

NESMEYANOV, A.N., akademik; KRAVTSOV, D.N.

p-Dimethylaminophenylmercury derivatives of nitroanilines and nitronaphthylamines. Dokl. AN SSSR 137 no.3:614-617 Mr 61.
(MIRA 14:2)

1. Institut elementoorganicheskikh soyedineniy AN SSSR.
(Mercury organic compounds) (Aniline)
(Naphthylamine)

21499

E/020/61/137/004/024/031
B103/B208

15 8114

2209, 1372, 1407

AUTHORS:

Freydlina, R.Kh., Corresponding Member AS USSR,
Chukovskaya, Ye.Ts., Tsao-I, and Nesmeyanov, A.N.,
Academician

TITLE:

Telomerization and polymerization of ethylene with silicon
hydrides in the presence of titanium tetrachloride

PERIODICAL: Doklady Akademii nauk SSSR, v. 137, no. 4, 1961, 885 - 888

TEXT: The authors studied the telomerization of ethylene with: I) sili-
co-chloroform, II) methyl dichloro-silane, and III) triethyl silane in
the presence of $TiCl_4$ which catalyzes (initiates) these reactions accord-
ing to the formula $CH_3SiCl_2H + nCH_2=CH_2 \rightarrow CH_3SiCl_2(CH_2CH_2)_nH$. They used
a steel autoclave in which the reaction was carried out under pressure and
by heating. Ethylene was found to be telomerized smoothly and with a good
degree of conversion in cases I and II. In case I, some telomer homologs
with the structure $SiCl_2C_nH_{2n+1}$, where $n = 2, 4, 6, 8$, were isolated from

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the mixture of telomerization products. The constants of these substances (Table 2) and of their methylation products (Table 3) are in good agreement with those previously obtained by the authors (Ref.2, DAN, 113, 120, 1957). The normal structure of their alkyl groups was confirmed by infrared spectra. Ad II. A mixture of telomer homologs with a structure $\text{CH}_3\text{SiCl}_2\text{C}_n\text{H}_{2n+1}$ was formed at 180 - 200°C and at a maximum pressure of 280 atm. This reaction is complicated by the formation of liquid hydrocarbons due to ethylene polymerization. Table 4 gives the constants of some methyl-alkyl dichloro-silanes with $n = 2, 4, 6, 8$. Ad III. At 130°C, ethylene is polymerized to polyethylene with no telomers being formed. This difference in the course of the reaction is said to be due to a different reducing power of the individual silicon hydrides studied. Triethyl silane, e.g., contains electron-donor groups bound to silicon, and is therefore a more powerful reducing agent than trichloro-silane and methyl-dichloro-silane. This might be the reason why these silicon hydrides with TiCl_4 yield products that are reduced to a different extent. X-ray structure analysis (performed at laboratoriya rentgenostrukturnogo analiza (Laboratory of X-Ray Structural Analysis) and laboratoriya fiziki polimerov

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(Laboratory of Polymer Physics) of the Institut elementoorganicheskikh sovedineniy (Institute of Elemental-organic Compounds) disclosed that the polyethylene obtained by the authors is identical with low-pressure polyethylene and the product obtained by diazomethane decomposition (X-ray pictures of the two latter polymers were made available by V.A. Sergeyev). Thermomechanical analysis showed a melting point of 135°C for the authors' polyethylene, which also corresponds to low-pressure polyethylene. Its molecular weight was 26670, determined from the viscosity in tetrahydro-naphthalene at 135°C. This indicates that the authors' polyethylene is practically identical with the two polyethylenes mentioned (analogous data in Ref. 4, S. Nitshe, Khimiya i tekhnologiya polimerov, 1960, p. 54). There are 2 figures, 4 tables and 6 references: 5 Soviet-bloc and 1 non-Soviet-bloc.

SUBMITTED: December 8, 1960

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Telomerization and polymerization of ...

Table 2

Соедине- ние	Э.Т. кип., °C		n_D^{20}		d_4^{20}		MR	
	набд.	лит. данные	набд.	лит. данные	набд.	лит. данные	набд.	вычисл.
C ₂ H ₅ (Cl)	87	87-100	1,4566	1,4522	1,2264	1,1677	34,08	33,61
C ₂ H ₅ (Cl)	158	148-152	1,4558	1,4460	1,1685	1,1084	42,92	42,71
C ₂ H ₅ (Cl)	87 (30 мм)	87-90	1,4486		1,1082		32,58	32,12
C ₂ H ₅ (Cl)	102 (10 мм)	87 (10 мм)	1,4480	1,4480	1,0768	1,0764	31,61	31,61

Таблица 3

Table 3

Соединение	Э.Т. кип., °C		n_D^{20}		d_4^{20}		MR	
	набд.	лит. данные	набд.	лит. данные	набд.	лит. данные	набд.	вычисл.
C ₂ H ₅ (CH ₂) ₂	82	82	1,4020	1,4026	0,8028	0,8040	34,75	34,82
C ₂ H ₅ (CH ₂) ₂	115	115	1,4035	1,4030	0,7167	0,7184	44,42	44,12
C ₂ H ₅ (CH ₂) ₂	161-168	169	1,4102	1,4154	0,7618	0,7622	59,57	59,51
C ₂ H ₅ (CH ₂) ₂	83 (10 мм)	82,8 (10 мм)	1,4225	1,4262	0,7571	0,7581	62,76	62,76

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Соединение	Выход, %	3 Т. кип., °C		20 n _D		20 d ₄		MR Tab4	
		найд.	лит. данные	найд.	лит. данные	найд.	лит. данные	найд.	вычисл.
C ₂ H ₅ SiCl ₂ CH ₃	18	100,5	100	1,4190	1,4240	1,0644	1,0655	33,94	33,87
C ₂ H ₅ SiCl ₂ CH ₃	18	149	147-148	1,4320	1,4312	1,0212	1,0190	43,45	43,26
C ₂ H ₅ SiCl ₂ CH ₃	25	90 (81 мм)	91 (82 мм)	1,4390	1,4396	0,9992	0,9991	52,95	52,59
C ₂ H ₅ SiCl ₂ CH ₃	13	99 (8 мм)	94 (8 мм)	1,4450	1,4449	0,9884	0,9781	62,32	61,88

Legend to Tables 2-4: 1) Compounds, 2) yield, %, 3) boiling point, 4) found, 5) from published data.

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S/020/61/137/005/020/026
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AUTHORS: Freydina, R.Kh, Corresponding Member AS USSR,
Martirosyan, G.T. and Nesmeyanov, A.N., Academician

TITLE: Addition of trichlorobromomethane to compounds of the
structure $R(C_6H_5)_2 ECH = CH_2$ (where $R = C_6H_5, CH_3$;
 $E = Sn, Si, C$)

PERIODICAL: Doklady Akademii nauk SSSR, v. 137, no. 5, 1961, 1129 - 1132

TEXT: The authors studied the capability of rearrangement of the radicals:
 $(C_6H_5)_3Sn\dot{C}HCH_2CCl_3$, $(C_6H_5)_3Si\dot{C}HCH_2CCl_3$ and $(C_6H_5)_2\overset{\underset{CH_3}{|}}{C}\dot{C}HCH_2CCl_3$ in solution

and in the presence of benzoyl peroxide, where the phenyl is subjected to
a 1.2-migration from the metal atom to a carbon atom. For this purpose
the authors investigated the addition of trichlorobromomethane to 1) vi-
nyl triphenyl stannane, 2) vinyl triphenyl silane, and 3) 3,3-diphenyl-
butene-1. In the cases 1) and 2), the addition takes place very smoothly.

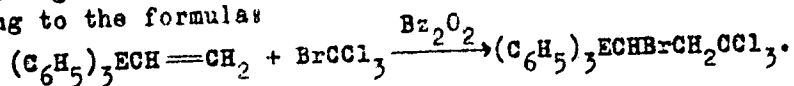
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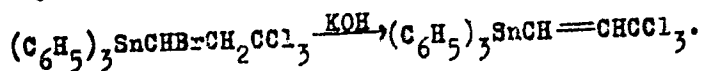
Addition of trichlorobromomethane ...

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Not rearranged addition products are formed in nearly quantitative yield according to the formula:



The structure of the resultant compounds is confirmed by the missing E—Br bond (negative test with AgNO_3) and by the behavior of the resultant adducts with respect to alcoholic alkali. The organotin compound is not hydrolyzed, but dehydrobrominated according to the formula:



Ad 1). After distilling off the excess BrCCl_3 14.3 g of a dense oil were left from which crystalline δ, δ, δ -trichloro- α -bromo-propyl triphenyl stannane was isolated by dissolution in absolute alcohol and cooling to -40°C . This was completely neutralized over night with KOH in ethanol at room temperature. Crystals of δ, δ, δ -trichloropropen-1-triphenyl-stannane precipitated. Ad 2). δ, δ, δ -trichloro- α -bromo-propyl triphenyl

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Addition of trichlorobromomethane ...

silane was obtained in an analogous manner, which did not react with AgNO_3 and remained unchanged when treated for 20 hr with alcoholic alkali.

