

NESHCHYANOV, A.N., akademik.

On the border line between sciences. Nauka i zhizn' 25 no.3:1-2
K: '58. (MIRA 11:4)

1. Prezident AN SSSR. (Science)

NESMEYANOV, A.N., akademik

Chemistry is the science of abundance. Tekh.nol. 26 no.8:8-9 '58.
(MIRA 11:9)

1. Prezident AN SSSR.
(Polymers)

MESENYANOV, A.N., akademik

Scientific front. Tekh.mol. 26 no.10:10-11 '58. (MIRA 11:11)

1. AN SSSR.

(Research)

AUTHORS: Nesmeyanov, A. N., Perevalova, E. G., (Moscow) 74-27-1-1/4

TITLE: Cyclopentadienyl Compounds of Metals and Compounds Related to Them (Tsiklopentadiyenil'nyye soyedineniya metallov i rodstvennyye soyedineniya)

PERIODICAL: Uspekhi Khimii, 1958, Vol. 27, Nr 1, pp. 3-56 (USSR)

ABSTRACT: Initially the author deals with the problem of the possible separation of organic iron compounds. In 1951 - 1952 a special class of metalorganic compounds (special as to their structure and properties) was discovered. When trying to synthesize dicyclopentadienyl, $C_5H_5 - C_5H_5$, Kealy and Fauson obtained a substance containing iron and hydrogen, which later was called ferrocene and which attracted the attention of all chemists. In the course of the further investigation of the dicyclopentadienyl derivatives also the problem of the limits of the possibility of applying the theory of valence became topical. A detailed description of the methods of obtaining dicyclopentadienyl compounds of the metals is following. On the physical properties and the structure of the ferrocene: The first investigations showed that its

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structure, as assumed by Fauson, 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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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

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NESMEYANOV, A. N.

30-1-2/39

AUTHOR: Nesmeyanov, A. N., Academician

TITLE: On the Launching of the First Artificial Earth Satellite
(K zapusku pervykh iskustvennykh sputnikov zemli).

PERIODICAL: Vestnik AN SSSR, 1958, Vol. 28, Nr 1, pp. 5-7 (USSR)

ABSTRACT: Whole epochs in the history of mankind can be named after discoveries or inventions. These epochs are, however, short. Thousands of years separated the stone age from the bronze age and the same is the case with respect to the latter and the iron age. Only some decades were, however, necessary to change over from the age of steam and the railroads to that of combustion engines and electricity. Many of such important dates or periods remained unnoticed because, at that time, they were not understood. The following dates of this kind are mentioned:

- 1) March 6, 1869, when, in the course of a meeting of the Russian Chemical Society, D. I. Mendeleev and N. A. Menshutkin delivered a short report on the discovery of the periodic system of elements.
- 2) In the summer of 1882 the first aircraft, constructed by Mozhaykiy, which was heavier than air, took place.

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3) On March 12, 1896 A. S. Popov, at a meeting of the Russian Physical and Chemical Society, demonstrated his device for wireless telegraphy.

4) In 1895 K. E. Tsiolkovskiy was the first to suggest producing artificial earth satellites.

The technical difficulties which arose when the first cosmic flight was carried out in practice were the following: A powerful driving mechanism had to be constructed which would operate reliably for a sufficient length of time at extremely tense thermal conditions. It was further necessary to develop a light and solid rocket construction which would be able to withstand the great stresses during flight. The parameters of the construction of the rocket, of the driving mechanism, and its fuel had, together, to warrant a minimum rocker velocity of 8 km per second and thus to render conveying the earth satellite to an orbital height of some hundred kilometers possible. The 4. October 1957 marks the beginning of a new era, viz. the era in which man penetrated into interplanetary space. This success could be achieved only thanks to the high level of Soviet science. It was necessary to carry out investigations in the field of aerodynamics,

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supersonic velocities, as well as of radio remote control, and theoretical work had to be performed concerning the dynamics of rocket motion and automatic control. New, light, solid, and refractory materials had to be found, as well as fuels of high calorific content. For the scientific apparatus of the earth satellite it was necessary to provide light, small gabarit constructions. The ionosphere, cosmic radiation, tensional modifications of the magnetic field at great heights, and many problems can now for the first time in history be observed and investigated by means of earth satellites (above the air atmosphere). Besides, also very interesting investigations concerning the behavior of living beings are carried out in great heights. All these investigations may be looked upon as a preparation for flights to the moon and other planets. The launching of artificial earth satellites may therefore be described as the beginning of a new era in the history of mankind, i. e. the cosmic era.

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1. Satellite-Launching

RESHEVYANOV, A.N., akademik

Great conquest of Soviet science. Vest. AN SSSR 28 no.11:3-9 N '58.
(MIRA 11:12)

(Artificial satellites) (Science)

VASIL'YEV, M.; GUSHCHEV, S.; RESMEYANOV, A.N., akademik; SECHERBAKOV, D.I., akademik;
ENGEL'GARDT, V.A., akademik; ZHENEBAK, A.R., prof.; LEBNEDEV, S.A.,
akademik; ZENKEVICH, L.A.; GRADOV, A.S.; GOLODOVSKIY, M.G., prof.;
SFANYUKOVICH, K.P., prof.

Ahead with the dream! Znan.sila 33 no.12:24-25 D '58.
(MIRA 11:12)

1. Chlen-korrespondent AN SSSR (for Zendeovich). 2. Direktor Nauchno-
issledovatel'skogo instituta proyektirovaniya obshchestvennykh zdaniy
i sooruzheniy (for Gradv).
(Science)

NESMEYANOV, A.N., akademik

Tasks of the Academy of Sciences of the U.S.S.R. and acceleration in the development of the chemical industry and particularly the production of synthetic materials and articles from them for the satisfaction of the demands of the population and the necessities of the national economy. Priroda 47 no.9:3-14 S '58. (MIRA 11:9)

1. President AN SSSR.
(Macromolecular compounds) (Chemical industries)

NESMEYANOV, A. N.

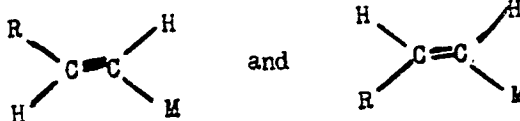
20-1-28/58

AUTHORS: Nesmeyanov, A. N., Academician
Reutov, O. A., Knoll', P.

