. 7. Rearrangement of the dimethylbenzyl(ferrocenylmethyl)ammonium chloride under the action of nucleophilic reagents

SOURCE: AN SSSR. Izvestiya. Ser. khim., no. 1, 1964, 62-69

TOPIC TAGS: ferrocenylmethyl compounds, reactivity, rearrangement, ferrocenylmethyl group, stabilizing action, isomerization, intramolecular reduction, carbanion stabilization, nucleophilic reagents dibutyllithium

ABSTRACT: The comparative stabilizing action of the benzyl and the ferrocenyl rings on an adjacent carbanion center was determined from the rearrangement products. Dimethylbenzyl(ferrocenylmethyl) ammonium chloride (I) rearranges in the presence of dibutyllithium to (alpha-phenyl-beta-ferrocenylethyl)-dimethylamine (II), 72% yield. In the presence of potassium amide, conversion is 50%, with benzyl-

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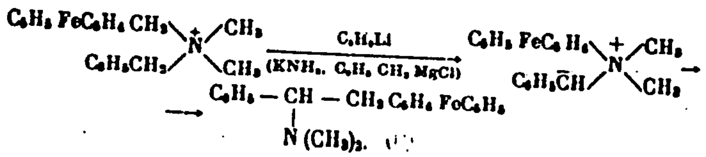
ACCESSION NR: AP4010040

magnesium chloride, 21%.



Thus the benzene ring stabilizes the adjacent anion center more than the ferrocenyl ring does. A new type of isomerization was observed in the reaction with dibutyllithium; N,N,N', N'-tetramethyl-alpha,beta-diphenylethylene diamine and 1,2-diferrocenylethane were produced in addition to II, the amount of II decreasing on prolonging the reaction. The following intramolecular reduction of the ammonium nitrogen is suggested:

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ACCESSION NR: AP4010040

"Authors express deep appreciation to A. N. Nesmeyanov for attention to the work and valuable advice." Orig. art. has: 10 Equations.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR Moskovskiy gosudarstvenny*y universitet im. M. V. Lomonosova (Institute of Organometallic Compounds, Academy of Sciences SSSR Moscow State University)

SUBMITTED: 06Sep62 DATE ACQ: 14Feb64 ENCL: 00

SUB CODE: CH NR REF SOV: 006 OTHER: 005

Card 3/3

S/0062/64/000/001/0070/0073

ACCESSION NR: AP4010041

AUTHORS: Usty*nyuk, Yu.A.; Perevalova, E.G.; Nesmeyanov, A.N.

TITLE: The reactive ability of compounds containing the ferrocenylmethyl group Report No.8. Wittig rearrangement in a series of ferrocenylcarbinol ethers

SOURCE: AN SSSR. Izvestiya. Ser. khim., no.1, 1964, 70-73

TOPIC TAGS: ferrocenylmethyl group, Wittig rearrangement, ferrocenylcarbinol ethers, butyl lithium, lithium ether linkage, ether isomerization, anionic center stabilization, 1 phenyl 2 ferrocenylethanol, 2 phenyl 1 ferrocenylethanol, 1,2 diferrocenylethanol, 1,2 diferrocenylethylene

ABSTRACT: In continuation of earlier work, this rearrangement was studied for the benzylferrocenylmethyl and bisferrocenylmethyl ethers under the influence of butyllithium and tetrahydrofuran. During reaction with the first compound a 55% yield of 1-phenyl-2-ferrocenylethanol-1 was obtained without formation of its 2-phenyl-1-ferrocenyl-

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ACCESSION NR: AP4010041

ethanol isomer, while reaction of the second yielded 1,2-diferrocenylethanol. The latter rearrangement proceeded with less ease, with a yield of only 23% and a 27% residue of unchanged starter ether. The product of the second rearrangement was converted into 1,2-diferrocenylethylene by dehydration; this latter is a red crystalline substance, m.p. 264-265, soluble in hot benzene, toluene and chloroform. The new data confirmed earlier findings, i.e., that the ferrocenyl nucleus will stabilize the adjoining carbonation center to a lesser degree than the benzene ring. The laboratory procedure, the products obtained, and their description and IR spectra are reported. "The authors wish to thank O.T. Nikitina for determining the molecular weight." Orig. art. has: 4 formulas.

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk SSSR (Institute of Organoelemental Compounds, Academy of Sciences SSSR); Moskovskiy gosudarsteny*i universitet im. M.V. Lomonosova (Moscow State University)

SUBMITTED: 10Sep62 DATE ACQ: 14Feb64 ENCL: 00

SUB CODE: CH NR REF SOV: 004 OTHER: 004

Card 2/2

33264
S/062/62/000/001/005/011
B106/B101

5 3700

AUTHORS: Nesmeyanov, A. N., Perevalova, E. G., and Nesmeyanova, O. A.

TITLE: Mechanism of ferrocene formation in electrophilic and homolytic reactions of iodoferrocene and mercury derivatives of ferrocene

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 1, 1962, 47 - 52

TEXT: In almost all electrophilic and homolytic reactions of iodoferrocene and mercury derivatives of ferrocene, ferrocene is formed as an unexpected by-product. The mechanism of ferrocene formation was studied with the aid of some reactions of diferrocenyl mercury. When boiling diferrocenyl mercury with metallic sodium for 15 min in absolute benzene and subsequently carboxylating the reaction mixture with dry ice, no ferrocene carboxylic acid was obtained but ferrocene (10% of the theoretical value) besides a large portion of the initial product. Reaction of diferrocenyl mercury with $SnCl_2$ in petroleum ether gave 15% of

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B106/B101

Mechanism of ferrocene formation...

ferrocene besides metallic mercury. Reaction of diferrocenyl mercury with $CuCl_2$ in dioxane yielded an inseparable mixture of chloroferrocene and ferrocene. Reaction of copper chloride with 1,1'-di-(mercury chloride ferrocene yielded a mixture of dichloro ferrocene and ferrocene containing much more ferrocene which could be isolated from the mixture. The formation of ferrocene can be explained in all these cases, if a ferrocenyl radical is assumed to be involved, which either splits a hydrogen atom from the solvent, or, if the latter is absent, even from the ferrocene derivatives. The formation mechanism of this ferrocenyl radical is unclear. The radical can not be formed by thermal splitting of diferrocenyl mercury because the latter withstands long heating in benzene. Results of previous studies of the authors show that in electrophilic substitution of mercury in diferrocenyl mercury according to the pattern $(C_5H_5FeC_5H_4)_2Hg \xrightarrow{RX} C_5H_5FeC_5H_4R + (C_5H_5)_2Fe$ the yield of ferrocene decreases with increasing readiness of substitution. The formation of ferrocene during the decomposition of diferrocenyl mercury in the presence of palladium black without solvent, previously observed by two of the present authors, can be attributed to the fact that a ferrocenyl radical is formed as an intermediate product which splits a hydrogen atom from