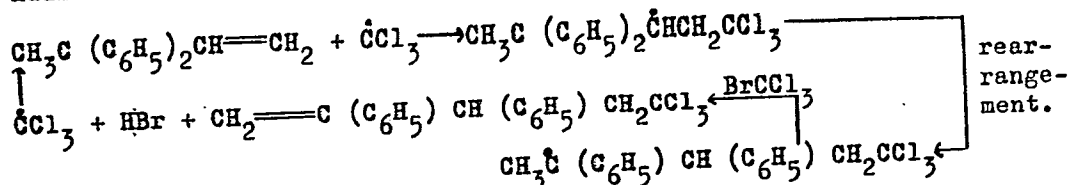
Ad 3). The addition is difficult. 66% of the initial diphenyl butene were recovered in unchanged state after boiling of the reaction mixture for 20 hr and repeated addition of benzoyl peroxide. As the principal product yielded an unsaturated compound with the empirical formula $\text{C}_{17}\text{H}_{15}\text{Cl}_3$ (5,5,5-trichloro-2,3-diphenyl pentene-1). The following resulted by ozonolysis: Formaldehyde and a ketone $\text{C}_{16}\text{H}_{13}\text{Cl}_3\text{O}$ from the crystals of which a 2,4-dinitrophenyl hydrazone $\text{C}_{22}\text{H}_{17}\text{Cl}_3\text{N}_2\text{O}_4$ was formed with 2,4-dinitrophenyl hydrazine. These data correspond to a compound: $\text{CH}_2=\text{C}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{CCl}_3$ (III) which may be formed according to the formula:

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Addition of trichlorobromomethane . . .



Simultaneously with III, a saturated adduct (bromide) was formed in low yield, whose structure has not been studied. The authors summarize that radicals $(\text{C}_6\text{H}_5)_3\text{E}\dot{\text{C}}\text{HCH}_2\text{CCl}_3$ (E = Sn, Si) are not rearranged under comparable conditions, whereas radicals $(\text{C}_6\text{H}_5)_2\text{C}(\text{CH}_3)\dot{\text{C}}\text{HCH}_2\text{CCl}_3$ were rearranged. The reasons for this different behavior may be a) a low stability of the first radical, as compared with the initial radicals $(\text{C}_6\text{H}_5)_3\text{E}\dot{\text{C}}\text{HCH}_2\text{CCl}_3$, or b) the Sn- and Si-atoms are less able to impart the effect caused by an odd electron at the adjacent carbon atom to the phenyl group. There are 9 references: 1 Soviet-bloc and 8 non-Soviet-bloc. The 3 most recent references to English language publications

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Addition of trichlorobromomethane ...

read as follows: D. Seyferth (Ref. 2: J.Org.Chem.Soc., 22, 1252, 1957),
E.A. Benkeser, E.W. Bennet, E.A. Huckner (Ref. 3: J.Am.Chem.Soc., 79,
6253, 1957), S.D. Rosenberg, A.I. Gibbons et.al. (Ref. 7: J.Am.Chem.Soc.,
79, 2137, 1957).

SUBMITTED: December 24, 1960

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15 8114 2209
24 3600 (1035, 1138, 1482)

S/020/61/157/006/013/020
B103/B217

AUTHORS: Nesmeyanov, A. N., Academician, Korshak, V. V., Corresponding Member AS USSR, Voevodskiy, V. V., Corresponding Member AS USSR, Kochetkova, N. S., Sosin, S. L., Materikova, R. B., Bolotnikova, T. N., Chibrikin, V. M., and Bazhin, N. M.

TITLE: Synthesis and some optical-magnetic properties of polyferrocenes

PERIODICAL: Doklady Akademii nauk SSSR, v. 137, no. 6, 1961, 1370-1373

TEXT: The authors studied the magnetic properties of ferrocene derivatives: 1) of the polyferrocenylenes (Table 1, nos. 1-6), 2) the polydiisopropylferrocene (Table 1, nos. 7-8), 3) the polymethano- and 4) the polyethanopolyferrocenes (Table 1, nos. 9-13). They were synthesized by: A) Polyrecombination. To 1) and 2). 1 mole ferrocene (or of its diisopropyl homolog) was treated with 1 mole tertiary butyl peroxide in nitrogen atmosphere at 200°C. 1) and 2) are assumed to be formed as follows: the Butoxyl and methyl radicals formed during peroxide decomposition separate the hydrogen from ferrocene (or the α -hydrogen). The radicals thus formed

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Synthesis and some ...

recombine and form linear 1) or 2), easily soluble in benzene. An insoluble polymer (Table 1, nos. 5-6) with a two- or tridimensional network structure is formed simultaneously. The conversion of ferrocene to high-molecular products amounted to 25%. Nos. 1-3 have a softening temperature of 290-300°C and are a dark-red powder, whereas nos. 5-6 had their softening temperature at about 400°C and were light-yellow. B) Polyalkylation of ferrocene by methylene chloride and 1,2-dichloroethane in the presence of anhydrous aluminum chloride. Aluminum chloride solution in 50 ml of dihalogen alkane was added gradually to 40 g ferrocene dissolved in 250 ml dry dihalogen alkane. The mixture was stirred for 6 hr at the boiling temperature of the solvent. The next day, 10 g aluminum chloride in 25 ml dihalogen alkane were added and treated for 6 hr as above. The mixture was decomposed by ice and HCl and treated with sodium sulfite. The obtained 3) and 4) were well soluble in benzene, differed, however, by their solubility in ether. Table 1 shows the molecular weights, the always equal g-factor and the magnetic characteristics of all substances produced. The decomposition temperature of 9-13 was 115-120°C. All substances are amorphous powders, nos. 9 and 10 light-yellow, no. 11 grey-brown. Nos. 10 and 11 are of a chemical composition similar to that of no. 9 (pentaethanodiferrocene).

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They consist possibly of 2 and 4 molecules similar to the latter, connected by ethane bridges. 4-5 methylenes in the molecule of nos. 12 and 13 belong to 2 ferrocene radicals. They do not contain halogen. The infrared spectra of nos. 9-13 have frequencies within the range $1000-1100\text{ cm}^{-1}$. To 1). Derivatives 1) having a π -conjugation between the ferrocene links give a signal the electron paramagnetic resonance (e-p-r), similarly to the poly-aromatic hydrocarbons. This cannot be explained by the presence of a corresponding quantity of the oxidized form of the ferricinium cation. Table 1 shows that also polymers in which the ferrocene links are separated by the $-\text{CH}_2-\text{CH}_2-$ group give an e. p. r. signal. It is known that the delocalization of the unpaired electrons between the two phenyl rings is not prevented by this group. In the substances described here, which give an e. p. r. signal, this signal is the smaller, the smaller the number of ferrocene links is. This signal vanishes in 2). Polymers with a low molecular weight give no e. p. r. signal in the solution (benzene), but in solid state. This is explained by the fact that the intramolecular interactions cause in solid state a conjugation of the adjacent polymer molecules. This causes for its part an e. p. r. signal. All polymers

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giving this signal show a single symmetrical line of the e. p. r. of the Lorenz type. The 1) obtained from the reaction A yields a wide e. p. r. line of 120-160 oersteds, its width being dependent on the polymer structure. This line becomes broader on reducing the measuring temperature. Its width is changed most considerably in low-molecular polymers. The authors believe the nature of the measured signals to be unclarified, they cannot maintain that the number N of the unpaired electrons per 1 member, determined by a comparison with the standard, corresponds to their actual number. N may, however, be a certain characteristic of the magnetic properties of the system (nos. 2-4). N reaches an anomalous size in the insoluble polymer no. 5. This is assumed to be connected with a collective effect of the ferromagnetic type. The ultraviolet (UV-) spectra of 1) dissolved in n-octane, which give an e. p. r. signal in solid state, differ from the ultraviolet spectra of such that give no signal in solid state. In the first case the UV-spectrum agrees completely with that of ferrocene dissolved in CCl_4 . It was proved for these spectra (Ref. 7) that the charge transfer takes place here under formation of an ion pair $\text{Fer}^+\text{CCl}_4^-$. On the contrary, the UV-spectrum of such 1) that give no e. p. r. signal is similar

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to that of ferrocene in a neutral solvent (n-octane), i. e. under conditions under which the charge is not transferred. Finally, the authors point out that their results concerning the UV-spectra apparently confirm the "pseudoferrromagnetism" of the polynucleotides and of the polyaromatic hydrocarbons (Refs. 5 and 8). There are 1 figure, 1 table, and 8 references: 7 Soviet-bloc and 1 non-Soviet-bloc. The only reference to English-language publication reads as follows: J. C. D. Brand, Ref. 7: Trans. Farad. Soc., 53, 894, 1957.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR
(Institute of Elemental-organic Compounds of the Academy of Sciences, USSR)

SUBMITTED: December 20, 1960

Legend to Table 1. I) Current number, 1-4) linear polyferrocenylene, 5-6) insoluble polyferrocenylene, 7) polydiisopropylferrocene, linear, 8) like 7, insoluble, 9-11) condensation products of ferrocene with Di-1,2-chloroethane, 12-13) with methylene chloride, 14) ferricinium cation. II) Substance, III) molecular weight, IV) g-factor, V-VI) line width, oersted

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FREYDLINA, R.Kh.; KOST, V.N.; VASII'YEVA, T.T.; NESMEYANOV, A.N., akademik

Homolytic isomerization of 1-fluoro-1, 1-dichloro-2-bromopropene.
Dokl. AN SSSR 137 no.6:1385-1388 Ap '61. (MIRA 14:4)

1. Institut elementoorganicheskikh soyedineniy AN SSSR. 2. Chlen-
korrespondent AN SSSR (for Freydlina).
(Propene)

NESMEYANOV, A.N., akademik; RUBINSHTEYN, A.M.; SLCNIMSKIY, G.L.; SLINKIN,
A.A.; KOCHETKOVA, N.S.; MATERIKOVA, R.B.