TITLE: The Employment of the Isotopic Method in Studying the Stereochemistry of Replacement Reactions at the Olefinic Carbon Atom (Izucheniye stereokhimiicheskikh reaktsiy zameshcheniya u olefinovogo atoma ugleroda s pomoshch'yu izotopnogo metoda).

PERIODICAL: Doklady AN SSSR, 1958, Vol. 118, Nr 1, pp. 99-102 (USSR).

ABSTRACT: Together with Borisov the first author (reference 1) established the following rule: electrophile and homolytic replacement reactions take place under conservation of the cis- and trans-configuration. This rule was derived in the study of the metal exchange in the series of stereoisomeric organometallic compounds of the type:



By employing the method of isotopes the authors in this paper directly proved the correctness of this rule. As example of electrophile reactions they studied the interaction of trans- and cis-β-

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chlorovinyl-mercury chloride with sublimate labelled with radioactive mercury Hg^{203} . The reactions were carried out in an acetone solution in the cold. In both cases the isotopic equilibrium was soon obtained (within 5 minutes). The stereochemical initial configuration of the chlorovinyl group was on that occasion strictly conserved. As homolytical reactions they studied the interaction of metallic mercury labelled with Hg^{203} with trans- and cis- β -chlorovinyl-mercury chlorides, as well as that with bis-trans- and bis-cis- β -chlorovinyl-mercury. All 4 above-mentioned organo-mercury compounds readily react in acetone in the cold with finely distributed metallic mercury. The isotopic equilibrium is attained after some hours. The configuration of the chlorovinyl groups is always conserved in this connection. During the interaction of the metallic mercury with trans- and cis- β -mercuryvinylchlorides a side reaction takes place under formation of calomel and acetylene. This is an example of the double reactivity which is so very characteristic of all β -chlorovinyl-organometallic compounds. The two electrophile and the two first homolytical reactions require an additional discussion. The observed stereochemistry of these 4 reactions was not the result of one but of several processes. It may be stated that these 4 reac-

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The Employment of the Isotopic Method in Studying the Stereochemistry of Replacement Reactions at the Olefinic Carbon Atom. 20-1-28/58

tions do not proceed over the equilibrium, but that $\overset{\text{H}}{\text{Hg}}\text{Cl}_2$ and $\overset{\text{H}}{\text{Hg}}$ directly react with the β -chlorovinyl-mercury chlorides. Thus the results obtained here are a direct proof of the conservation of the configuration at the olefinic carbon atom during the electrophile and homolytical replacement reactions. An experimental part with the usual data follows. There are 4 references, 3 of which are Slavic.

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

SUBMITTED: October 22, 1957.

AVAILABLE: Library of Congress.

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Nesmeyanov, A. N.

AUTHORS: Nesmeyanov, A. N., Academician, Rybinskaya, M.I., 20-2-25/60

TITLE: A Direct Synthesis of the 4-Substituted Salts of 1-Azadehydroquinolysinium (Pryamoy sintez 4-zameshchennykh soley 1-azadegidrokhinoliziniya).

PERIODICAL: Doklady AN SSSR, 1958, Vol. 118, Nr 2, pp. 297-298 (USSR)

ABSTRACT: The authors recently published (reference 1) the method of synthesis of the salts of 4-alkyl-1-azadehydroquinolysinium. It is based on the condensation of α -aminopyridine with acyl-acetaldehyde-acetalene (reference 2) and on the subsequent ring closure of the obtained condensation-products by means of concentrated acids (HBr, HClO₄). In the present paper the authors considerably simplified this method by showing that the same compounds may be produced by a direct condensation of β -chlorovinylketones with α -aminopyridine under the influence of 70% perchloric acid. The acyl-acetaldehyl-acetals (reference 2) readily developing from β -chlorovinylketones enter this type of hypercycle-closure-reaction with the same result. This variant of the method under review may win independent importance, as the first homologue of the series of acyl-acetal-aldehyde-acetals, namely aceto-acetaldehyl-acetal, recently became a tech-

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A Direct Synthesis of the 4-Substituted Salts of 1-Azadehydro- 20-2-25/60
quinolysinium.

nical product and may easily be produced from diacetylene (ref. 3,4). The method of synthesis worked out here also yielded the possibility of producing 4-phenyl-1-azadhydroquinolysinium-perchlorate. The structure of the produced salts was proved earlier (reference 1). No 2-substituted isomers were found in these two cases. Production methods (2 respectively), yields and constants for perchlorates of 4-methyl-, 4-propyl- and 4-phenyl-1-azadhydroquinolysinium are given in the experimental part. There are 4 references, 2 of which are Slavic.

SUBMITTED: September 18, 1957

AVAILABLE: Library of Congress

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NESMEYANOV A. N.

20-3-26/59

AUTHOR: Nesmeyanov, A. N., Academician
Vol'kenau, N. A., Vil'chevskaya, V. D.

TITLE: Intramolecular Acylation in the Ferrocene Series
(Vnutrimolekulyarnoye atsilirovaniye v ryadu ferrotsena).
The Cyclization of γ -Ferrocenyl Substituted Acids and
Ketoacids (Tsiklizatsiya γ -ferrotsenilzameshchennykh kislot
i ketokislot).