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33264
S/062/62/000/001/003/015
Mechanism of ferrocene formation... B106/B101

other radicals or from diferrocenyl mercury. To find out whether this was also true for reactions in solvents without hydrogen, the behavior of the ferrocenyl radical in CCl_4 was investigated. An unambiguously radical reaction was already observed when diferrocenyl mercury was heated in absolute CCl_4. This reaction led to the formation of mercury chloride ferrocene (57%), ferrocene (22%), and resins which, in addition to carbon, iron, and hydrogen, also contained chlorine and mercury (in the atomic ratio of 10-12 : 1). When heating diferrocenyl mercury in absolute CCl_4 in the presence of hydroquinone and benzoyl peroxide, neither resins nor mercury chloride ferrocene were formed, but only 12 and 3% ferrocene, respectively, whereas the bulk of diferrocenyl mercury did not react. Addition of antioxidants or radical sources inhibited the reaction, which indicates the chainlike nature of the process. Thus, the following pattern is suggested for the reaction between diferrocenyl mercury and CCl_4:

$$C_5H_5FeC_5H_4^{\cdot} + (C_5H_5FeC_5H_4)_2Hg \rightarrow C_5H_5FeC_5H_5 + C_5H_5FeC_5H_4-Hg-C_5H_4FeC_5H_4^{\cdot}$$

$$C_5H_5FeC_5H_4-Hg-C_5H_4FeC_5H_4^{\cdot} + CCl_4 \rightarrow C_5H_5FeC_5H_4-Hg-C_5H_4FeC_5H_4CCl_3 + Cl^{\cdot}$$

$$Cl^{\cdot} + C_5H_5FeC_5H_4-Hg-C_5H_4FeC_5H_5 \rightarrow C_5H_5FeC_5H_4HgCl + C_5H_5FeC_5H_4^{\cdot}$$

Card 3/4

S/062/62/000/010/001/003
B144/B186

AUTHORS: Nesmeyanov, A. N., Perevalova, E. G., and Shilovtseva, L. S.

TITLE: Aminomethylation of phenyl, tolyl, and chloro ferrocenes

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 10, 1962, 1767 - 1772

TEXT: Phenyl, p-tolyl, and chloro ferrocenes were aminomethylated with N,N,N',N'-tetramethyl diamino-methane in glacial acetic acid in the presence of H_3PO_4 by heating between 110 and 115°C in an N_2 stream for 12 hr. The mixture was then diluted with the same amount of H_2O, the non-converted initial products were extracted with benzene, and the solution was alkalized with 40% NaOH. The end products were extracted with ether and chromatographed on Al_2O_3 impregnated with formamide. The quantitative composition of N,N-dimethyl-amino-methyl ferrocenes were determined by paper chromatography.

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S/062/62/000/010/001/0C3
B144/B186

Aminomethylation of phenyl,...

Initial ferrocene	Amino isomers			Iodine methylates	
	number, type	R_f in benzene	% of total amines	m.p., °C	in IR spectrum 1000-1100 cm^{-1}
phenyl	1 heterocyclic	0.14	82	90-95	-
	2 homocyclic	0.38;	15	143-145	1004; 1104
		0.81	3	167-170	1103; 1106
p-tolyl	1 heterocyclic	0.26	83	95-99	-
	1 homocyclic	0.57	17	172-175	1004, 1106
chloro	1 heterocyclic	*0.22	80	185-190	-
	1 homocyclic	*0.32	11	163-166	1006; 1104
	1 mixed		9		

* $CHCl_3:C_6H_6$ = 1:1

Thus the aminomethylation was effected mainly (~5:1) in the non-substituted cyclopentane dienyl ring; this was shown also by the IR spectra of iodomethylate of the substances obtained. The spectra of heterocyclic isomers showed no 1000-1100 cm^{-1} bands. Iodomethylates were obtained by converting amines with twice the methyl iodide excess in benzene; their compositions and gross formulas are given. An excess of 1,1'-methyl-p-tolyl ferrocene,

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S/062/62/000/010/001/003
B144/B186

Aminomethylation of phenyl,...

$C_{18}H_{18}Fe$ (m.p. 93 - 95°C) was obtained from the iodomethylate of 1,1'-(N,N-dimethyl aminomethyl)-p-tolyl ferrocene by reduction with sodium amalgam. There are 2 tables.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova (Moscow State University imeni M. V. Lomonosov)

SUBMITTED: March 7, 1962

Card 3/3

41638

S/062/62/000/010/002/003
B144/B186

11 2131
11 2219

AUTHORS: Nesmeyanov, A. N., Perevalova, E. G., Yur'yeva, L. P., and Grandberg, K. I.

TITLE: Direct cyanidation of ferrocene derivatives

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 10, 1962, 1772 - 1777

TEXT: Bromo, nitro, acetyl, phenyl, p-nitrophenyl ferrocenes (F') and phenyl ferrocenyl sulfone were cyanidated; ferricinium borofluoride (I) and ferricinium chloro platinate (II) were synthesized and I was cyanidated. Bromo, phenyl, and p-nitrophenyl-F' were cyanidated by a method given in Dokl. AN SSSR, 135, 1402 (1960). The cyanidation of phenyl-F' yielded 88.5% phenyl ferrocene carbonic acid nitrile, $C_{17}H_{13}NFe$, a reddish-brown, oily substance with the composition C 71.06, 71.05; H 4.97, 5.00;, and N 5.19, 5.30%. The IR absorption bands at 1004 and 1106 cm^{-1} showed the homocyclic structure of this nitrile. The substance was converted into the amide $C_{17}H_{15}NOFe$ by adding KOH and H_2O_2 (yield 32%;

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m.p. 155.5 - 156.5°C), as it does not crystallize. A heterocyclic nitrile, $C_{11}H_8BrNFe$ was obtained by cyanidating bromo-F' (yield: 78%; m.p. 91-92°C; C 45.62, 45.92; H 2.88, 3.09; Br 27.83, 27.67; N 5.00, 5.00; Fe 19.32, 19.46%). Cyanidation of p-nitrophenyl-F' yielded dark red, resin-like crystals of a heterocyclic nitrile, $C_{17}H_{12}NO_2Fe$ (m.p. 134 - 135°C; C 61.42, 61.40; H 3.55, 3.74; N 8.21, 8.37; Fe 16.54, 16.46%). Cyanidation of nitro and acetyl-F' yielded only 3 and 18% by heating for 2 and 6.5 hrs, respectively, even with a considerable excess of $FeCl_3$ and HCN. Treatment of 1.5 g phenyl ferrocenyl sulfone with 4.6 g $FeCl_3$, 60 mg tetrahydrofuran, and 3 ml liquid HCN, yielded 52% heterocyclic phenyl sulfone ferrocenyl carbonic acid nitrile, $C_{17}NO_2SFe$, (m.p. 141 - 141.5°C; C 58.30, 58.51; H 3.88, 4.11; N 4.17, 4.39; S 9.02, 9.13; Fe 15.97, 16.10%). Cyanidation of F'-carbonic acid nitrile with a considerable excess of $FeCl_3$ and HCN added to it, increased the yield in dinitrile from 27 to 62%. F' was also cyanidated immediately into the dinitrile of 1,1'-ferrocene dicarbonic acid (yield: 68%). Experiments with an equimolecular F'-mononitrile mixture showed that cyanidation into mononitriles is much easier than into