Magnetic susceptibility of polyalkenopolyferrocenes and polyferro-
cenylenes. Dokl.AN SSSR 138 no.1:125-126 Ky-Je '61.
(MIRA 14:4)

1. Institut elementoorganicheskikh soyedineniy AN SSSR.
(Ferrocene--Magnetic properties)

NESMEYANOV, A.N., akademik; VIL'CHEVSKAYA, V.D.; KOCHETKOVA, N.S.

o-Carboxybenzoylferrocene reactions. Dokl.AN SSSR 138 no.2:390-392
My '61. (MIRA 14:5)

1. Institut elementoorganicheskikh soydeineniy Akademii nauk SSSR.
(Ferrocene)

BRATNINA, E.M.; MINACHEVA, M.Kh.; FREYDLINA, R.Kh.; NESMEYANOV, A.N.,
akademik

Cobalt, nickel, and manganese alcoholates. Dokl. AN SSSR 138 no.3:
598-600 My '61. (MIRA 14:5)

1. Institut elementorganicheskikh soedineniy AN SSSR. 2. Chlen-
korrespondent AN SSSR (for Freydina).
(Alcoholates)

FREYDLINA, R.Kh.; TARENT'YEV, A.B.; PETROVA, R.G.; NESMEYANOV, A.N., akademik

Regroupment of radicals in the reactions of thiols with polyhalo-
propenes. Dokl. AN SSSR 138 no.4:859-862 Je '61. (MIRA 14:5)

1. Institut elementorganicheskikh soyedineniy AN SSSR. 2. Chlen-
korrespondent AN SSSR (for Freydlina).
(Mercapto compounds) (Propene) (Radicals (Chemistry))

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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

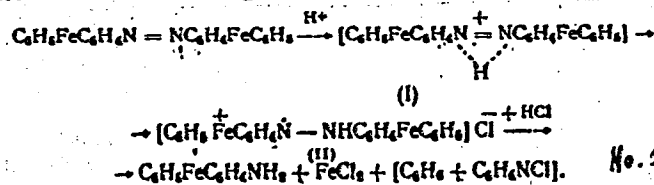
TEXT: The authors synthesized azoferrocene, examined its interaction with reagents transforming azobenzene into benzidine, and studied the behavior of azoferrocene under the conditions of the production of hydrazo compounds and their subsequent benzidine rearrangement. Azo derivatives of ferrocene were 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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benzidine-type compounds under the action of strong acids (conditions of benzidine formation from azobenzene). The action of concentrated HCl or H₂CO₄ 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. Ferrocenyl amine and fission products of the ferrocene ring were obtained from II by acid action:



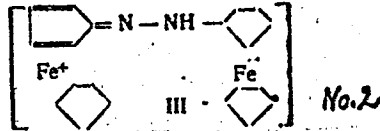
The authors assume that the ion of II has a III structure:

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(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

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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, its²⁵³¹⁷

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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 quinoid-type structures. In the case of ferrocene derivatives, similar transition states cannot be of the same character. The specificity 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 "quinoid" 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)

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11.2205

AUTHORS: Freydlina, R. Kh., Corresponding Member AS USSR, Braynina, E. M., and Nesmeyanov, A. N., Academician

TITLE: Synthesis of mixed chelate cyclopentadienyl compounds of zirconium

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 138, no. 6, 1961, 1369-1372

TEXT: The authors continued their studies on transformation reactions of chelate compounds of transition metals (Ref.5: Izv. AN SSSR, OKhN, 1957, 43; Ref.6: ibid. 1960, 59; Ref.7: ibid. 63), and studied the interaction of sodium cyclopentadienide with zirconium dichloride diacetyl acetyl acetate. They obtained the mixed compound $C_5H_5(C_5H_7O)_2ZrCl$ which also forms in almost quantitative yields by interaction between dicyclopentadienyl zirconium dichloride and an excess of acetyl acetone. The authors assume that this type of reactions might be a way of synthesizing analogous mixed zirconium compounds containing other chelate groups. The substances synthesized by the authors are colorless, crystalline, and soluble in chloroform at room temperature, in benzene and tetrahydrofuran when heated,
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25341

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B103/B215

Synthesis of mixed ...

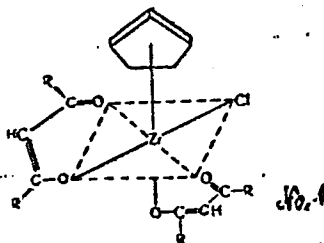
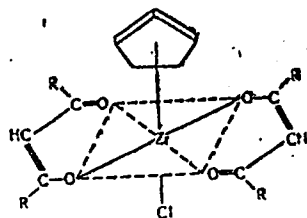
and insoluble in petroleum ether. Their properties are similar to those of dihaloid dicyclopentadienyl compounds of zirconium. The authors assume that the zirconium compounds of the substances produced are of octahedral structure. Should this assumption be correct, they probably correspond to

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25341

S/020/61/138/006/017/019
B103/B215

Synthesis of mixed ...



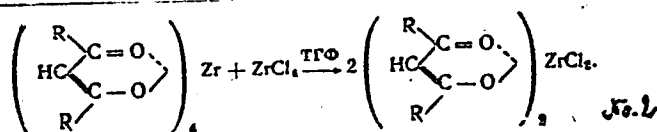
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2504

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B103/B215

Synthesis of mixed ...

given for cis- and trans-isomers. The authors thank L. A. Kazitsina (spektral'naya laboratoriya Moskovskogo universiteta (Spectral Laboratory of Moscow University)) for taking the infrared absorption spectra which are not in disagreement with the assumed structure of the above-mentioned mixed compound. The authors developed a simple method of synthesizing hitherto hardly obtainable chelate zirconium compounds which serve as initial substances for mixed compounds. It is based upon the interaction of zirconium tetrachloride with complete chelate zirconium compounds:



(TFE = tetrahydrofuran). The experimental part describes the production of the following compounds: (1) Dicyclopentadienyl zirconium dichloride whose isolation (G. Wilkinson, P. L. Pauson et al. (Ref.1: J. Am. Chem.

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2534E

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B103/B215

Synthesis of mixed ...

Soc., 75, 1011 (1953)); G. Wilkinson, J. M. Birmingham (Ref.2: ib. 76, 4281 (1954)) was simplified by the authors and whose yield was increased. (2) Diacetyl acetate cyclopentadienyl zirconium monochloride forms: (A) by heating substance (1) together with acetyl acetone for 2 hr at 70-80°C and reduced pressure; (B) from zirconium dichloride diacetyl acetate (synthesis of the latter see below, item (4)) in nitrogen atmosphere by 2 hr stirring at room temperature with equimolar amounts of sodium cyclopentadienide. (3) Dibenzoyl acetate cyclopentadienyl zirconium monochloride. A benzene solution of (1) with benzoyl acetone was heated for 15 hr at 95-100°C and reduced pressure. (4) Zirconium dichloride diacetyl acetate from zirconium tetraacetyl acetate and zirconium tetrachloride by 2 hr stirring at 40°C. (5) Zirconium dichloride dibenzoyl acetate produced from zirconium tetrabenzoyl acetate in analogy to (4). Syntheses (1) and (3)-(5) were carried out in tetrahydrofuran. There are 10 references: 4 Soviet-bloc and 6 non-Soviet-bloc. Two references to English-language publications see above: the third one reads as follows: L. T. Reynolds, G. Wilkinson, J. Inorg. and Nucl. Chem. 9, 86 (1959). X

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Synthesis of mixed ...

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S/020/61/138/006/017/019
B103/B215

X

ASSOCIATION: Institut elementoorganicheskikh soyedineniy (Institute of
Elemental Organic Compounds)

SUBMITTED: February 4, 1961

Card 6/6

NESMEYANOV, A.N., akademik; TOLSTAYA, T.P.; GRIB, A.V.

Tri-n-aminotriphenyloxonium cation as a structural analog of
parafuchsin. Dokl. AN SSSR 139 no.1:114-116 JI '61. (MIRA 14:7)

1. Moskovskiy gosudarstvennyy universitet im. M.V. Lomonosova.
(Oxonium compounds) (Parafuchsin)

5375025856
S/020/61/139/004/016/025
B 103/B206

AUTHORS: Nesmeyanov, A. N., Academician, Pelevanova, 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, 888-891

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

Properties of phenyl ferrocene

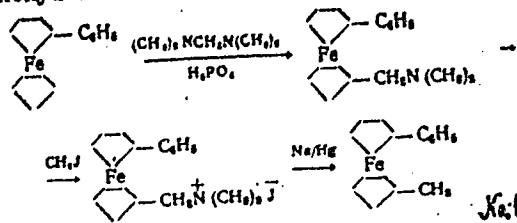
acetic acid and 4 g of H_3PO_4 , cooled to $10^\circ C$, 2.25 g (0.019 mole) of tetramethyldiaminoethane is gradually added, and then 4 g (0.015 mole) of phenyl ferrocene. The reaction mass was stirred for 1 hr at room temperature and for 10 hr at $110 - 115^\circ C$ in a nitrogen current and subsequently 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 $150-160^\circ C/3$ 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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Properties of phenyl ferrocene

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 $70 - 75^\circ\text{C}$. Since in the infrared spectrum of the methiodide which was produced from the distilled ripal 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).