PERIODICAL: Doklady AN SSSR, 1958, Vol. 118, Nr 3, pp. 512-514 (USSR)

ABSTRACT: This kind of acylation was proved by the authors in the ferrocene series (ref. 1). The present work is an extension and continuation of it. By interaction between ferrocene and the anhydride of chlorine of β -carbomethoxypropionic acid β -carbomethoxypropionyl-ferrocene was produced and from this β -carboxypropionyl-ferrocene. With the latter substance no cycle could be formed by the action of polyphosphoric- or sulfuric acid. Then it was reduced to ω -carboxypropyl-ferrocene according to Klemmensen. This was easily cyclisated by heating with polyphosphoric acid. On this occasion keto-hydro-indenyl-cyclo-pentadienyl-iron was formed. Its structure was proved by: 1.- The production of a derivative after the

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Intramolecular Acylation in the Ferrocene Series.
The Cyclization of γ -Ferrocenyl Substituted Acids and Ketoacids

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ketogroup; 2.- Bromination which lead to pentabromo-cyclopentan, that is to say a non-substituted cyclopentadienyl-ring was proved in the molecule; 3.- The infrared spectrum (1008 and 1106 cm^{-1}). Furthermore the cyclization with α -carboxy-benzoyl-ferrocene was investigated. Contrary to the ferrocenyl substituted keto acids of the aliphatic series α -carboxybenzoylferrocene can easily be cyclisated with polyphosphoric- and concentrated sulfuric acid. On the same conditions this occurs also with α -carbomethoxybenzoylferrocene. Thus a complete analogy with benzene derivatives is observed. As is known benzoyl-propionic acid can not be cyclisated while α -benzoyl-benzoe acid easily forms anthraquinone with simple heating. The results mentioned above prove the final conclusion (ref. 1) that ferrocenyl substituted carboxylic acids are subjected to an intra-molecular acylation and this in the same cyclopentadienyl ring which already contains a substituent. The same applies even for the α -carboxybenzoyl-ferrocene in which this ring is already somehow deactivated by the CO-group in it. β -carboxypropionyl ferrocene can not at all be

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cyclized. The reason for this has still to be found.
An experimental part with the usual data follows.
There are 4 references, 3 of which are Slavic.

ASSOCIATION: Institute for Elementary-Organic Compounds AN USSR
(Institut elementoorganicheskikh soedineniy Akademii nauk
SSSR).

SUBMITTED: August 10, 1957

AVAILABLE: Library of Congress

Card 3/3

AUTHORS: Nesmeyanov, A. N.; Member of the Academy, 20-119-2-27/60
Ferevalova, E. G.; Nesmeyanova, O. A.

TITLE: Diferrocenyl Mercury Reactions
(Reaktsii diferrotsenilrtuti)

PERIODICAL: Doklady Akademii Nauk SSSR, 1958, Vol. 119, Nr 2,
pp. 288-291 (USSSR)

ABSTRACT: As it was proved already the ferrocene mercury derivatives produced by the authors for the first time (ref 1) can be used for the synthesis of the ferrocene derivatives. The authors produced haloid ferrocenes by means of reactions with iodine and bromine (ref 2). In the present paper the interaction of the derivative mentioned in the title with triphenyl chloromethane, with haloid anhydrides of the carboxylic and sulfonic acids, with thiocyanogen (in statu nascendi) and with selenium tetrabromide was utilized. Diferrocenyl mercury reacts with triphenyl chloromethane under not rigorous conditions and produces ferrocenyl triphenylmethane with a yield of 18% of the theoretically possible yield and a small amount of ferrocene.

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Biferrocenyl Mercury Reactions

Reaction takes place under greater difficulties with sulfonic acids chloranhydrides. Thus, differrocenylsulfone and phenyl ferrocenylsulfone are produced in a yield of 5-6 % on the heating of differrocenyl mercury with chloranhydrides of the ferrocene and benzene sulfonic acid. On this occasion 35-38 % of the differrocenyl mercury are converted into ferrocene. Reaction with acetyl chloride takes place even under greater difficulties. Acetyl ferrocene only forms in a yield of 1 % and ferrocene forms in great quantities as described above. Differrocenyl 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 sulfonic acid phenyl ferrocenyl sulfone forms in a yield of 22 %. Differrocenyl mercury forms a complex with thiocyanogen excess. If the latter is processed by means of a watery solution of sodium thiosulfate differrocenyl disulfide forms in a yield of 15 % calculated with reference to the mercury compound which entered reaction. 12 % of the differrocenyl mercury remain unchanged. Probably the originally formed

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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 substitution 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.

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AUTHORS: Nesmeyanov, A. N., Member, Academy of Sciences, USSR, Borisov, A. Ye., Novikova, E. V. 20-119-3-29/65

TITLE: Conservation of Propenyl Radical Configuration in Metal to Metal Transition Reactions (Sokhraneniye konfiguratsii propenil'nogo radikala v reaktsiyakh perekhoda ot metalla k metallu)

PERIODICAL: Doklady Akademii Nauk SSSR, 1958, Vol. 119, Nr 3, pp. 504-505 (USSR)

ABSTRACT: The authors continue their papers on the stereochemistry of the atom exchange reactions (ref 1). The atoms are connected with the olefine-hydrocarbon. The authors realized several transitions of the cis- and correspondingly of the trans-propenyl-radical in starting from the stereo-isomeric 1-bromo-1-propenes (table 1). These bromides were transformed by action of lithium in ether at +5 to -7°C into corresponding stereoisomeric lithium-propenyl compounds and further into several propenyl-organometallic compounds of Hg, Sn and Tl by subsequent exchange reactions at reduced temperatures. Corresponding stereoisomers of acrotic acid were formed

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Metal Transition Reactions

by CO_2 action. The configuration of the initial bromo-propene is known as well as the configuration of the crotonic- and isocrotonic acid. The configuration of the two compounds of lithium-propenyl which were formed by lithium action on an ether solution of a corresponding bromo-propene at 5 to -70°C was proved by the presence of frequencies 700 and 1623 cm^{-1} in the infrared spectrum which belong to the substances formed by cis-bromo-propene, whereas in the same spectrum of its stereoisomer frequencies 975 and 1645 cm^{-1} occur. This characterizes the first organolithium substance as cis-, the latter as a trans-isomer. The exchange reactions of these isomers of lithium-propenyl with HgBr_2 and TlBr_3 passed under conservation of their configurations, exactly like all other exchange reactions of the metals investigated by the author. This is proved by the delimitation of the trans-formation region of the cis-lithium-propenyl from the domain of the trans-lithium compound and by the method of even and uneven cycles (ref 1). The transitions 6,7; 7,8; 5; 7, 8, 12, 11, 5; 7, 8, 12, 11, 9, 6 and 11, 9, 10