Direct cyanidation of ferrocene... S/062/62/000/010/002/003
B144/B186

dinitriles. I was synthesized by passing BF_3 through a benzene solution of 5.58 g F' with 1.62 g quinone. It is a dark violet crystalline substance, $C_{10}H_{10}BF_4Fe$, which is easily soluble in H_2O, acetone, and nitromethane (C 44.06, 44.16; H 3.65, 3.75; F 28.15, 28.43%). II was obtained from aqueous ferricinium ferrichloride solution and chloroplatinic acid; it is a bluish black, crystalline substance, $(C_{10}H_{10}Fe)_2PtCl_6$, which is moderately soluble in H_2O and, when heated, decomposes into methanol and nitromethane forming F' (C 30.39, 30.22; H 2.77, 2.73; Cl 27.42, 27.06%). When cyanidating I, $2(C_5H_5)_2Fe^+BF_4^- + HCN \rightarrow C_5H_5FeC_5H_4CN + Fe(C_5H_5)_2 + 2HBF_4$, 44% of the initial compound was converted into nitrile, and 45% was reduced into F'.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova
(Moscow State University imeni M. V. Lomonosov)

SUBMITTED: March 7, 1962

Card 3/3

NESMEYANOV, A.N.; PEREVALOVA, E.G.; SHILOVTSEVA, L.S.; TYURIN, V.D.

Ferrocenylmethylation by means of N,N-dimethylaminomethylferrocene and its iodomethylate. Izv.AN SSSR. Otd.khim.nauk no.11:1997-2001 N '62. (MIRA 15:12)

1. Moskovskiy gosudarstvennyy universitet im. M.V. Lomonosova.
(Ferrocene)

NESMEYANOV, A.N.; PEREVALOVA, E.G.; YUR'YEVA, L.P.; GRANDBERG, K.I.

Direct cyanation of ferrocene derivatives. Izv. AN SSSR.Otd.khim. nauk no.10:1772-1777 O '62. (MIRA 15:10)

1. Moskovskiy gosudarstvennyy universitet im. M.V.Lomonosova. (Ferrocene) (Hydrocyanic acid)

S/062/62/000/011/006/021
B101/B144

AUTHORS: Nesmeyanov, A. N., Perevalova, E. G., Shilovtseva, L. S., and Tyurin, V. D.

TITLE: Ferrocenyl methylation by means of N,N-dimethyl aminomethyl ferrocene and its iodo methylate

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 11, 1962, 1997 - 2001

TEXT: The following syntheses were made with N,N-dimethyl aminomethyl ferrocene (A), trimethyl(ferrocenyl-methyl) ammonium iodide (B), and dimethyl-ethyl(ferrocenyl-methyl) ammonium bromide (C):- (1) Reaction of B with $Na_2S \cdot 10H_2O$ on a boiling water bath and extraction with ether produced di-(ferrocenyl-methyl) sulfide, yield 54%, m.p. 107 - 108°C (with decomposition). The IR spectrum contained absorption bands at 1000 and 1104 cm^{-1}. (2) Di-(ferrocenyl methyl) disulfide, yield 33%, m.p. 125-127°C (with decomposition), was obtained from B and NaSH, the latter being produced by bubbling H_2S through NaOH solution. (3) The synthesis of ferro-

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S/062/62/000/011/006/021
B101/B144

Ferrocenyl methylation by means of...

cenyl methyl acetate was made in three ways: (a) Reaction of B with glacial acetic acid at 90 - 95°C in N_2 atmosphere, yield 25%, m.p. 74-76°C, IR absorption bands at 997, 1104, and 1740 cm^{-1}. A compound soluble in benzene, (gross formula $C_{12}H_{12}Fe$, m.p. 115-135°C) formed at 110-150°C; it was not further investigated. (b) Reaction of C with sodium acetate at 150-155°C in vacuum (7 mm Hg), yield 39%, m.p. 75-76°C. (c) Reaction of A with acetic anhydride, yield 89%. The compound obtained by (c) was, as to m.p. and IR spectrum, identical with the compounds obtained by reactions (a) and (b). (4) Reaction of A with methyl benzoate in N_2 atmosphere at 130 - 135°C, and extraction with benzene, produced ferrocenyl methyl benzoate, yield 50%, m.p. 132-135°C, IR bands at 1003, 1098, 1700 cm^{-1}. (5) Reaction of A with methyl anthranilate produced ferrocenyl methyl anthranilate, yield 46%, m.p. 123-124°C, IR bands at 996, 1102, 1686 cm^{-1}. (6) Heating of B with ethyl acetate at 120-125°C produced, instead of the expected ferrocenyl methyl acetate, ferrocenyl carbinol ethyl ether, yield 42%, b.p. 68-70°C/0.3 mm Hg, n_D^{20} 1.5840. The IR bands at 1002, 1106 cm^{-1}

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proved the existence of a nonsubstituted cyclopentadienyl ring. Bands of an ester carbonyl group were not observed. (7) B with butyl acetate produced ferrocenyl carbinol butyl ether, yield 35%, m.p. 31.5-32.5°C, b.p. 105-106°C/2 mm Hg, n_D^{20} 1.5695. IR bands at 1004 and 1104 cm^{-1}. (8) Heating of B with piperidine at 110°C produced N-(ferrocenyl-methyl) piperidine, yield 94%, m.p. 84.5 - 85.5°C, IR bands at 1002, 1103, 1303 cm^{-1}. Reaction of A with piperidine did not lead to a substitution of the dimethyl amino radical. (9) N-(ferrocenyl-methyl) morpholine was obtained from B and morpholine at 120-130°C, yield 95%, m.p. 74-75°C, IR bands at 1006, 1104 cm^{-1}. (10) N-(ferrocenyl-methyl) aniline was obtained from B and aniline in boiling aqueous solution, yield 75%, m.p. 84-84.5°C, IR bands at 1000, 1106, 1602, 1552-1566, 3930 cm^{-1}. (11) N-(ferrocenyl-methyl) phthalimide was obtained from B and potassium phthalimide in dimethyl formamide solution at 130-140°C, yield 97%, m.p. 209-210°C (with decomposition), IR bands at 1000, 1102, 1706, 1758 cm^{-1}. (12) Ferrocenyl methyl amine was obtained from N-(ferrocenyl-methyl) phthalimide and hydrazine hydrate heated at 80-90°C in N_2 atmosphere, by precipitation with NaOH, b.p.

Ferrocenyl methylation by means of...

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108-110°C/0.3 mm Hg, n_D^{20} 1.6510, IR bands at 1002, 1106, 3288, 3368 cm^{-1}. This compound decomposes in air. Bubbling of HCl through its benzene solution yielded ferrocenyl methyl amine hydrochloride, decomposition temperature 233-235°C.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova (Moscow State University imeni M. V. Lomonosov)

SUBMITTED: April 2, 1962

Card 4/4

PEREVALOVA, E.G.; BUBIN, S.P.; SMIRNOVA, S.A.; NESMEYANOV, A.N.,
akademik

Redox potentials of heteroannual disubstituted ferrocenes.
Dokl. AN SSSR 155 no. 4:857-860 Ap '64. (MIRA 17:5)

1. Moskovskiy gosudarstvennyy universitet im. Lomonosova i
Institut elementoorganicheskikh soyedineniy AN SSSR.

S/062/62/000/012/005/007
B117/B101

AUTHORS: Nesmeyanov, A. N., Perevalova, E. G., Yur'yeva, L. P., and Denisovich, L. I.