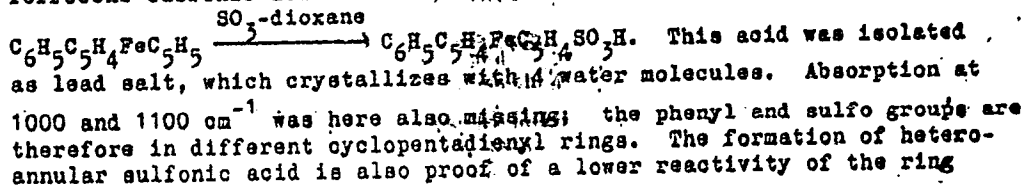


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Properties of phenyl ferrocene

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.

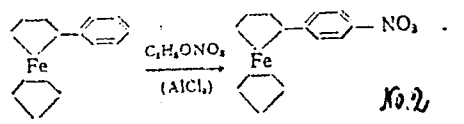


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 B103/B206

Properties of phenyl ferrocene

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. 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).



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Properties of phenyl ferrocene

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

NESMEYANOV, A.N., akademik; KRAVTSOV, D.N.

p-Dimethylaminophenylmercury derivatives of oxyazo compounds and
quinone phenylhydrazones. Dokl. AN SSSR 140 no.6:1334-1337 0
'61. (MIRA 14:11)

1. Institut elementoorganicheskikh soyedineniy AN SSSR.
(Mercury) (Azo compounds) (Quinone)

NESMEYANOV, Andrey Nikolayevich; DRAGUNOV, E.S., red. izd-va; POLYAKOVA, T.V.,
tekh. red.

[Vapor pressure of chemical elements] Davlenie para khimicheskikh
elementov. Moskva, Izd-vo Akad. nauk SSSR, 1961. 395 p.
(MIRA 14:7)

(Chemical elements) (Vapor pressure)

33263
S/062/62/000/001/002/015
B106/B101

53700

AUTHORS: Nesmeyanov, A. N., Sazonova, V. A., and Drozd, V. N.

TITLE: Influence of the carboxyl and carbomethoxy groups on the substitution of halogen in ferrocene compounds

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 1, 1962, 45 - 47

TEXT: This work has been undertaken to ascertain whether halogen in ferrocene derivatives is easily substituted in the presence of carboxyl and carbomethoxy groups. Oxidation of 1'-bromo-1-acetylferrocene with iodine in absolute pyridine yielded 1'-bromoferrocene-1-carboxylic acid (recrystallized from aqueous alcohol, m. 154-158°C (decomposition), 41% yield). The bromium of this compound is completely exchanged for the acetoxy group when boiling with copper acetate in aqueous alcohol for 15 min. The yield of 1'-acetoxyferrocene-1-carboxylic acid (yellow crystals from benzene-hexane, m. 126-130°C (decomposition), readily soluble in water) was 60% of the theoretical value. The reaction product did not contain initial carboxylic acid. (The nephrite test was negative before

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Influence of the carboxyl and ...

purification of the product). The methyl ester of 1'-bromoferrocene-1-carboxylic acid (recrystallized from n-hexane, m. 68-69.5°C), obtained by esterification of the acid with diazomethane in 96% yield, reacts less readily with copper acetate under the same conditions than the relevant acid: After 30-min reaction, chromatography on aluminium oxide revealed 45% of the initial methyl ester besides the expected product, the methyl ester of 1'-acetoxyferrocene-1-carboxylic acid (m. 45.5-47°C, 16% yield). The methyl ester of 1'-acetoxyferrocene-1-carboxylic acid is partially decomposed during the chromatographic process. The fact that the carboxyl group, contrary to other electron-acceptor groups, increases the mobility of a halogen bound to the ferrocene system is explained as follows: The copper salt of 1'-bromoferrocene-1-carboxylic acid, formed at the beginning of the reaction, forms a coordinate bond, Cu...Br, whereby the C-Br bond is polarized and the halogen may be exchanged for the acetoxy group. This behavior is similar to the aromatic carboxylic acids ortho-substituted by halogen, which, in the presence of copper compounds, also exchange the halogen readily for nucleophilic groups. These facts can not be attributed to simple activating effects of the carboxyl group since the halogen is not as reactive in the relevant benzene carboxylic acids para-substituted by

X

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Influence of the carboxyl and ...

halogen. The easy substitution of the halogen is mainly due to the polarity of the C-X bond, which is increased by the coordinate bond Cu...X. Steric factors may prevent the formation of the inner complex and thus lower the halogen mobility. The student A. K. Prokof'yev is mentioned. There are 1 table and 5 references: 1 Soviet and 4 non-Soviet. The three references to English-language publications read as follows: V. Weinmayer, USA Patent 2683157 (1954), Chem. Abstrs., 49, 10364a (1955); A. A. Goldberg, J. Chem. Soc., 1952, 4368; W. R. H. Hurlley, J. Chem. Soc., 1929, 1870.

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

SUBMITTED: July 3, 1961

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33264

S/062/62/000/001/003/015

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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Mechanism of ferrocene formation...

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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 diphenyl mercury because the latter withstands long heating in benzene. Results of previous studies of the authors show that in electrophilic substitutions of mercury in diferrocenyl mercury according to the pattern

$$(\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4)_2\text{Hg} \xrightarrow{\text{RX}} \text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{R} + (\text{C}_5\text{H}_5)_2\text{Fe}$$

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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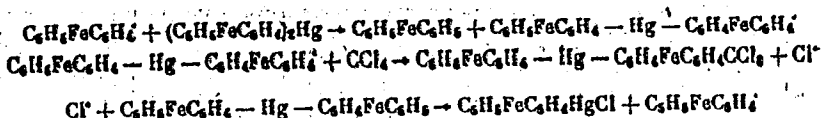
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Mechanism of ferrocene formation...

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 :



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Mechanism of ferrocene formation...

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It is concluded that the ferrocenyl radical forms readily and possesses an extremely high selectivity to hydrogen. The combination of two ferrocenyl radicals is not very pronounced. It occurs when heating iodoferrocene with copper without solvent, and also to an insignificant degree, when splitting diferrocenyl mercury in the presence of palladium black. Papers of A. N. Nesmeyanov, V. A. Sazonova, and V. N. Drozd (Dokl. AN SSR 130, 1030 (1960)), and of G. A. Razuvayev et al. (G. A. Razuvayev, M. S. Fedotov, Zh. obshch. khimii 22, 484 (1952); G. A. Razuvayev, M. S. Fedotov, Sb. statey po obshchey khimii, M.-L., Izd. AN SSSR, 2, 1517 (1953); G. A. Razuvayev, M. S. Fedotov, T. N. Zaychenko, N. A. Kul'viyskaya, ibid., p. 1514) are mentioned. There are 1 table and 9 references: 8 Soviet and 1 non-Soviet. The reference to the English-language publication reads as follows: M. Rausch, M. Vogel, H. Rosenberg, J. Organ. Chem. 22, 900 (1957). X

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

SUBMITTED: July 19, 1961

Card 4/4

33265

S/062/62/000/001/004/015
B106/B101

5 3700 1273

AUTHORS: Yemel'yanova, L. I., Vinogradova, V. N., Makarova, L. G.,
and Nesmeyanov, A. N.

TITLE: Synthesis of aromatic germanium compounds by reaction of
diaryl mercury with germanium diiodide

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh
nauk, no. 1, 1962, 53-59

TEXT: Organic germanium compounds were synthesized by reaction of GeI_2 with diphenyl, di-p-tolyl, di-m-tolyl, di-o-tolyl, di-p-chloro-phenyl, di-m-chloro-phenyl, di-o-chloro-phenyl, di-p-bromo-phenyl, di-o-bromo-phenyl, di-p-methoxyphenyl, di-p-ethoxyphenyl, di-o-ethoxyphenyl, and di- β -naphthyl mercury. The reaction takes place when boiling equimolecular amounts of GeI_2 and Ar_2Hg in toluene for 15-30 min. The reaction products contain Hg , Hg_2I_2 , HgI_2 , $\text{GeO}_2(\text{GeI}_4)$, ArHgI , sometimes part of the initial Ar_2Hg , and the organogermanium compounds Ar_2GeI_2 , Ar_3GeI , and ArGeI_3 . The main products are the relevant diarylated germanium compounds which are obtained in a

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B106/B101

Synthesis of aromatic germanium ...

yield of 40-75%, related to the admixture of aryl radical. Compounds of the Ar₄Ge type are not formed. The composition of the reaction products suggests that the reaction $\text{Ar}_2\text{Hg} + \text{GeI}_2 \rightarrow \text{Ar}_2\text{GeI}_2 + \text{Hg}$ (I) takes place as the main reaction. Ar₃Ge is probably formed by further reactions following the pattern $\text{Ar}_2\text{Hg} + \text{Ar}_2\text{GeI}_2 \rightarrow \text{Ar}_3\text{GeI} + \text{ArHgI}$ (II). This reaction is facilitated by the fact that both reactants are present in a dissolved form. In the presence of orthosubstituents in the Ar₂Hg molecule complicating reaction (II), no Ar₃GeI is formed. In some cases, a small amount of ArGeI₃ is formed, probably owing to the reaction $\text{ArHgI} + \text{GeI}_2 \rightarrow \text{ArGeI}_3 + \text{Hg}$ (III). In a special experiment, the reaction of equimolecular amounts of C₆H₅HgI and GeI₂ boiled in toluene for 15 min was investigated. Similar to the reactions with Ar₂Hg, metallic mercury was deposited immediately. Apart from a small portion of the initial C₆H₅HgI, the reaction products contained 31.09% of C₆H₅GeI₃, 50.63% of (C₆H₅)₂GeI₂, Hg, Hg₂I₂, and GeI₄. Obviously, C₆H₅HgI reacts with GeI₂ like (C₆H₅)₂Hg.