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Conservation of Propenyl Radical Configuration in Metal
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actually contain in the transformation series of trans-lithium-propenyl and the corresponding transformations 18, 19; 19, 20, 17; 19, 20, 24, 17; 23, 24; 23, 21, 22 - 2, 3, 5, 6 terms; they are cyclic, i.e. they return each time to the initial stereoisomer, independently of the number of terms. Therefore each probability of reactions with inversions of configuration is excluded. Thus the above material once more confirms the rule concerning the conservation of configuration in electrophil or homolytical substitutions of an olefine-hydrocarbon (ref 3) put up by the authors. The transformations 1, 13, 8, 20, 11 and 23 are here apparently homolytical, whereas the others are electrophil. There are 1 table, and 8 references, 5 of which are Soviet.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk
SSSR (Institute of Elemental-organic Compounds AS USSR)

SUBMITTED: November 20, 1957

Card 3/3

AUTHORS: Neameyanov, A. N., Member, Academy of Sciences, USSR, Borisov, A. Ye., Novikova, N. V. 20-119-4-23/60

TITLE: Preservation of Configuration of the Propenyl Radical in the Reactions of Cis- and Trans-Propenyl Lithium With Oxo-Compounds (Sokhraneniye konfiguratsii propenil'nogo radikala v reaktsiyakh tsis- i transpropenillitiya s oksosoyedineniyami)

PERIODICAL: Doklady Akademii Nauk SSSR, 1958, Vol. 119, Nr 4, pp. 712-715 (USSR)

ABSTRACT: In previous reports (ref. 1) the authors proved that the reactions of electrophilic and homolytic exchange usually take place with the conservation of geometrical configuration, at the olefine-carbon atom which is responsible for the cis-, trans-isomerism. This was proved in numerous cases of metal-metal exchange. It is the object of the present paper to show that this is possible in the case of an electrophilic substitution of a metal atom by a carbon atom in the reactions mentioned in the title. The production method of the isomers in question is described; their constants are given. A corresponding quantity of ketone or aldehyde was introduced to 200 ml of dry ether of an ether

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Reactions of Cis- and Trans-Propenyl Lithium With Oxo-Compounds

solution of the two isomers mentioned in the title, stirred for two hours, and decomposed by a saturated solution of ammonium chloride. The reaction product which was dried by means of potash was distilled. Reaction products of the two isomers with acetone, acetophenone, benzophenone, p-chlorobenzophenone, as well as with acetaldehyde and benzaldehyde were investigated, too. In the case of interaction of ketones with cis-propenyl lithium corresponding tertiary alcohols are formed from the last mentioned compound; with aldehydes, however, secondary alcohols with a cis-configuration; trans-propenyl lithium forms here corresponding trans-compounds. The configurations of the products were determined from the oscillation frequencies of the infra red absorption spectra (table 1). ~~Undistilled~~ products have exactly the same frequencies. The configuration was confirmed additionally by the known catalytic affiliation of two hydrogen atoms to the acetylene derivatives in a cis-position (ref. 4) for the cis-isomer of the 1-methyl-butene-2-ol-1. The cis- and trans-isomers of further dimethyl-butenes were also identified as p-nitrobenzoates (table 2). Thus the configuration of the

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Reactions of Cis- and Trans-Propenyl Lithium With Oxo-Compounds

olefine radical is conserved also in the reactions mentioned in the title, in an analogous way as described by the authors in ref. 5. Thus the general importance of the initially mentioned rule is proved. There are 2 tables and 5 references, 2 of which are Soviet.

SUBMITTED: November 20, 1957

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20-119-5-30/59

AUTHORS: Nesmeyanov, A. N., Member, Academy of Sciences, USSR, Perevalova, E. G., Churanov, S. S., Nesmeyanova, O. A.

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 $\text{Fe}(\text{C}_5\text{H}_4\text{SO}_3)_2 \cdot \text{Pb} \cdot 4\text{H}_2\text{O}$ with phosphorus trichloride they obtained monochlor anhydride $\text{ClSO}_2\text{C}_5\text{H}_4\text{FeC}_5\text{H}_4\text{SO}_3\text{H}$. 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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The Reactions of Ferrocene Sulfonic Acids

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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 $\text{Fe}[\text{C}_5\text{H}_4\text{SO}_2\text{H}(\text{C}_2\text{H}_5)_2]_2$ was produced. From ferrocene monosulfochloride they produced diethylamide, the sodium salt of sulfonic 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 $1000-1110 \text{ cm}^{-1}$ (taken by L. A. Kazitayna 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 lie in different cyclopentadiene rings. The authors did not succeed in replaining the sulf-

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group by a hydroxyl (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 formate); 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 substitutions, to a high degree in the same cyclopentadienyl ring and to a much lower degree in the other ring (ref 1). 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.

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The Reactions of Ferrocene Sulfonic Acids

10-119-5-0100

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

SUBMITTED: January 16, 1958

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SOV/20-120-4-29/67

AUTHORS: Nesmeyanov, A. N., Member, Academy of Sciences, USSR
Rybinskaya, M. I.

TITLE: The Interaction of β -Cyanovinyl Ketones With Secondary Amines
(O vzaimodeystvii β -tsianvinilketonov s vtorichnymi aminami)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol. 120, Nr 4, pp. 793-796
(USSR)

ABSTRACT: In a recently published paper the authors reported on the synthesis of up to now unknown derivatives of acrylonitrile: β -cyanovinyl ketones (Ref 1). Even the preliminary results from the examination of the interaction of those substances with nucleophilic agents show a high electrophilic activity of their double binding. It is interesting that among the 2 competing groups $>C=O$ and $-C\equiv N$ it is the carbonyl group which determines the orientation of addition. The addition proceeds opposite to the direction of the reactions of cyanoethylation by acrylonitrile. This offers quite different possibilities of synthesis in the use of β -cyanovinyl ketones (β -acyl-acrylonitriles). In this paper in connection with the investigation of the reaction mentioned in the title an inter-