TITLE: Reaction between ferrocene carboxylic acid nitrile with organometallic compounds and production of di- and triferrocenyl-methyl compounds

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 12, 1962, 2241-2243

TEXT: Reaction of ferrocene carboxylic acid nitrile with ethyl magnesium bromide yielded propionyl ferrocene (m.p. 38-39°C) and the same reaction with methyl magnesium iodide yielded acetyl ferrocene (m.p. 85-86°C). The ketone yield was found to be 70 and 80% at a considerable Grignard reagent excess. Diferrocenyl ketone (m.p. 210-211°C, yield 55-60%) was obtained from reaction between ferrocenyl lithium and ferrocene carboxylic acid nitrile. Differrocenyl ketone was used for synthesizing compounds of the triferrocenyl methane series, not hitherto described. The reaction of diferrocenyl ketone with ferrocenyl lithium yielded 60% triferrocenyl

Card 1/2

37383

S/020/62/143/006/016/024
B106/B138

5.3700

AUTHORS: Gubin, S. P., and Perevalova, E. G.

TITLE: Formal redox potentials of monosubstituted ferrocenes

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 143, no. 6, 1962, 1351-1354

TEXT: The formal redox potentials of 30 monosubstituted ferrocenes were determined by potentiometric titration with potassium bichromate in a mixture of acetic acid and aqueous perchloric acid. Relative quantitative data were thus obtained on the effect of substituents on the oxidation of the ferrocene nucleus to the ferricinium cation. The determinations were conducted by the method of J. G. Mason and M. Rosenblum (Ref.2: J. Am. Chem. Soc., 82, 4206 (1960)) at 25 ± 0.1°C in nitrogen atmosphere. Table 1 shows the results. The differences of the logarithms of the equilibrium constants for the reactions of substituted and unsubstituted ferrocene were calculated from the corresponding potentials (Column 4, Table 1) and compared with the constants σ^* and σ^0 according to Taft (Ref. 10: M. S. N'yumen, Prostranstvennyye effekty v organicheskoy khimii (M. S. Newman, Steric effects in organic chemistry), IL, 1960, 591), and σ_m and

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Formal redox potentials of...

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B106/B138

published statement that hydrogen and alkyl substituents cannot interact with the reaction center by the field effect mechanism (Ref. 9: V. A. Pal'm, Usp. khim., 30, 1069 (1961)). The interaction by the field effect mechanism occurs over a shorter distance, which leads to an increase in the absolute value of ρ. Academician A. N. Nesmeyanov is thanked for cooperation and advice. There are 1 figure and 1 table. The most important English-language references read as follows: T. Kuwana, D. E. Bublitz, G. Hoh, J. Am. Chem. Soc., 82, 5811 (1960); H. H. Jaffe, Chem. Rev., 53, 191 (1953); D. S. Trifan, R. Baskai, Tetrahedron Letters, 1960, no. 13, 1; J. D. Roberts, R. A. Carboni, J. Am. Chem. Soc., 77, 5554 (1955).

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova (Moscow State University imeni M. V. Lomonosov)

PRESENTED: December 12, 1961, by A. N. Nesmeyanov, Academician

SUBMITTED: November 9, 1961

Card 3/5

Formal redox potentials of...

S/020/62/143/006/016/024
B106/B138

Table 1. Formal redox potentials of monosubstituted ferrocenes $C_5H_5FeC_5H_4X$ (formulas do not take account of changes in the reaction medium).

Legend: (I) E_{f_o}, v (according to a standard calomel electrode); (II) m., °C; (III) $\frac{b., {}^oC}{mm\ Hg}$; (IV) under decomposition; ^{2} calculated from the formula $(E_o^X - E_o^H)/0.0591 = \log K/K_o$; ^{3} only the primary σ_n values obtained from the dissociation constants of the corresponding p-substituted benzoic acids have been used; ^{4} the potentials of these compounds differ slightly from published data; the potential differences between ferrocene and phenyl ferrocene, and between ferrocene and p-nitrophenyl ferrocene, are constant within the error limits of the experiment; ^{5} from published data; ^{6} the value for the $-COOC_2H_5$ group from published data has been used. In olumn 2: изо = iso; м = m; п = p.

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S/020/62/147/002/015/021
B106/B101

AUTHORS: ~~Perevalova, E. G.,~~ Gubin, S. P., Smirnova, S. A., Nesmeyanov, A. N., Academician

TITLE: Redox properties of compounds containing two ferrocenyl groups

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 147, no. 2, 1962, 384-387

TEXT: The authors studied the effect produced by one ferrocene ring on the redox properties of a second ferrocene ring bound to the first either directly (diferrocenyl) or by groups Y of different conductivity (-Hg-, -CH_2-, -CH_2-CH_2-, -CH_2-O-CH_2-, -CH_2-$N^+(CH_3)_2$-CH_2-). They measured the first and second redox potentials E'_{f_0} and E''_{f_0} (Table 1). The significance of E'_{f_0} and E''_{f_0} is evident from the following scheme:

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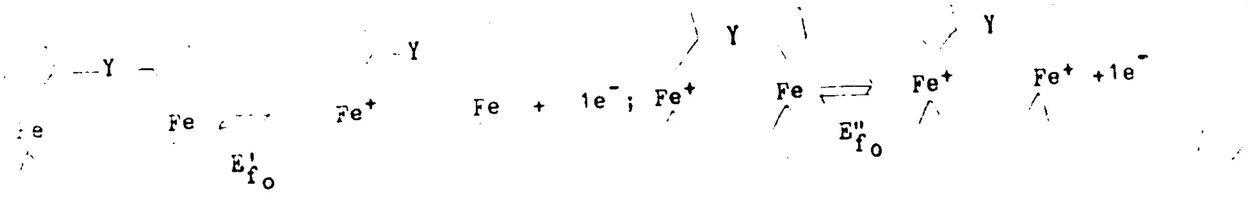
B106/B101

Redox properties of compounds ...



Under the chosen conditions diferrocenyl was oxidized at one Fe atom only. When two ferrocene rings interact, the electron density increases at the ring oxidized. The redox potentials indicate that the methylene group transfers to the other nucleus; hardly any of the electron-donor effect of the ferrocenyl group, whereas the effect of the positively charged ferricinium ion is transferred even across bridges of 3 atoms. The investigations covered also how some substituents in the methyl group of methyl ferrocene affect the redox potentials (Table 2): in this case, too, the effect of electron-acceptor substituents was transferred via the methylene group to a notably greater extent than that of electron-donor substituents. There are 4 figures and 2 tables. The most important English-language references are: R. W. Taft Jr., J. Am. Chem. Soc., 75,

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Redox properties of compounds ... S/020/62/147/002/015/021
B106/B101

4231 (1953); H. H. Jaffe, Chem. Rev., 53, 191, (1953).