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Synthesis of aromatic germanium ...

following the pattern $C_6H_5HgI + GeI_2 \rightarrow C_6H_5GeI_3 + Hg$;

$C_6H_5HgI + C_6H_5GeI_3 \rightarrow (C_6H_5)_2GeI_2 + HgI_2$; $2HgI_2 + GeI_2 \rightarrow GeI_4 + Hg_2I_2$.

The influence of the reaction conditions on the degree of arylation and on the yield of organogermanium compounds was also studied. Quantitative proportions and, above all, the sequence of combination of the reactants affect both the yield and the degree of arylation. To achieve a predominant formation of Ar_2GeI_2 , Ar_2Hg must be added in portions to a small GeI_2

excess. An attempt to alkylate Ar_3GeI completely by boiling for many hours with the equimolecular amount of Ar_2Hg in absolute xylene failed. Ar_2Hg

reacted only with Ar_3GeI to form $ArHgI$. The simultaneous formation of

$(Ar_3Ge)_2O$ is probably caused by the oxidation of the $ArGe$ radical by

atmospheric oxygen. Separation of the organogermanium iodides, especially Ar_3GeI and Ar_2GeI_2 , is sometimes difficult owing to their similar

solubility. Therefore, the reaction products, or the residues remaining after the separation of the principal amounts of iodides were hydrolyzed in

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B106/B101

Synthesis of aromatic germanium ...

some cases from the mother liquors, and the resulting aryl germanium compounds were separated in the form of oxides. The molecular weight of some soluble diaryl germanium oxides was determined cryoscopically in benzene. There are 1 table and 9 references: 1 Soviet and 8 non-Soviet. The three most recent references to English-language publications read as follows: O. H. Johnson, D. M. Harris, J. Amer. Chem. Soc. 72, 5564 (1950); F. C. Whitmore, R. J. Sobatzki, J. Amer. Chem. Soc. 55, 1128 (1933); J. K. Simons, E. C. Wagner, J. H. Müller, J. Amer. Chem. Soc. 55, 3705 (1933).

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR (Institute of Elemental Organic Compounds of the Academy of Sciences USSR)

SUBMITTED: July 17, 1961

Table. Organic germanium compounds.

Legend: (1) substance; (2) m., °C; (3) obtained here; (4) according to published data; (5) solvent for crystallization; (8) n-heptane;

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33981
S/062/62/000/002/009/013
B117/B138

15. 8150

AUTHORS: Nesmeyanov, A. N., and Kritskaya, I. I.

TITLE: 1,2-diferrocenyl-1,2-diphenyl ethane and 1,1-diferrocenyl-1,2-diphenyl ethane

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 2, 1962, 352 - 354

TEXT: It is shown that the condensation products of ferrocene and aldehydes described in Ref. 1 (Izv. AN SSSR. Otd. khim. n. 1956, 253; A. N. Nesmeyanov, L. A. Kazitsina, B. V. Lokshin, and I. I. Kritskaya, Dokl. AN SSSR, 117, 433 (1957)) have the structure of symmetric 1,2-diferrocenyl ethanes. This structure was confirmed by Rinehart and co-workers (Ref. 2, see below), who showed that $\overset{\cdot}{\text{C}}\text{H}_2\text{CH}_2\overset{\cdot}{\text{C}}$ ($\overset{\cdot}{\text{C}}$ = ferrocenyl radical) is formed over the stage $\overset{\cdot}{\text{C}}\text{H}_2\text{OH}$ carbonium cation $\overset{\cdot}{\text{C}}\text{H}_2^+$, which is evidently converted by inner reduction into the doubling radical $\overset{\cdot}{\text{C}}^+\text{CH}_2$. This viewpoint was experimentally confirmed when 1,2-diferrocenyl ethane was produced under the effect of

Card 1/2

1,2-diferrocenyl-1,2-diphenyl...

33981
S/062/62/000/002/009/013
B117/B138

FeCl_3 on $\text{C}_6\text{H}_5\text{CH}_2\text{Li}$ (Ref. 4: A. N. Nesmeyanov, E. G. Perevalova, and Yu. A. Ustynyuk, Dokl. AN SSSR, 133, 1105 (1960)) and under the action of $\text{ClCH}_2\text{CH}_2\text{Cl}$ on ferrocene in the Friedel-Crafts reaction (Ref. 3):

A. N. Nesmeyanov, N. S. Kochetkova, and R. B. Materikova, Dokl. AN SSSR, 136, 1096 (1961)). Diferrocenyl ethanes are also formed by the condensation of ferrocene with benzaldehyde. Benzoyl ferrocene reduced according to Clemmensen yielded the unsymmetric 1,1-diferrocenyl-1,2-diphenyl ethane. In addition to the desired hydrocarbons, this reaction yields also pinacolines and the respective hydrocarbons, obviously over the pinacone stage. There are 6 references: 3 Soviet and 3 non-Soviet. The most recent reference to English-language publications reads as follows: ~~Ref. 2: K. L. Rinehart,~~ Ch. J. Michejda, P. A. Kittle, J. Amer. Chem. Soc. 81, 3162 (1959). ✓

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR
(Institute of Elemental Organic Compounds of the Academy of
Sciences USSR)

SUBMITTED: June 29, 1961

Card 2/2

NESMEYANOV, A.N.; KRAVTSOV, D.N.

Aryl mercury derivatives of keto enols and phenols. Izv. AN
SSSR. Otd. khim. nauk no. 3:431-438 Mr '62. (MIRA 15:3)

1. Institut elementoorganicheskikh soedineniy AN SSSR.
(Mercury compounds) (Ketones) (Phenols)

NESMEYANOV, A.N.; ANISIMOV, K.N.; KOLOBOVA, N.Ye.

Some chemical properties of butadiene iron tricarbonyl. *Izv. AN SSSR Otd.khim.nauk* no.4:722-724 Ap '62. (MIRA 15:4)

1. Institut elementoorganicheskikh soedineniy AN SSSR.
(Iron organic compounds)

S/189/62/000/005/002/006
D204/D307

AUTHORS: Genov, L. Kh., Nesmeyanov, A. N., and
Priseikov, Yu. A.

TITLE: The rate of evaporation of thallium selenide
(TlSe)

PERIODICAL: Moscow. Universitet. Vestnik. Seriya II,
Khimiya, no. 5, 1962; 34-35

TEXT: The above was measured between ~ 430 and 570°K , on
TlSe made by reacting equivalent amounts of Tl (containing
Tl²⁰⁴) and Se in a sealed quartz tube, at 400°C over 24 hours.
The vapor pressure P was measured on an apparatus described
earlier by the authors (Ref. 2: Dokl. AN SSSR, 140, No. 1, 159,
1961) determining the amount of condensate by the quantity of
Tl²⁰⁴ and calculating the rate of evaporation, P , and heat of
sublimation ΔH_{T} by methods described in the same, earlier

Card 1/2

S/189/62/000/005/002/006
D204/D307

The rate of...

work. It was assumed that the vapor consisted of an equivolar mixture of Tl_2Se and Tl_2Se_3 . The vapor pressure was determined by (1) the effusion method (effective surface of aperture = $7.82 \times 10^{-4} \text{ cm}^2$), and (2) the evaporation from an open surface (area = 1.68 cm^2). From the results, the relationships (1) $\log P = 9.9638 - \frac{7384.6}{T}$ ($\Delta H_T = 33.56 \text{ kcal/mol}$), and (2) $\log P = 11.3501 - \frac{8613.3}{T}$ ($\Delta H_T = 39.41 \text{ kcal/mol}$) were developed. The results are not in agreement with those of M. G. Shakhtakhtinskiy and A. A. Kuliyeu (Ref. 3: Fizika metallov i metallovedeniya, IX, No. 2, 202, 1960) and indicate that the coefficient of evaporation is not equal to unity. There is 1. table. ✓

ASSOCIATION: Kafedra radiokhimii (Department of Radio-chemistry)

SUBMITTED: March 27, 1961

Card 2/2

NESMEYANOV, A.N.; RYBINSKAYA, M.I.

Synthesis and rearrangements of β -azidovinyl ketones. *Izv. AN SSSR. Otd.khim.nauk no.5:816-820 My '62.* (MIRA 15:6)

1. Institut elementoorganicheskikh soedineniy AN SSSR.
(Ketone)

NESMEYANOV, A.N.; FIRSOVA, L.P.; REYNKHARDT, M.; FORYS', M.;
KURGANOVA, S.Ya.