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esting difference between aliphatic and aromatic β -cyano-
vinyl ketones is pointed out. Aryl- β -cyanovinyl ketones yield
amine addition products (even in case of a great excess of
amines) attached to the double binding. The products can be
easily crystallized. After a longer period of storing, how-
ever, they become changeable. They are nitrils of α -amino- α -
-ketocarboxylic acids. In the case of action of concentrated
HCl on nitril- α -(N-piperidyl) of β -benzoyl-propionic acid the
hydrolysis proceeds under formation of the corresponding acid;
the latter is isolated as a stable chloroanhydrate. By the
action of ethylene oxide on this chloroanhydrate α -(N-piperi-
dil)- β -benzoyl-propionic acid was isolated which was identical
with that obtained from a counter-synthesis of β -benzoyl-
acrylic acid and piperidine (Ref 2). By means of hydrolysis
of nitril of α -(N-morpholy)- β -benzyl-acrylic acid the amide
of the corresponding acid was obtained under the same condi-
tions. The investigations of β -acyl-acrylic acids have
hitherto not been very successful. The method the authors
applied to clarify their structure is simple and may in future
be used for the determination of the structure of other addi-
tion products to the double binding. Under similar circum-

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The Interaction of β -Cyanovinyl Ketones With Secondary Amines

stances methyl- β -cyanovinyl ketone behaves differently. It brings about an exchange of the CN-group for the amino group. There are 1 table and 9 references, 2 of which are Soviet.

SUBMITTED: February 28, 1958

1. Ketones--Chemical reactions
2. Amines--Chemical reactions

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SOV/20-120-5-33/67

AUTHORS: ~~Vasmeryanov, A. M.~~ Member, Academy of Sciences, USSR,
Lutsenko, I. F., Khomutov, R. M.

TITLE: The Production of Metallic Derivatives of Vinyl Alcohol
(Polucheniye metallicheskih proizvodnykh vinilovogo spirta)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol. 120, Nr 5, pp.1049-1051
(USSR)

ABSTRACT: The most interesting characteristic feature of the α -mono-mercurated carbonyl compounds is their capacity of reacting in two directions (with respect to C and to O) and of forming 2 series of derivatives. In the first case the reaction products correspond to a direct substitution of the Hg-atom, in the second case the reaction center of the molecule is transferred since the Hg-C and C-O bonds are well developed (Refs 1-4). In the present paper the authors report on a new group of reactions investigated by them in which the reaction center is transferred as well. These reactions make possible an easy transition from C-metal derivatives of carbonyl compounds to their O-metal derivatives, especially the metal derivatives of the most simple enol - of vinyl alcohol. In order to ob-

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The Production of Metallic Derivatives of Vinyl Alcohol

tain lithium- and sodium vinylates the authors carried out experiments with the dissociation of the monomercurated acetaldehyde by means of metallic lithium and sodium into benzene and toluene which, however, failed. The authors succeeded, however, in obtaining the two vinylates in the individual state by means of the dissociation of the Hg-C bond of the aldehyde- and ketone mercury derivatives by alkali metal solutions in liquid ammonia. The obtained compounds are colorless crystalline substances. Lithium vinylate is soluble in ether and benzene, sodium vinylate, however, is not. The simple methods of synthesis of mercury-bis-acetaldehyde (Ref 5) worked out by the authors and a slight dissociation of the latter by alkali metals in liquid ammonia rendered accessible the hitherto not described most simple metal enolates. At present the authors are of the opinion that the dissociation of the Hg-C bond during an experiment in which the aldehyde- and ketone mercury salts were symmetrized by means of various complex formers passes an intermediate stage of the enolate formation. This enolate may be easily hydrolyzed in a water medium, when aldehyde or ketone, respectively, is split off.

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00700-120-5-13/67

The Production of Metallic Derivatives of Vinyl Alcohol

The Hg- bond is disrupted in the ethers of the mercaptated carboxylic acids under analogous conditions, even with potassium chloride, in order to isolate the metal derivatives of vinyl alcohol by means of an exchange reaction of the metal chloride with halogeno-organic ketalsdehyde the authors eliminated the water medium. They carried out the reaction between anhydrous ferric chloride and mercury chloride acetate in dry acetone. The composition and the structure of the ferric vinylate oxynolapide $Hg_2-ClOFe(OH)Cl$ obtained was proved by analysis and oxidizing. There are 10 references, 7 of which are soviet.

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

SUBMITTED: March 7, 1958

- 1. Alcohols (Polymerized)--Chemical reactions
- 2. Vinyl compounds--Chemical reactions
- 3. Vinyl compounds--Synthesis
- 4. Alkali metals--Chemical reactions

Card 3/3

TITLE: Polyvinyl Alcohol

AUTHORS: Nesmeyanov, A. N., Member, Academy of Sciences, USSR, SOV/20-120-6-27/59
Perévalova, E. G., Beynoravichute, Z. A., Malygina, I. L.

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

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

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Reactions of 1,1'-Dimethyl Ferrocene

SOV/20-120-6-27/59

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

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influence of the methyl groups. Moreover, the initial mixture was hydrogenized under pressure in the presence of skeleton nickel (Ref 11). 4 alkyl cyclopentanes were isolated by means of distillation. There are 13 references, 7 of which are Soviet.

SUBMITTED: March 12, 1958

1. Ferrocenes--Chemical reactions

Card 3/3

AUTHORS: Mesmeyanov, Nik. A., Reutov, O. A. 20-120-6-28/59

TITLE: Functional Derivatives of Ferrocene-1,1'-Dicarboxylic Acid
(Funktsional'nyye proizvodnyye ferrotsen-1,1'-dikarbonovoy kisloty)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol. 120, Nr 6,
pp. 1267 - 1270 (USSR)

ABSTRACT: Although the acid mentioned in the title was produced already in 1952 (Ref 1) its derivatives remained unknown with two exceptions (Refs 1,2). In the present paper the authors obtained a number of these derivatives. They are: a) the chlorine anhydride b) from the latter an amide (V) was produced, c) methyl ether of the carbamido-ferrocene-1'-carboxylic acid (VII); d) the above amides (V), and (VII) as well as the amide of ferrocene carboxylic acid can be converted into the corresponding nitriles by heating in acetic anhydride. By heating the acid (VII) at 140° for 20 minutes e) 1-cyano ferrocene-1'-carboxylic acid (VIII) formed in a yield of 55%; f) the nitrile of ferrocene-1,1'-dicarboxylic acid (IX) was obtained in a yield of 30% by heating the amide of this acid in acetic anhydride at 100° during 6 hours; g) by heating the amide of ferrocene carboxylic acid in acetic anhydride at 140° during 40 minutes the nitrile of this

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SOV/20-121-1-32/55

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

TITLE: The Synthesis of Methyl Ferrocene (Sintez metilferrotsena)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol. 121, Nr 1, pp. 117-118
(USSR)

ABSTRACT: In recent time various mono- and dialkyl ferrocenes were de-
scribed which were produced by means of a direct alkylation of
ferrocene in the presence of aluminum chloride (Refs 1-4) or
by reduction of the corresponding ketones (Ref 5) or acids
(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

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The Synthesis of Methyl Ferrocene

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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 35,5 - 36,5°. These last data are undoubted. The reasons for the mentioned divergence are explained later. There are 9 references, 6 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

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SOV/20-121-3-23/47

AUTHORS: Mesnyanov, A. N., Member, Academy of Sciences, USSR,
Kritskaya, I. I.