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova (Moscow State University imeni M. V. Lomonosov)

SUBMITTED: July 18, 1962

Table 1. Redox potentials of compounds with two ferrocenyl groups $C_5H_5FeC_5H_4$-Y-$C_5H_4FeC_5H_5$ (in v, related to the standard calomel electrode). Legend: (1) melting point, °C; (2) diferrocenyl; * * obtained by reduction of diferrocenyl ketone; (3) with decomposition.

Table 2. Redox potentials of some monosubstituted ferrocenes $C_5H_5FeC_5H_4CH_2X$. Legend: (1) v, related to the standard calomel electrode; * mean deviation from the E_{f_0} values indicated ±0.003 v

Card 3/4

NESMEYANOV, A.N.; PEREVALOVA, E.G.; YUR'YEVA, L.P.; GRANDBERG, K.I.

Synthesis of ferrocene derivatives from nitriles of ferrocenecarboxylic acids. Izv.AN SSSR.Ser.khim. no.8:1377-1380 Ag '63. (MIRA 16:9)

1. Moskovskiy gosudarstvennyy universitet im. Lomonosova.
(Ferrocene) (Nitriles) (Ferrocenecarboxylic acid)

L 12852-63 EWP(j)/EPF(c)/EWT(m)/BDS Pr-4/Pc-4 RM/WW
ACCESSION NR: AP3002287 S/0062/63/000/006/1036/1045

63
62

AUTHOR: Perevalova, E. G.; Usty*nyuk, Yu. A.; Nesmeyanov, A. N.

TITLE: The reactivity of compounds containing the ferrocenylmethyl group. Report 1. Hydrolytic cracking of tetravalent ammonium salts

SOURCE: AN SSSR. Izv. Otdeleniye khimicheskikh nauk, no. 6, 1963, 1036-1045

TOPIC TAGS: tetravalent ammonium salts, ferrocenylmethyl group, hydrolytic cracking, rate of hydrolysis

ABSTRACT: A series of tetravalent ammonium salts containing the ferrocenylmethyl group was synthesized, i.e. compounds of the type shown in the enclosure, where RCH sub 2 is methyl, ethyl, n-propyl, n-butyl, n-nonyl, benzyl, allyl, carboxymethyl, phenacyl or ferrocenyl methyl, and the anion X is chloro, bromo, iodo or picryl. Hydrolytic cracking of these compounds in alkaline, neutral and 50% aqueous dioxane solutions was studied: rate of hydrolysis was independent of anions and of solvent concentration, but increased with electron acceptor properties of the CH sub 2 R group. Hydrolysis proceeded according to the S sub N 1 mechanism with the intermediate formation of the ferrocenylmethyl cation. Orig. art. has: 9 tables, 8 formulas, and 1 figure.

Card 1/2 Moscow St. Un.

PEREVALOVA, E.G.; USTYNYUK, Yu.A.; NESMEYANOV, A.N.

Reactivity of compounds containing a ferrocenylmethyl group. Report No.4: Reaction of ferrocenylmethyllithium. Izv. AN SSSR. Ser. khim. no.11:1967-1972 N '63.

Reactivity of compounds containing a ferrocenylmethyl group. Report No.5: Preparation of organolithium compounds with α-ferrocenyl alkyl groups. Ibid.:1972-1977 (MIRA 17:1)

1. Moskovskiy gosudarstvennyy universitet imeni Lomonosova.

L 12728-63 EWP(j)/EPF(c)/EWP(q)/EWT(m)/BDS AFFTC/ASD Pc-4/Pr-4 RM/WW/JD/WB

ACCESSION NR: AP3002288 S/0062/63/000/006/1045/1049

69

68

AUTHOR: Perevalova, E. G.; Usty*nyuk, Yu. A.; Nesmeyanov, A. N.

TITLE: Reactivity of compounds containing a ferrocenylmethyl group. Report 2. Regeneration of tetravalent ammonium salts, containing ferrocenylmethyl radical, with sodium amalgam by Emde

14

SOURCE: AN SSSR. Izv. Otdeleniye khimicheskikh nauk, no. 6, 1963, 1045-1049

TOPIC TAGS: ferrocenylmethyl group, trimethyl ferrocenylmethyl ammonium iodide, dimethylallyl ferrocenylmethyl ammonium iodide, dimethylbenzyl ferrocenylmethyl ammonium iodide, sodium amalgam

ABSTRACT: The reduction of trimethyl-, dimethylallyl-, and dimethylbenzyl ferrocenylmethyl ammonium iodide with sodium amalgam by the method of Emde and coworkers (Arch. Pharm. v. 247, 1909, 333, 314, 351; v. 249, 1911, 111, 118, 166; Liebigs Ann. Chem. 391, 1912, 88) was investigated. The ferrocenylmethyl group split off from the N of the tetravalent ammonium much more readily than the methyl, much less readily than the benzyl, and at about the same rate as the allyl group. Hence, ferrocene group stabilizes the neighboring radical center less than the benzyl, and more than the methyl radical, and about equally to the double bond of

Card 1/2

PEREVALOVA, E.G.; USTYNYUK, Yu.A.; USTYNYUK, L.A.; NESMEYANOV, A.N.

Reactivity of compounds containing a ferrocenylmethyl group. Report No.6: Steric effects in reactions of alkylation by quaternary ammonium salts. Izv. AN SSSR. Ser. khim. no.11: 1977-1985 N '63. (MIRA 17:1)

1. Moskovskiy gosudarstvennyy universitet imeni Lomonosova.

ACC NR: AP7012431 SOURCE CODE: UR/0062/66/000/008/1467/1469

AUTHOR: Nesmeyanov, A. N. Perevalova, E. G.; Yur'yeva, L. P.; Gosteyeva, G. N.

ORG: Institute of Heteroorganic Compounds, AN SSSR (Institut elementoorganicheskikh soyedineniy AN SSSR)

TITLE: Synthesis of nitriles of phenylferrocenecarboxylic acids

SOURCE: AN SSSR. Izvestiya. Seriya khimicheskaya, no. 8, 1966, 1467-1469

TOPIC TAGS: organic nitrile compound, chemical separation, phenylferrocenecarboxylic acid

SUB CODE: 07

ABSTRACT: The authors describe an improvement on an earlier method for separating mixtures of amides of isomeric phenylferrocenecarboxylic acids, prepared by the hydrolysis of the reaction products of the cyanation of phenylferrocene. The individual amides of the isomeric phenylferrocenecarboxylic acids were converted to the corresponding nitriles. The nitrile of p-ferrocenylbenzoic acid was also prepared from the amide of p-ferrocenylbenzoic acid and used as a standard in gas chromatographic analysis of the mixture of nitriles of 1,2-, 1,3-, and 1,1'-phenylferrocenecarboxylic acids, obtained in the cyanation of phenylferrocene. Orig. art. has: 2 formulas and 1 table. [JPRS: 40,422]

UDC: 542.91+542.957+621.785.666

Card 1/1 0932 1377

ACC NR: AP7012420 SOURCE CODE: UR/0062/66/000/011/1938/1943

AUTHOR: Nesmeyanov, A. N.; Perevalova, E. G. Tyurin, V. D.; Gubin, S. P.