Preparation of indole tagged with carbon-14 by the hot synthesis
method. Radiokhimiya 4 no.6:739-740 '62. (MIRA 16:1)
(Indole) (Carbon--Isotopes)

NESMEYANOV, A.N.; BORISOV, A.Ye.; BORISOVA, A.I.

Alkenyl derivatives of arsenic. Izv.AN SSSR.Otd.khim.nauk
no.7:1199-1203 J1 '62. (MIRA 15:7)

1. Institut elementoorganicheskikh soyedineniy AN SSSR.
(Arsenic organic compounds) (Unsaturated compounds)

S/062/62/000/007/008/013
B117/B180

AUTHORS: Borisov, A. Ye., Abramova, A. N., and ~~Nesmeyanov, A. N.~~

TITLE: Propenyl stereoisomers of phosphorus

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 7, 1962, 1258 - 1261

TEXT: The reaction of cis and trans propenyl lithium with phosphorus trichloride yielded tri(cis)- and tri(trans propenyl)phosphine, and the reaction of isopropenyl lithium with phosphorus trichloride yielded tri(isopropenyl)phosphine. The resulting phosphorus derivatives and methyl iodide yielded the corresponding phosphonium iodides $R_3P \cdot CH_3I$ and together with the sublimate and β -chloro-vinyl mercury chloride formed complex $R_3P \cdot HgCl_2$ -type compounds. The configurations of the synthesized compounds were determined from their infrared spectra. Compounds with intense absorption lines of non-planar vibrations of the CH groups with a double bond in the $960 - 975 \text{ cm}^{-1}$ range and with C=C bond frequencies of

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Propenyl stereoisomers of phosphorus

S/062/62/000/007/008/013
B117/B180

$\sim 1630 \text{ cm}^{-1}$ were assumed to be trans isomers. Compounds with intense absorption lines of non-planar vibrations of the CH group in the $917 - 930 \text{ cm}^{-1}$ range and with C=C bond frequencies of 1615 cm^{-1} were assumed to have cis configurations. 12 hrs heating at $80 - 105^\circ\text{C}$ or ultraviolet irradiation had no effect on the trans isomer, but $\sim 40\%$ of the cis isomer was converted into trans isomers by the irradiation. Attempts to synthesize R_5P -type propenyl compounds of phosphorus failed. There is 1 table.

ASSOCIATION: Institut elementoorganicheskikh sovedineniy Akademii nauk SSSR (Institute of Elemental Organic Compounds of the Academy of Sciences USSR)

SUBMITTED: February 2, 1962

Card 2/2

S/062/62/000/007/012/013
B117/B180

AUTHORS: Nesmeyanov, A. N., Nogina, O. V., and Surikova, T. P.

TITLE: Alkylation of bis(cyclopentadienyl)titanium dichloride
 $(C_5H_5)_2TiCl_2$ PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh
nauk, no. 7, 1962, 1314TEXT: The authors are the first to have achieved aromatic substitution
in cyclopentadienyl titanium derivatives by means of $(C_5H_5)_2TiCl_2$.

Alkylation of bis(cyclopentadienyl)titanium dichloride took place under
the action of ethylene on a $(C_5H_5)_2TiCl_2$ solution in chloroform at a
pressure of 30 atm without the catalyst $AlCl_3$. Double sublimation in
vacuo yielded $C_{10}H_4(C_2H_5)_6TiCl_2$. Diethyl-bis(cyclopentadienyl)titanium
dichloride $C_{10}H_8(C_2H_5)_2TiCl_2$ was obtained under the same conditions in the
presence of $AlCl_3$. Monoethyl-bis(cyclopentadienyl)-titanium dichloride

Card 1/2

S/062/62/000/007/012/013
B117/B180

Alkylation of bis...

$C_{10}H_9(C_2H_5)TiCl_2$ was obtained without $AlCl_3$ by the action of triethyl amine on $(C_5H_5)_2TiCl_2$. The infrared spectra of the resulting compounds showed bands characteristic of methyl and methylene groups. [Abstracter's note: Essentially complete translation.]

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk SSSR (Institute of Elemental Organic Compounds of the Academy of Sciences USSR)

SUBMITTED: May 17, 1962

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38533

8/063/62/007/003/001/003
A057/A126

15.8/50

AUTHOR: Nesmeyanov, A.N., Academician

TITLE: The chemistry of ferrocene

PERIODICAL: Zhurnal vsesoyuznogo khimicheskogo obshchestva imeni D.I. Mendeleeva, v. 7, no. 3, 1962, 249 - 263

TEXT: The author discusses the chemistry of ferrocene, a member of new, specific metalorganic systems, and considers only investigations carried out by his coworkers. He discusses separately each typical reaction carried out with ferrocene, presenting corresponding reaction schemes for sulphonation, acylation, Friedel-Craft alkylation and electrophilic substitutions. Furthermore, he analyzes the condensation process of ferrocene with aldehydes. Mercuration, metalization of ferrocene by alkyl-lithium, and alkyl-, or aryl-sodium are mentioned and also arylation reactions with diazo compounds. Three different methods were developed by the author to determine the structure of ferrocene. Syntheses by means of mercury compounds show that mercury behaves like an electron-acceptor substitute. In contrast to benzene, dialkylferrocenes with dif-

Card 1/3

The chemistry of ferrocene

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A057/A126

ferent rings show that electrophilic substitutes enter differently into the second, or third position in relation to the alkyl group. Metalization of alkylferrocenes occurs into the ring and not into the chain like in toluene. The acyl-electron acceptor group shows a directing function in conversions of ferrocene, while the phenyl group acts as electron acceptor in phenylferrocene. Variations of the acidic properties of the carboxylic acids of ferrocene were investigated in earlier papers by O.A. Reutov and the author. Substitutes which are in the second cyclopentadienyl ring affect the dissociation constant over the whole ferrocene molecule. Alkyls, as electron donors, decrease the acidic properties in the same order as in the meta position in the benzene ring. The effect of electron-acceptor substitutes is much higher. Some interesting effects of the ferrocene substitute were observed on the basic properties of aniline. Ferrocene shows, besides several characteristics common with benzene, many differences to aromatic compounds which are discussed in the present paper. The ferricine cation cannot receive electrophilic attacks, i.e., it cannot be sulfurized, mercurized, etc., but does not receive nucleophilic attacks, either thus being different from pyridine, for instance. Hence, specific reactions could be observed. Concluding the author states that the chemistry of ferrocene

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The chemistry of ferrocene

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is only a part of the great complex of non-classic structures, which are now in the beginning of being explored. There are 27 figures.

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X

S/062/62/000/008/013/016
B101/B180

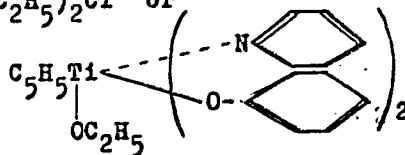
AUTHORS: Nesmeyanov, A. N., Nogina, O. V., and Dubovitskiy, V. A.

TITLE: Data on the titanium - cyclopentadienyl ring bond in $C_5H_5Ti(OC_2H_5)_3$ and $(C_5H_5)_2Ti(OCOCH_3)_2$

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 8, 1962, 1481-1483

TEXT: Using the method of A. K. Fischer, G. Wilkinson (J. Inorg. and Nucl. Chem. 2, 149, (1956)) the ionic nature of the Ti bond in sandwich compounds was checked by reaction with $FeCl_2$ or Fe (II) acetyl acetonate, in argon atmosphere, and tetrahydrofuran solvent at $65^\circ C$. Results:

(1) no ferrocene is formed from $(C_5H_5)_2TiCl_2$, $(C_5H_5)_2Ti(C_6H_5)_2$, $C_5H_5TiCl_3$, $C_5H_5Ti(OC_2H_5)Cl_2$, $C_5H_5Ti(OC_2H_5)_2Cl$ or



Card 1/2

Data on the titanium - ...

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(synthesized for the first time, report printing). (2) ferrocene is formed from $C_5H_5Ti(OC_2H_5)_3$ and $(C_5H_5)_2Ti(OCOCH_3)_2$. (3) the ionic nature of the bond in $C_5H_5Ti(OC_2H_5)_3$ and $(C_5H_5)_2Ti(OCOCH_3)_2$ was further demonstrated by the ease with which these compounds hydrolyze in the presence of water at 60-80°C. (4) The compound $C_5H_5Ti(OC_2H_5)_2Cl$ was synthesized for the first time by reaction between CH_3COCl and $C_5H_5Ti(OC_2H_5)_3$; b.p. 113-114°C/0.5 mm Hg, n_D^{20} 1.5812, d_4^{20} 1.2253. There are 2 tables.

ASSOCIATION: Institut elementoorganicheskikh sovedineniy Akademii nauk SSSR (Institute of Elemental Organic Compounds of the Academy of Sciences USSR)

SUBMITTED: February 17, 1962

Card 2/2

NESMEYANOV, A.N.; ANISINOV, K.N.; VALUYEVA, Z.P.

Mercury derivatives of cyclopentadienyl and methylcyclopentadienylmanganese tricalbony. *Izv. AN SSSR. Otd. khim. nauk no. 9:1683-1684, 3 '62.*
(MIRA 15:10)

1. Institut elementoorganicheskikh soyedineniy AN SSSR.
(Mercury compounds) (Manganese) (Cyclopentadiene)

3/062/62/000/010/001/003
B144/B186

AUTHORS: Nesmeyanov, A. ^NG., 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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Aminomethylation of phenyl,...