TITLE: Stereochemistry of σ, π -Conjugation (Stereokhimiya σ, π -sopryazheniya). α -Chloromercury Camphenilone (α -khlormerkurkamfenilon)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol. 121, Nr 3, pp. 477-480 (USSR)

ABSTRACT: At the beginning of 1950 the author mentioned first carried out exchange reactions with several factors of those atoms (or groups) which are connected with the carbon atom at the top of the bridge of a bicyclic system. (Ref 1). Several phenomena of inertia of the atom in this position are explained by Bredt's rule (Ref 3). One of these phenomena is e.g. the fact that dehydration and dehydrohaloidation at the expense of the atoms H, Hal, OH at the top of the bridge are impossible. Other phenomena, however, such as the incapability of decarboxylating β -ketonic acids with a carboxyl at the top of the bridge further the incapability to exchange camphenilone hydrogens for deuterium (even in presence of bases, Ref 4) demand already special evidence; namely that

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Stereochemistry of σ, π -Conjugation.
 α -Chloromercury Camphenilone

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the decarboxylation reaction of β -ketoic acids and the deuterio exchange in ketones undergo a stage of enolization. There is obviously no relation between the incapability of exchange of the haloid at the top of the bridge and Brett's rule. It could be explained by the necessity of the Walden inversion in the case of nucleophilic exchange. The Walden inversion, however, is impossible with the rigid system at the top of the bridge. The fact that the incapability of exchange of the atoms at the top of the bridge cannot be explained made the first author believe that the axes of σ - and π -clouds of electrons have to be parallel for a complete manifestation of the σ, π -conjugation and that the conjugation is eliminated if the axes are in vertical position to each other (Ref 1). This paper represents an example for the re-examination of this hypothesis. Correy and Sneed (Ref 5a) published (1950) a similar theory apparently without having known reference 1. α -Chloromercury camphenilone which was synthesized by the authors has a mercury atom. It is added to the carbon atom at the top of the bridge which is at the same time an α -atom in its relation to the carbonyl. This

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Stereochemistry of σ, π -Conjugation.
o-Chloromercury Camphenilone

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mercury atom has a considerable reactivity which by far exceeds that of mercury in its alkyl compounds. The authors proved that this considerable inertia of the system $\text{Hg}-\text{C}=\text{C}=\text{O}$ neither depends on the Walden inversion nor on Bredt's rule. The only remaining explanation is the elimination of the conjugation of the $\text{Hg}-\text{C}-$ and $\text{C}=\text{O}$ -bindings as a result of the vertical position of the axes of the clouds of electrons and the elimination of the possibility of penetration into each other. The regularity found in 1950 and now supported by further evidence is more comprehensive than Bredt's rule. There are 13 references, 6 of which are Soviet.

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk SSSR
(Institute of ~~Elemental Organic Compounds, AS USSR~~)

SUBMITTED: April 21, 1958

Card 3/3

AUTHORS: Nasmevanov, A. N., Member, Academy of Sciences, USSR, Pecherskaya, K. A., Akhramovich, A. N., Minakova, L. M. SOV/20-121-4-24/54

TITLE: Stereochemistry of σ, π - Conjugation (Stereokhimiya σ, π -sopryazheniya) Autooxidation of Rigid Allyl Systems (Avtookisleniye zhestkikh allil'nykh sistem)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol. 121, Nr 4, pp. 660 - 663 (USSR)

ABSTRACT: In earlier papers the authors proved (Ref 1) that in rigid (zhestkiy) bicyclic structures C — H and C — Hg- bindings on the top of the bridge of such structures, in an α -position to the carbonyl, are not activated by the carbonyl. Neither is under acid action the mercury of α -chloromercury camphenylone and of mercury-bis- α -camphenylone is substituted nor does an exchange for Hg^{203} and $HgCl_2$ take place. In camphenylone the α -hydrogen atom is neither treated with nitrous acid nor sulfonated nor brominated. The σ, π -conjugation of the system A-C-C=O is usually eliminated when the σ -axis of binding is at right angle to the π -surface.

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Stereochemistry of σ, π -Conjugation. Autooxidation
of Rigid Allyl Systems

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The aim of this paper is it to clarify if there are similar conditions for the elimination of H-C-C=C-conjugation as were proved by the authors for H-C-C=O-conjugation. For this purpose they investigated such terpene hydrocarbons with respect to their capacity of being oxidizable. In terpene hydrocarbons (thanks to a methylene bridge) the C — H-binding in α -position to the double binding seems to be spatially attached to the latter, namely bornylene (I), camphene (II) and δ -fenchene. Referring to the above mentioned these hydrocarbons are compounds with a rigid structure. It could be proved that these hydrocarbons do not absorb any oxygen after they are kept many hours at temperatures of 40, 60 and 80° in presence of such active initiators as cobalt and manganese stearates. After oxidation they were recovered from the solution in unchanged state. Under such conditions non-rigid allyl systems are easily oxidized by molecular oxygen be it in presence or absence of an initiator. This fact was experimentally proved in the case of related compounds with a non-rigid structure. Thus it could be proved by means of experiments that in the

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Stereochemistry of σ, π -Conjugation. Autooxidation
of Rigid Allyl Systems

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case of the homolytical σ, π -conjugation the influence of
the same spatial factors occurs as in heterolytical con-
jugations. There are 1 table and 15 references, 7 of which
are Soviet.