ORG: Moscow State University im. M. V. Lomonosov (Moskovskiy gosudarstvennyy universitet)

TITLE: Metallation of alkylferrocenes

SOURCE: AN SSSR. Izvestiya. Seriya khimicheskaya, no. 11, 1966, 1938-1943

TOPIC TAGS: ferrocene, lithium compound, ferrocenyllithium

SUB CODE: 07

ABSTRACT: The metallation of methyl-, ethyl-, and n-propylferrocene with excess n-butyllithium at room temperature was studied. Mixtures of mono- and dimetallated alkylferrocenes were obtained. The monometallated alkylferrocenes were found to possess a heteroannular structure. The mixture of mono- and dimetallated alkylferrocenes, after carboxylation, were converted to a mixture of mono- and dicarboxylic acids. Metallation of alkylferrocenes proceeded with greater difficulty than that of ferrocene itself. Approximately 2-2.5 times as much of the monometallated alkylferrocene was formed as of the dimetallated derivative. The metallated alkylferrocenes were also used for the synthesis of heteroannular nitroalkylferrocenes by the reaction with propyl nitrate. Nitromethyl-, nitroethyl-, and nitropropylferrocenes were obtained in low

Card 1/2 UDC: 542.91 + 547.1'3 + 546.72

0932 1356

ACC NR: AP7012420

yields. No dinitro-compounds were isolated. Orig. art. has: 3 formulas, 4 tables. [JPRS: 40,422]

2/2

L 35318-66 EWT(m)/EWP(j) RM

ACC NR: AP6026891 SOURCE CODE: UR/0062/65/000/012/2120/2124

22

C

AUTHOR: Nesmeyanov, A. N.; Perevalova, E. G.; Nikitina, T. V.; Kuznetsova, N. I.

ORG: Moscow State University im. Lomonosov (Moskovskiy gosudarstvennyy un[illegible])

TITLE: Behavior of m- and p- ferrocenylhydrazobenzenes under conditions of benzidine rearrangement

SOURCE: AN SSSR. Izvestiya. Seriya khimicheskaya, no. 12, 1965, 2120-2124

TOPIC TAGS: benzidine, benzene, substituent, ferrocene, molecular structure, chemical reaction

ABSTRACT: This is a continuation of a previous investigation. The effect of ferrocenyl as a substituent on the benzidine rearrangement of hydrazobenzene was studied. It was established that ferrocenyl as a substituent on the benzene ring complicates benzidine rearrangement: m- and p-ferrocenylhydrazobenzenes under the conditions of benzidine rearrangement generally get disproportionated rather than rearranged, i.e. the end-product is ferrocenylamine and azoferrocene. Compounds of the benzidine type do not form. These findings indicate that the introduction of the ferrocenyl substituent -- whether in the para or in the meta position -- into the hydrazobenzene molecule impedes benzidine rearrangement to such an extent that disproportionation becomes the main trend of the reaction. [JPRS: 36,455]

SUB CODE: 07 / SUBM DATE: 29Jul63 / ORIG REF: 003 / OTH REF: 005

Card 1/1 UDC: 542.957+546.72

0976 2649

L 35324-66 EWT(m)/EWP(j) RM

ACC NR: AP6026892 SOURCE CODE: UR/0062/65/000/012/2124/2128

35

AUTHOR: Nesmeyanov, A. N.; Perevalova, E. G.; Nikitina, T. V.; Kuznetsova, N. I. B

ORG: Moscow State University im. M. V. Lomonosov (Moskovskiy gosudarstvennyy universitet)

TITLE: Effect of hydrochloric acid on the azo derivatives of ferrocene

SOURCE: AN SSSR. Izvestiya. Seriya khimicheskaya, no. 12, 1965, 2124-2128

TOPIC TAGS: hydrochloric acid, ferrocene, organic azo compound, chemical synthesis, nitrobenzene, chemical decomposition, condensation reaction, chemical reduction, amine

ABSTRACT: **A study was made of the effect of conc. HCl on benzenoazoferrocene and m- and p-ferrocenylazobenzenes -- azo derivatives of ferrocene synthesized by condensation of nitrobenzene with ferrocenylamine and m- and p-ferrocenylanilines. It is shown that conc. HCl causes benzenoazoferrocene to decompose and form Fe-free substances; products of benzidine-type rearrangement have not been detected. Conc. HCl transforms m- and p-ferrocenylazobenzenes into ferrocenylaniline, aniline and substances isomeric to ferrocenylhydrazobenzene. In this case the ferrocenylazobenzenes are protonated and decompose, to form $FeCl_2$, which then reduces the second molecule of the protonated ferrocenylazobenzene to a hydrazo compound. The hydrazo compound is either further reduced to amines or gets disproportionated and rearranged.**
[JPRS: 36,455]

SUB CODE: 07 / SUBM DATE: 29Jul63 / ORIG REF: 006 / OTH REF: 003

Card 1/1 UDC: 542.957+546.72

L 35316-66 EWT(m)/EWP(j) RM

ACC NR: AP6026898 SOURCE CODE: UR/0062/65/000/012/2196/2198

22
B

AUTHOR: Reshetova, M. D.; Yarysheva, L. M.; Perevalova, E. G.; Nesmeyanov, A. N.

ORG: Moscow State University im. Lomonosov (Moskovskiy gosudarstvennyy universitet)

TITLE: Synthesis of certain substituted ferrocenylcarbinols

SOURCE: AN SSSR. Izvestiya. Seriya khimicheskaya, no. 12, 1965, 2196-2198

TOPIC TAGS: chemical synthesis, ferrocene, hydrolysis, methylation

ABSTRACT: This is a continuation of a previous investigation (PEREVALOVA), which deals with the synthesis of heteroannular chloro-, bromo- and cyano-(alpha-oxyethyl) ferrocenes and (alpha-oxypropyl) ferrocene by reducing the corresponding acylferrocenes with $LiAlH_4$. The compounds thus obtained were; 1,1'-chloracetylferrocene, 1,1'-chloro(alpha-oxyethyl)ferrocene, 1,1'-bromo(alpha-oxyethyl)ferrocene, 1,1'-cyano(alpha-oxyethyl)ferrocene, and 1,1'-carbomethoxy(alpha-oxyethyl)ferrocene. 1,1'-cyano(alpha-oxyethyl) ferrocene was converted to 1,1'-carbomethoxy(alpha-oxyethyl)ferrocene by alkaline hydrolysis and subsequent methylation with diazomethane.
[JPRS: 36,455]

SUB CODE: 07 / SUBM DATE: 05Apr65 / ORIG REF: 002 / OTH REF: 002

Card 1/1 UDC: 542.91+547.1'3

0916 2656

L 36507-66 EWT(m)/EWP(j) RM

ACC NR: AP6017876 (A) SOURCE CODE: UR/0062/66/000/005/0832/0839

AUTHOR: Perevalova, E. G.; Grandberg, K. I.; Zharikova, N. A.; Gubin, S. P.; Nesmeyanov, A. N.