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Initial ferrocene	Amino isomers			Iodine methylates	
	number, type	R _f in benzene	% of total amines	m.p. in IR spectrum C 1000-1100 cm ⁻¹	
phenyl	1 heterocyclic	0.14	82	90-95	-
	2 homocyclic	0.38; 0.81	15 3	143-145 167-170	{ 1004; 1104 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		

* CHCl₃:C₆H₆ = 1:1

Thus the aminomethylation was effected mainly (~5:1) in the non-substituted cyclopentane diene 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, Card 2/3

Aminomethylation of phenyl,...

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B144/B186

$C_{18}H_{10}Fe$ (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

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Card 3/3

L1638

S/062/62/000/010/002/003
B144/B18611.2131
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%; Card 1/3

Direct cyanidation of ferrocene...

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

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

Card 2/3

Direct cyanidation of ferrocene...

S/062/62/000/010/002/003
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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, $\text{C}_{10}\text{H}_{10}\text{BF}_4\text{Fe}$, 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, $(\text{C}_{10}\text{H}_{10}\text{Fe})_2\text{PtCl}_6$, 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, $2(\text{C}_5\text{H}_5)_2\text{Fe}^+\text{BF}_4^- + \text{HCN} \rightarrow \text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{CN} + \text{Fe}(\text{C}_5\text{H}_5)_2 + 2\text{HBF}_4$, 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

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

AUTHORS: Nesmeyanov, A. N., Kritskaya, I. I., and Antipina, T. V.

TITLE: Application of adsorption chromatography when working with ferrocene derivatives

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 10, 1962, 1777 - 1783.

TEXT: The formation of keto groups on the central C atom was observed when chromatographing ferrocenes (F'). More detailed studies were made of this phenomenon in aralkyl-F', F'CH₂Ar, and in ferrocenyl carbinols, F'CH(OH)R (R being Ar, Alk), chromatographed on "chromatographic" Al₂O₃ (ГОСТ 2962-54 (GOST 2962-54); pH 6.7 - 7; H₂O 3% by weight) and on ACM (ASM) and KGM (KSM) silica gel in air. The acidity of the adsorbents was determined by H. A. Benesi's method (J. Amer. Chem. Soc. 78, 5490 (1956)). Al₂O₃:aralkyl-F' yielded a distinct amount of keto derivatives; benzyl-F', for example, yielded ~13% benzoyl-F' after 92 hrs contact at room temperature. Alkyl-F'
Card 1/3

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Application of adsorption...

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B144/B186

became oxidized only in traces, if at all. With a contact time of 120 - 200 hrs, the ferrocenyl aryl carbinols $F'CH(OH)C_6H_5$, $F'[CH(OH)C_6H_5]_2$, and $F'CH(OH)CH_3$ yielded respectively 92, 76.8, and 34%. Dehydration at $300^\circ C$ in an N_2 stream increased the catalytic activity of Al_2O_3 . The degree of oxidation decreased when Al_2O_3 had been exposed to air or CO_2 for a considerable time, but reducing the contact time of $F'CH_2C_6H_5$ from 90 to 4 hrs increased the $F'CO_2C_6H_5$ yield from 13 to 32% when air or O_2 was blown through the adsorption column. There was no oxidation when Al_2O_3 was treated with alkali. When Fe had not been separated from SiO_2 , oxidation of alkyl and aralkyl- F' and of diferrocenyl ethanes easily occurred, forming ferricinium cations of F' derivatives with electron-donor substituents. Ferrocenyl carbinols were disproportionated and etherified. This reaction depended on the acidity of SiO_3 . 1,1'-di-(α -hydroxy benzyl)- F' was not disproportionated, but yielded 55% of the internal ether besides small amounts of $F'(CO_2C_6H_5)_2$ and ferrocinium cations. Polyaryl methyl

Card 2/3

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Application of adsorption...

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B144/B186

carbinols yielded ether under the same conditions. Benzhydrol for example, gave 41% of dibenzhydryl ether. The oxidations described are important especially for chromatographing small amounts. The conditions and results of 41 experiments are given in a table. There is 1 table.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR (Institute of Elemental Organic Compounds of the Academy of Sciences USSR). Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova (Moscow State University imeni M. V. Lomonosov)

SUBMITTED: March 26, 1962

Card 3/3

S/062/62/000/011/002/021
B101/B144

AUTHORS:

Nesmeyanov, A. N., Kursanov, D. N., Setkina, V. N.,
Kislyakova, N. V., and Kochetkova, N. S.

TITLE:

Study of hydrogen exchange in nonbenzoidic aromatic systems
(cenes). Communication 1. Hydrogen exchange of ferrocene,
and mono- and diacetyl ferrocene, with acids

PERIODICAL:

Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh
nauk, no. 11, 1962, 1932 - 1936

TEXT: An investigation was made of the hydrogen exchange between the following, dissolved in benzene: ferrocene, acetyl ferrocene, diacetyl ferrocene, or toluene and trifluoro deuterio acetic acid at 25°C, and of ferrocene with deuterio sulfuric acid. In acetylated ferrocenes, the deuterium added on the acetyl group was removed by 160 - 170 hrs standing in 10% alcoholic KOH solution, and the amount of deuterium added on the cyclopentadienyl rings was determined from the density of the water obtained when the compound was burned. The compound : acid : benzene ratio was 1 : 3 : 20. Experiments with CF_3COOD gave the following rate constants

Card 1/2

Study of hydrogen exchange in...

S/062/62/000/011/002/021
B101/B144

for the exchange reaction (sec^{-1}): ferrocene $1.6 \cdot 10^{-4}$; acetyl ferrocene $1.5 \cdot 10^{-7}$; diacetyl ferrocene $7.7 \cdot 10^{-8}$; toluene $3 \cdot 10^{-8}$. Under the given conditions, benzene did not react with CF_3COOD . A 50% hydrogen exchange between ferrocene and D_2SO_4 occurred after 5 min. But no isotopic equilibrium was established because part of the ferrocene oxidizes to ferricinium ion, which does not react with D_2SO_4 , as has been shown by special experiments. On the other hand, deuterium phosphoric acid had no oxidizing action; here the exchange proceeded until reaching equilibrium. There are 6 tables. ✓

ASSOCIATION: Institut elementoorganicheskikh sovedineniy Akademii nauk SSSR (Institute of Elemental Organic Compounds of the Academy of Sciences USSR)

SUBMITTED: March 28, 1962

Card 2/2

NESMEYANOV, A.N.; KOCHETKOVA, N.S.; VIL'CHEVSKAYA, V.D.; SHEVCHUK, Yu.N.;
SENYAVINA, L.B.; STRUCHKOVA, M.I.

o-Carboxy- and *o*-hydroxybenzoylferrocenes and their derivatives.
Izv. AN SSSR. Otd.khim.nauk no.11:1990-1996 N '62. (MIRA 15:12)

1. Institut elementoorganicheskikh soedineniya AN SSSR i
Institut khimii prorodnykh soedineniya AN SSSR.
(Ferrocene)

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 di-
methyl-ethyl(ferrocenyl-methyl) ammonium bromide (C):- (1) Reaction of B
with $\text{Na}_2\text{S} \cdot 10\text{H}_2\text{O}$ on a boiling water bath and extraction with ether produced
di-(ferrocenyl-methyl) sulfide, yield 54%, m.p. 107 - 108°C (with decom-
position). 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 pro-
duced by bubbling H_2S through NaOH solution. (3) The synthesis of ferro-

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Ferrocenyl methylation by means of...

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ferrocenyl methyl acetate was made in three ways: (a) Reaction of B with glacial acetic acid at 90 - 95°C in N₂ 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 C₁₂H₁₂Fe, 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 N₂ atmosphere at 130 - 135°C, and extraction with benzene, produced ferrocenyl methyl benzoate, yield 50%, m.p. 132-133°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_D²⁰ 1.5840. The IR bands at 1002, 1106 cm⁻¹

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Ferrocenyl methylation by means of...

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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. Card 3/4

Ferrocenyl methylation by means of...

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B101/B144

108-110°C/0.3 mm Hg, n_D^{20} 1.6310, 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

5/062/62/000/011/005/021
B101/B144

AUTHORS: Nesmeyanov, A. N., Kochetkova, N. S., Vil'chevskaya, V. D.,
Sheynker, Yu. N., Senyavina, L. B., and Struchkova, M. I.

TITLE: o-Carboxy- and o-hydroxy benzoyl ferrocenes and their
derivatives

PERIODICAL: Akademiya nauk SSSR. - Izvestiya. Otdeleniye khimicheskikh
nauk, no. 11, 1962, 1990 - 1996

TEXT: The IR and UV spectra of the following compounds were studied:
o-carboxy benzoyl ferrocene (A); o-hydroxy benzoyl ferrocene (B) synthesized
from salicyl chloride and ferrocene in the presence of $AlCl_3$ in CH_2Cl_2

solution at 45 - 50°C; o-methoxy benzoyl ferrocene (C) obtained by
methylating B with dimethyl sulfate, yield 96%; o-acetoxy benzoyl ferrocene
(D) obtained by acetylating B with acetic anhydride, yield 95%; o-hydroxy
benzyl ferrocene (E) obtained by reducing B with zinc amalgam, yield 77%;
o-methoxy benzyl ferrocene (F) obtained by methylating E with dimethyl
sulfate, yield 94%; o-hydroxy phenyl ferrocenyl carbinol (G) obtained by
reducing B with $LiAlH_4$, yield 90%; and o-methoxy ferrocenyl carbinol (H)

Card 1/3

o-Carboxy- and o-hydroxy...