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk SSSR
(Institute of Elemental-Organic Compounds, AS USSR) Belorusskiy
gosudarstvennyy universitet im.V.I.Lenina (Belorussian State
University imeni V.I.Lenin)

SUBMITTED: April 21, 1956

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SOV/20-122-3-22/57

AUTHORS:

Nesmeyanov, A. N., Member, Academy of Sciences, USSR,
Yemel'yanova, L. I., Makarova, L. G.

TITLE:

The Synthesis of Aromatic Germanium Compounds by Means of Aryl
Diazonium Borofluorides (Sintez aromaticheskikh soyedineniy
germaniya posredstvom arildiazoniyborofloridov)

PERIODICAL:

Doklady Akademii nauk SSSR, 1958, Vol 122, Nr 3, pp 403-404
(USSR)

ABSTRACT:

The aromatic tin and lead compounds were produced by the first author and his collaborators (Ref 1). In the case of tin mainly diarylated derivatives were formed. In the case of the decomposition of double salts of tin chloride and of the aryl diazonium chlorides by metallic tin powder the best, however, not high yields (23%) were obtained if $Ar=C_6H_5$. Higher yields of diaryl dichloro stannates (up to 40%) were obtained in the case of the decomposition of the substances mentioned last in the title by zinc dust under the presence of tin chloride in acetone. For organolead compounds the decomposition of the substances mentioned last in the title by metallic lead powder furnishes the best results, (Ref 3) the same holds for a lead-sodium alloy

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The Synthesis of Aromatic Germanium Compounds by Means of Aryl Diazonium
Borofluorides

(Ref 4) in acetone. In contrast to SnCl_4 and PbCl_4 GeCl_4 forms no double salts with aryl diazonium chlorides. The substances mentioned last in the title were decomposed under the presence of GeCl_4 . Zinc dust proved to be the best reducing metal, acetone the best solvent. Monoarylated germanium compounds are formed as the result of the reaction. Under these conditions germanium does not form compounds of higher degrees of arylation. The aryl trichloro germanium varieties were isolated and analyzed as anhydrides of the aryl germanic acids. The latter form non-melting colorless powders. Anhydrides of the aryl germanic acids with $\text{Ar}=\text{C}_6\text{H}_5$, $p\text{-CH}_3\text{OC}_6\text{H}_4^-$, $p\text{-C}_2\text{H}_5\text{OC}_6\text{H}_4^-$, $p\text{-BrC}_6\text{H}_4^-$, $p\text{-ClC}_6\text{H}_4^-$ were produced. The anhydride of the phenyl germanic acid was obtained with a yield of 28% of the theoretically possible yield; the yields of other anhydrides were smaller. In a kind of experimental part (not denoted as such) the other data are given. There are 1 table and 4 references, 4 of which are Soviet.

SUBMITTED: June 11, 1958

Card 2/3

AUTHORS: ~~Neznanov, A. N.~~, Member, Academy of Sciences, USSR, Tolstaya, T. P., Isayeva, L. S. SOV/20-122-4-21/57

TITLE: The Synthesis of Aromatic Organometallic Compounds of Bismuth Via Diazocompounds (Sintez aromaticheskikh metalloorganicheskikh soyedineniy vismuta cherez diazoyedineniya)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol 122, Nr 4, pp 614 - 617 (USSR)

ABSTRACT: The synthesis of organometallic compounds by the decomposition of diazonium salts by means of metal powders (suggested by the first author, Ref 1) has hitherto been realized for the production of these compounds by means of the following metals Hg (Ref 1), Tl (Ref 2), Sn (Ref 3), Pb (Ref 4), Sb (Ref 5), and Bi (Refs 6 - 9). The authors investigated systematically the decomposition of the diarylbromonium borfluorides by metal powder and found that the results of these reactions are to a great extent similar to the results of corresponding reactions with aryl diazonium borfluorides. This experience was used in the case of the decomposition of the aryl diazonium salts as well, and the analogy was

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The Synthesis of Aromatic Organometallic Compounds
of Bismuth Via Diazocompounds

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confirmed. The decomposition of aryl diazonium borfluorides in acetone by the powder of metallic bismuth led to good yields of the tri-aryl-bismuth (30-50-70%) for various aromatic radicals. Thus were produced: triphenyl-bismuth, tri-p-tolyl-bismuth, tri-o-tolyl-bismuth, tri-p-chlorophenyl-bismuth, tri-m-tolyl-bismuth-dichloride, tri-p-bromphenyl-bismuth, tri-p-chlorphenyl-bismuth-dichloride, tri-p-carb-ethoxy-phenyl-bismuth-dichloride, tri-p-ethoxy-phenyl-bismuth, tri-m-nitro-phenyl-bismuth-dichloride, and tri-p-nitrophenyl-bismuth-dichloride. This synthesis process of the bismuth organic compounds via diazocompounds is supposed to be the best at present. Reference 13 gives a probable explanation of the reaction mechanism. There are 19 references, 11 of which are Soviet.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk
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The Synthesis of Aromatic Organometallic Compounds
of Bismuth Via Diazocompounds

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SUBMITTED: June 30, 1958

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5(3)
AUTHORS: Nesmeyanov, A. N., Academician, SOV/20-122-5-20/56
Freydlina, R. Kh., Corresponding Member, Academy of
Sciences, USSR, Belyavskiy, A. B.