ORG: Moscow State University im. M. V. Lomonosov (Moskovskiy gosudarstvennyy universitet); Institute of Organometallic Compounds, Academy of Sciences, SSSR (Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR)

TITLE: Electronic influence of ferrocenyl as a substituent

SOURCE: AN SSSR. Izvestiya. Seriya khimicheskaya, no. 5, 1966, 832-839

TOPIC TAGS: ferrocene, dissociation constant, aniline, benzoic acid, phenol, substituent, amine

ABSTRACT: By determining values of Hammett's σ, the authors studied certain electronic effects of ferrocenyl as a substituent. Using acid-base potentiometric titration, they determined the dissociation constants of p-, m-, and o-ferrocenylbenzoic acids, a series of substituted benzoic acids and ferrocenecarboxylic acid in 70% dioxane, and the dissociation constants of p-ferrocenylphenol and a series of p-substituted phenols in 50% ethanol. The basicity constants of p-, m-, and o-ferrocenylanilines, a series of p-substituted anilines, and ferrocenylamine in 80% ethanol were also determined. The data obtained were treated by the least-squares method, ρ values were calculated for the reaction series studied, σ values were found for ferro-

UDC: 541 + 541.49 + 547.1'3:541.132

Card 1/2

L 35327-66 EWT(m)/EWP(j) RM

ACC NR: AP6026836

SOURCE CODE: UR/0020/66/166/002/0374/0377

AUTHOR: Nefedova, M.N.; Kursanov, D.N. (Corresponding member AN SSSR); Setkina, V.N.; Perevalova, E.G.; Nesmeyanov, A.N. (Academician)

ORG: none

37
33
B

TITLE: Effect of substituents on the rate of isotopic hydrogen exchange in ferrocene derivatives

SOURCE: AN SSSR. Doklady, v. 166, no. 2, 1966, 374-377

TOPIC TAGS: ferrocene, electron donor, dissociation constant, substituent, reaction rate

ABSTRACT:

The authors determined the rate constants for acid isotopic exchange of hydrogen in six monosubstituted and four disubstituted ferrocenes. The relative rate constants K_{rel} were then calculated assuming unity for unsubstituted ferrocene. The substituents studied included both electron-donor and electron-acceptor types. An analysis of the resultant data shows that the effect of the substituent on the reaction rate in an aromatic compound may be described as a combination of induction and conjugation. The conjugation effect is much less important in this case than it is in electrophilic substitution in the benzene series. It was found that the substituent

Card 1/2

UDC: 546.11.2+542.957+546.72

L 35327-66

ACC NR: AP6026836

constants obtained from the dissociation constants for phenylacetic acids may be used as a quantitative index of the effect which the substituent has on the reaction rate. Curves for ln k/k_0 for all substituents studied show a linear correlation with those constants. Heterocyclic disubstituted derivatives lie on this same line if doubled values of substituent constants are used, i.e., the substituents have an additive effect within the limits of experimental error. The authors thank S.L. Portnova and G.P. Syrova for taking the nuclear resonance spectra. The authors further thank V.A. Pal'm and N.P. Gambaryan for participating in the discussions of the results. Orig. art. has: 1 figure and 1 table [JPRS: 36, 455]

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SUB CODE: 07 / SUBM DATE: 23Sep65 / ORIG REF: 013 / OTH REF: 010

Card 2/2

L 31360-66 EWP(j)/EWT(m) IJP(c) RM/WW

ACC NR: AP6021100 SOURCE CODE: UR/0062/66/000/002/0335/0337

50

B

AUTHOR: Nesmeyanov, A. N.; Perevalova, E. G.; Reshetova, M. D.

ORG: Moscow State University im. M. V. Lomonosov (Moskovskiy gosudarstvennyy universitet)

TITLE: Salts of N-(alpha-ferrocenylalkyl)pyridinium

SOURCE: AN SSSR. Izvestiya. Seriya khimicheskaya, no. 2, 1966, 335-337

TOPIC TAGS: pyridine, alcohol, esterification, solubility, chemical synthesis, organic nitrile compound, organic amide, ferrocene

ABSTRACT: The reaction of alcohols with p-toluenesulfochloride in pyridine is the method by which esters of p-toluenesulfonic acid are obtained. However, in some cases p-toluenesulfonates of pyridinium are formed instead; for example, with 2,4-dinitroresorcine or 2,4-dinitronaphthol. The authors found that ferrocenylcarbinol and substituted ferrocenylcarbinols react in this way. In the reaction of oxymethyl-, alpha-oxyethyl-, oxybenzyl, and 1,1'-cyano-(alpha-oxyethyl)ferrocene with p-toluenesulfochloride in absolute pyridine the authors obtained p-toluenesulfonates of the corresponding pyridiums. Salts of N-(alpha-ferrocenylalkyl)pyridiniums are soluble in water (except (ferrocenylbenzyl)pyridinium), alcohol, acetonitrile, and certain polar solvents. Nitriles of ferrocenylacetic, ferrocenylpropionic, and ferrocenyl (phenyl)acetic acids were obtained. Nitriles of the first two acids were hydrolysed to amides. The amides are stable upon standing in air, in contrast to the nitriles. Orig. art. has: 1 table. [JPRS]

SUB CODE: 07 / SUBM DATE: 19May65 / ORIG REF: 002 / OTH REF: 002

UDC: 542.1 + 547.1'3 + 546.72

Card 1/1 cc

L 27456-66 EWT(m)/EWP(j) RM

ACC NR: AP5027691 SOURCE CODE: UR/0062/65/000/010/1882/1884

AUTHOR: Nesmeyanov, A. N.; 44,55 Perevalova, E. G.; 44,55 Leont'yeva, L. I.; 44,55 Ustynyuk, Yu. A. 44,55

ORG: Moscow State University im. M. V. Lomonosova (Moskovskiy gosudarstvennyy universitet) 44,55

42
B

TITLE: Synthesis of 1,2-disubstituted ferrocenes 7,44,55

SOURCE: AN SSSR. Izvestiya. Seriya khimicheskaya, no. 10, 1965, 1882-1884

TOPIC TAGS: ferrocene, chemical reaction, desulfurization, chemical reduction

ABSTRACT: The reduction of 1,2-(2'-thia-4'-ketotetramethylene)ferrocene (I) was investigated in order to find suitable methods for the synthesis of homoannular disubstituted ferrocenes. I was desulfurized with Raney nickel to form 1,2-methylethyl- and 1,2-methylacetylferrocene. Reduction of I with lithium aluminum hydride gave 1,2-(2'-thia-4'-hydroxytetramethylene)ferrocene (II). Reduction of I in the presence of aluminum chloride gave 1,2-(2'-thiatetramethylene)-ferrocene, a small amount of II, and methylferrocene, and in one instance, 1,2-(2'-thia-3',4'-dehydrotetramethylene)ferrocene. Orig. art. has: 2 equations.