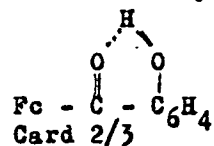
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B101/B144

obtained by methylating G with dimethyl sulfate, yield 93%. Ethers of the type $C_{10}H_9Fe-CH(OR)-C_6H_4OH$ were obtained by recrystallizing G in the corresponding alcohols. For $R = CH_3$, the m.p. was 119 - 120°C, the yield 89%; for $R = C_2H_5$, m.p. 117°C, yield 94%; and for $R = i-C_3H_7$, m.p. 79-80°C, yield 89%. The spectroscopic studies showed: (1) Both the crystallized and the dissolved A showed no tautomerism by ring closure. The structure of A is therefore open: $Fc-CO-C_6H_4$, (Fc = ferrocenyl), although in an

earlier study (Dokl. AN SSSR, 138, 390 (1961)) derivatives of the tautomeric

form $Fc-C(OR)-C_6H_4$ were also synthesized from this compound. (2) With B there is also no hydroxy quinone tautomerism, but an intramolecular H bond

is formed. There are 4 figures and 1 table. The most



o-Carboxy- and o-hydroxy...

S/062/62/000/011/005/021
B101/B144

important English-language reference is: R. L. Schaaf, J. Organ. Chem.,
27, 107 (1962).

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk
SSSR (Institute of Elemental Organic Compounds of the
Academy of Sciences USSR). Institut khimii prirodnykh
soyedineniy Akademii nauk SSSR (Institute of Chemistry of
Naturally Occurring Compounds of the Academy of Sciences USSR)

SUBMITTED: April 4, 1962

Card 3/3

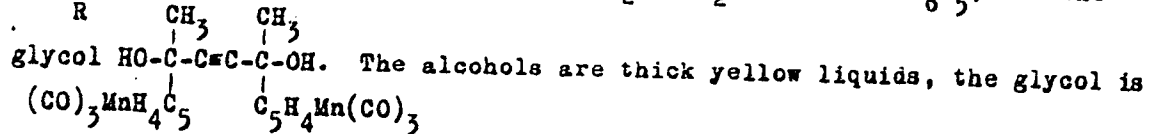
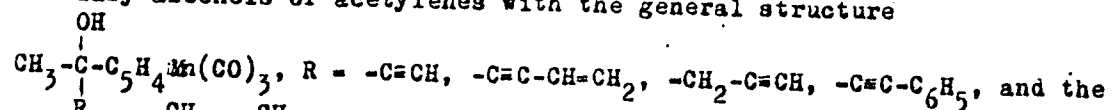
S/062/62/000/011/013/021
B101/B144

AUTHORS: ~~Nesmeyanov, A. N.~~, Anisimov, K. N., Kolobova, N. Ye., and Magomedov, G. K.

TITLE: Reaction of acetyl cyclopentadienyl manganese tricarbonyl with Grignard reagent and with Iotsich complex

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 11, 1962, 2072 - 2073

TEXT: Reaction of acetyl cyclopentadienyl manganese tricarbonyl with the corresponding Grignard reagents and with the Iotsich complex produced tertiary alcohols of acetylenes with the general structure



Card 1/2

Reaction of acetyl...

S/062/62/000/011/013/021
B101/B144

crystalline. The structures of the synthesized compounds were confirmed by the IR spectra. The relevant data will be published later. Compounds obtained: 2-hydroxy-2-cyclopentadienyl-manganese-tricarbonyl-butyne-3, yield 81%, b.p. 27°C/10⁻² mm Hg, n_D^{20} 1.5912, d_4^{20} 1.4131; 2,5-dihydroxy-2,5-bis-(cyclopentadienyl-manganese-tricarbonyl)-hexyne-3, m.p. 142 - 143°C without decomposition, yield 40%; 2-hydroxy-2-cyclopentadienyl-manganese-tricarbonyl-4-phenyl-butyne-3, yield 71%, b.p. 70°C/10⁻² mm Hg, n_D^{20} 1.6238, d_4^{20} 1.3386; 2-hydroxy-2-cyclopentadienyl-manganese-tricarbonyl-hexen-5-yne-3, yield 90%, b.p. 80°C/10⁻² mm Hg, n_D^{20} 1.5945, d_4^{20} 1.3307; 2-hydroxy-2-cyclopentadienyl-manganese-tricarbonyl-pentyne-4, yield 63%, b.p. 40°C/10⁻⁴ mm Hg, n_D^{20} 1.5850, d_4^{20} 1.3635. ✓

ASSOCIATION: Institut elementoorganicheskikh sovedineniy Akademii nauk SSSR
(Institute of Elemental Organic Compounds of the Academy of
Sciences USSR)

SUBMITTED: June 4, 1962
Card 2/2

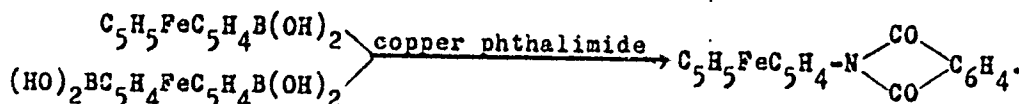
S/062/62/000/011/014/021
B101/B144

AUTHORS: Nesmeyanov, A. N., Sazonova, V. A., Gerasimenko, A. V., and Medvedeva, V. G.

TITLE: Reactions of ferrocenyl boric acids with copper phthalimide

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 11, 1962, 2073 - 2074

TEXT: The following reactions were carried out with ferrocenyl boric acid (I) and 1,1'-diferrocenylene diboric acid (II) in boiling pyridine for 10 - 15 min:



Styryl boric acid, phenyl boric acid, and p-anisyl boric acid react similarly with copper phthalimide. Compounds obtained: N-ferrocenyl phthalimide, yield from I: 47 %, from II: 29 %, m.p. 156 - 156.5°C; N-styryl phthalimide, yield 56 %; N-phenyl phthalimide, yield 19 %; and Card 1/2

Reactions of ferrocenyl boric...

S/062/62/000/011/014/021
B101/B144

N-p-methoxy phenyl phthalimide, yield 34 %.

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

SUBMITTED: June 4, 1962

↓

Card 2/2

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

AUTORS: 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. Diferrocenyl 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

Reaction between ferrocene...

S/062/62/000/012/005/007
B117/B1C1

carbinol $C_{31}H_{28}OFe_3$, m.p. 204-205°C (from benzene), molecular weight 617.

It is a yellow crystalline substance showing in its infrared spectrum a 3558 cm^{-1} band characteristic of the hydroxyl group. It is easily soluble in benzene and carbon tetrachloride, poorly soluble in ether, and insoluble in ethyl alcohol. If concentrated hydrochloric acid is added, it turns an intense green. Triferrocenyl carbinol, quite stable at room temperature, changes to a carmine-red substance of unknown structure when heated in benzene, melted or when chromatographed on Al_2O_3 over a long period. ✓

Triferrocenyl methane $C_{31}H_{28}Fe_3$ (59%) was synthesized by reducing triferrocenyl carbinol with zinc dust in acetic acid. It is a yellow infusible crystalline substance which decomposes at 200°C.

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

SUBMITTED: July 13, 1962

Card 2/2

NESMEYANOV, A. N.; NOGINA, O. V.; DUBOVITSKIY, V. A.

Alkylation of bis-(cyclopentadienyl) titanium dichloride by
means of acetyl chloride. Izv. AN SSSR Otd. khim. nauk no.12:
2254-2255 D '62. (MIRA 16:1)

1. Institut elementoorganicheskikh soedineniy AN SSSR.

(Titanium compounds) (Acetyl chloride)

NESMEYANOV, A.N., akademik; KRAVTSOV, D.N.

p-Dimethylaminophenylmercury derivatives of aminoazo compounds.
Dokl. AN SSSR 142 no.5:1088-1090 F '62. (MIRA 15:2)
(Azo compounds)
(Mercury compounds)

NESMEYANOV, A.N., akademik; KURSANOV, D.N.; SETKINA, V.N.; KISLYAKOVA, N.V.;
KOCHETKOVA, N.S.; MATERIKOVA, R.B.

Hydrogen isotope exchange of cyclopentadienylmanganesetricarbonyl.
Dokl. AN SSSR 143 no.2:351-353 Mr '62. (MIRA 15:3)

1. Institut elemento-organicheskikh soedineniy AN SSSR. 2. Chlen-
korrespondent AN SSSR (for Kursanov).
(Hydrogen--Isotopes)
(Cyclopentadiene)

NESMEYANOV, A.N., akademik; KOCHETKOVA, N.S.; MATERIKOVA, R.B.

Scission of cyclopentadienyl compounds of metals by
bromine and potassium hypobromite. Dokl. AN SSSR 147
no.1:113-116 N '62. (MIRA 15:11)

1. Institut elementoorganicheskikh soedineniy AN SSSR.
(Organometallic compounds)
(Cyclopentadiene) (Bromine)