Card 1/2 UDC: 542.91+547.35+546.72

L 27456-66

ACC NR: AP5027691

0

SUB CODE: OC/ SUBM DATE: 03Feb65/ ORIG REF: 002/ OTH REF: 002

Card 2/2 20

L 26555-66 EWP(j)/EWT(m)/T IJP(c) RM

ACC NR: AP6017363 SOURCE CODE: UR/0062/66/000/003/0556/0558

AUTHOR: Nesmeyanov, A. N.; Perevalova, E. G.; Leont'yeva, L. I.; Ustynyuk, Yu. A.

ORG: Moscow State University im. M. V. Lomonosov (Moskovskiy gosudarstvennyy universitet)

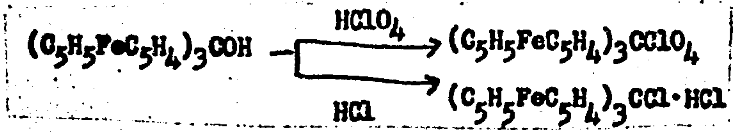
37
B

TITLE: Triferrocenylchloromethane hydrochloride

SOURCE: AN SSSR. Izvestiya. Seriya khimicheskaya, no. 3, 1966, 556-558

TOPIC TAGS: organic synthetic process, perchloric acid, perchlorate, hydrogen chloride, organoiron compound

ABSTRACT: The ionic triferrocenylmethylperchlorate and triferrocenylchloromethane hydrochloride were synthesized by reaction of triferrocenylcarbinol with perchloric acid in benzene and anhydrous HCl in ether, respectively.



$$(C_5H_5FeC_5H_4)_3COH \xrightarrow{HClO_4} (C_5H_5FeC_5H_4)_3CClO_4$$

$$(C_5H_5FeC_5H_4)_3COH \xrightarrow[HCl]{} (C_5H_5FeC_5H_4)_3CCl\cdot HCl$$

In polar solutions triferrocenylchloromethane hydrochloride decomposes to form ferrocenylfulvene. [JPRS]

SUB CODE: 07 / SUBM DATE: 22Jul65 / ORIG REF: 003 / OTH REF: 002

2

Card 1/1 UDC: 542.91+541.49+546.72

L 26554-66 EWP(j)/EWT(m)/T IJP(c) RM

ACC NR: AP6017364 SOURCE CODE: UR/0062/66/000/003/0558/0559

AUTHOR: Nesmeyanov, A. N.; Perevalova, E. G.; Leont'yeva, L. I.; Ustynyuk, Iu. A.

24
B

ORG: Moscow State University im. M. V. Lomonosov (Moskovskiy gosudarstvennyy universitet)

TITLE: Reactions of triferrocenylchloromethane hydrochloride 1

SOURCE: AN SSSR. Izvestiya. Seriya khimicheskaya, no. 3, 1966, 558-559

TOPIC TAGS: organoiron compound, chlorinated organic compound, organomagnesium compound, organosodium compound, organolithium compound, chemical reaction

ABSTRACT: Triferrocenylchloromethane hydrochloride reacts with nucleophilic reagents (organomagnesium and organosodium compounds, lithium aluminohydride, sodium methylate and sodium cyanide) to form the corresponding derivatives of triferrocenylmethane. [JPRS]

SUB CODE: 07 / SUBM DATE: 22Jul65 / ORIG REF: 002 / OTH REF: 001

2

Card 1/1 C UDC: 542.91+541.49+546.72

L 20351-66 EWT(m)/EWP(j) RM

ACC NR: AP6012083 SOURCE CODE: UR/0062/65/000/003/0580/0580

46

AUTHOR: Nesmeyanov, A. N.; Kozlovskiy, A. G.; Gubin, F. P.; Perevalova, E. G. B

ORG: Moscow State University im. M. V. Lomonosov (Moskovskiy gosudarstvennyy universitet); Institute of Organoelemental Compounds, AN SSSR (Institut elementoorganicheskikh soyedineniy)

TITLE: Protolysis of mercury derivatives of ferrocene

SOURCE: AN SSSR. Izvestiya. Seriya khimicheskaya, no. 3, 1965, 580

TOPIC TAGS: titrimetry, ferrocene, mercury compound, dioxane, chlorine compound

ABSTRACT: The Rate constants were determined for the protolysis of mercury derivatives of ferrocene — chloromercuroferrocene and diferrocene-mercury using hydrochloric acid in 90% (by volume) aqueous dioxane. The quantity of acid not entering into reaction was determined by potentiometric titration. The reaction rate in all cases is described by a second-order kinetic equation. The protolysis rate of diferrocene mercury is six times greater than the cleavage rate of di-p-anisylmercury under the same conditions. Orig. art. has: 1 table. [JPRS]

SUB CODE: 07 / SUBM DATE: 18Jan65 / ORIG REF: 002

UDC: 531.1+542.957

Cord 1/1 vmb

NESMEYANOV, A.N.; PEREVALOVA, E.G.; NIKITINA, T.V.; KUZNETSOVA, N.I.

Behavior of m- and p-ferrocenylhydrazobenzenes under conditions of benzidine rearrangement. Izv.AN SSSR.Ser.khim. no.12:2120-2124 '65.

Action of hydrochloric acid on azo derivatives of ferrocene. Izv.AN SSSR.Ser.khim. no.12:2124-2128 '65. (MIRA 18:12)

1. Moskovskiy gosudarstvennyy universitet im. Lomonosova. Submitted July 20, 1963.

RESHETOVA, M.D.; YARYSHEVA, L.M.; PEREVALOVA, E.G.; NESMEYANOV, A.N.

Synthesis of some substituted ferrocenylcarbinols. Izv.AN SSSR.Ser.khim. no.12:2196-2198 '65.

(MIRA 18:12)

1. Moskovskiy gosudarstvennyy universitet im. Lomonosova. Submitted April 5, 1965.

PEREVALOVA, E.G.; RESHETOVA, M.D.; GRANDBERG, K.I.; NESMEYANOV, A.N.

Synthesis of heteroannular alkylferrocenylcarbinols. Izv. AN
SSSR. Ser. khim. no.10:1901-1903 O '64. (MIRA 17:12)

1. Moskovskiy gosudarstvennyy universitet.

NESMEYANOV, A.N.; PEREVALOVA, E.G.; LEONT'YEVA, L.I.; USTYNYUK, Yu.A.

Synthesis of 1,2-disubstituted ferrocenes. Izv. AN SSSR. Ser.khim. no.10:1882-1884 '65. (MIRA 18:1)

1. Moskovskiy gosudarstvennyy universitet.

NESMEYANOV, A.N., akademik; KURSANOV, D.N.; NEFEDOVA, M.N.; SETKINA
V.N., PEREVALOVA, E.G.

Substitution of a proton for a halogen in ferrocene halides. Dokl.
AN SSSR 161 no.6:1349-1351 Ap '65. (MIRA 18:[illegible])

1. Institut elementoorganicheskogo sinteza AN SSSR. 2. Chlen-korrespondent AN SSSR (for Kursanov).