TITLE: Telomerization of Ethylene With Tetrachlorethylene
(Telomerizatsiya etilena s tetrakhloretilenom)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol 122, Nr 5,
pp 821 - 824 (USSR)

ABSTRACT: Non-polymerizable chlorine olefins cannot undergo
any polymerization, but they can enter a telomerization
reaction with olefins. In this reaction the chlorine
olefins serve as carriers of the chain of reaction
and supply the final groups for the telomer molecules.
Among the reactions of this kind the ones mentioned
in the title are of interest as means of synthesis
of tetrachloralkenes capable of reaction that
contain an even number of carbon atoms in the molecule
(Scheme (1)). It can be assumed that tetrachloralkenes
produced in this manner will make possible the synthesis
of various polyfunctional compounds of the even series

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Telomerization of Ethylene With Tetrachlorethylene

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(Ref 1). The reaction mentioned in the title must lead to the synthesis in one single stage of compounds containing a trichlorovinyl group (Patent in reference 2). In the reaction performed in the presence of benzoyl peroxide at 115° and 95 atmospheres only tetrachlorohexene boiling in a wide range was isolated. For this the authors used a pressure of between 50 and 200 atmospheres with and without water. Benzoyl peroxide, tertiary butyl peroxide, bis-iso-butyric acid azo-dinitrile and azo-amino-benzene were tested as initiators. In the presence of water a high conversion of tetrachlorethylene was obtained in all cases. Peroxides were the best initiators among the ones tested. Research showed that tetrachlorethylene is a carrier of the chain of reaction which is less capable of reaction as, for instance, carbon tetrachloride and chloroform. Thus, with the first substance a conversion of only 20% was obtained and only in case of repeated addition of the initiator during reaction. In case of an increase of pressure the content of higher tetrachloralkenes in the mixture

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Telomerization of Ethylene With Tetrachlorethylene

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of reaction products increases which indicates an inertness of tetrachlorethylene. By fractioning the mixture the lower $\alpha, \alpha, \beta, \omega$ -tetrachloralkenes ($n=1.2$) could easily be isolated in their individual shapes. Higher fractions contain by-products of the reaction which could not easily be separated. Still it was possible to obtain tetrachloralkenes with 4,6 and 8 carbon atoms in the molecule and to study some of these chemical transformations. **There are 3 references, 2 of which are Soviet.**

SUBMITTED: July 5, 1958

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SMIRNOVA, N.V.; NNSMEYANOV, A.N., akademik, glavnyy red.; TOPCHIYEV, A.V.,
akademik, ~~sen. glavnyy~~ red.; PASHKOVSKIY, Yu.A., red. izd-va;
MAKOGONOVA, I.A., tekhn. red.

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A.V., akademik, zam.glavnoho red.; BEREGAUT, V.G., red.izd-va;
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otv.red.; LIKHTEINSHTEYN, Ye.S., otv.red.; SHUNKOV, V.I., otv.
red.; MEL'NIKOVA, N.B., red.izd-va

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no.14) (MIRA 13:2)
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PRUSAKOVA, T.A., tekhn.red.; POLYAKOVA, T.V., tekhn.red.

[Selected works in four volumes] Izbrannye trudy v chetyrekh tomakh.
Moskva, Izd-vo Akad.nauk SSSR. Vol.4. 1959. 527 p. (MIRA 12:12)
(Chemistry)

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A.V., akademik, zamestitel' glavnogo red.; ISAKOVA, O.V., otv.red.;
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RESMEYANOV, Aleksandr Nikolayevich, akademik; REUTOV, O.A., otv.red.toma;
TOPCHIYEV, A.V., akademik, red.; KNUNYANTS, I.L., akademik, red.;
KABACHNIK, M.I., akademik, red.; FREYDLINA, R.Kh., red.; KAN, E.I.,
red.; LOSKUTOVA, I.P., red.izd-va; POLYAKOVA, T.V., tekhn.red.

[Selected works in four volumes] Izbrannye trudy v chetyrekh tomakh.
Moskva, Izd-vo Akad.nauk SSSR. Vol.1. 1959. 712 p. (MIRA 12:12)

1. Chleny-korrespondenty AN SSSR (for Reutov, Freydlina).
(Chemistry)

NESEMYANOV, Aleksandr Nikolayevich, akademik; KABACHNIK, M.I., akademik,
~~red. tom 1; TOPCHILIN, I.V., akademik, red.;~~ LOSKUTOVA, I.P.,
red. izd-va; PRUSAKOVA, T.A., tekhn. red.

[Selected works in four volumes] Izbrannye trudy v chetyrekh
tomakh. Moskva, Izd-vo Akad. nauk SSSR. Vol. 3. 1959. 748 p.
(MIRA 12:12)

(Chemistry)

~~NESMEYANOV, Aleksandr Nikolayevich, akademik; FREYDLINA, R.Kh., otv.red.
toma; TOPCHILIN, A.V., akademik, red.; POVAROV, L.S., red.izd-va;
PRUSAKOVA, T.A., tekhn.red.; POLYAKOVA, T.V., tekhn.red.~~

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tomakh. Moskva, Izd-vo Akad.nauk SSSR. Vol.2. 1959. 782 p.
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1. Chlen-korrespondent AN SSSR (for Freydlina).
(Chemistry)

SOV/180-59-1-1/29

AUTHORS: Nesmeyanov, A.N., Topchiyev, A.V. and Blagonravov, A.A.

TITLE: To Academician Lev Dmitriyevich Shevyakov (Akademiku L'vu Dmitriyevichu Shevyakovu)

PERIODICAL: Izvestiya Akademii Nauk SSSR, Otdeleniye tekhnicheskikh nauk, Metallurgiya i toplivo, 1959, Nr 1, p 3 (USSR)

ABSTRACT: The authors, on behalf of the Prezidium Akademii nauk SSSR (Presidium of the Academy of Sciences of the USSR) and the Otdeleniye tekhnicheskikh nauk AN SSSR (Technical-sciences section, AS USSR), congratulate

Card 1/1 Shevyakov on his 70th birthday and outline his work. They mention the rewards and honours he has received.

ASSOCIATION: Academy of Sciences of the USSR

21(0)
AUTHORS: Nesmeyanov, A. N., Academician, Tamm, I. Ye., Academician,
Nobel Prize Winner

SOV/29-59-1-3/26

TITLE: Academicians on the Future of Thermonuclear Energy (Akademiki
o budushchem termoyadernoy energii)

PERIODICAL: Tekhnika molodezhi, 1959, Nr 1, pp 4 - 4 (USSR)

ABSTRACT: Academician A. N. Nesmeyanov: Soviet scientists advance
successfully on the way towards domination of the thermo-
nuclear synthesis and the utilization of thermonuclear energy.
These are problems the solution of which will provide man-
kind with a source of energy to an unlimited extent and for
all times to come.
Academician I. Ye. Tamm, Nobel Prize winner: Methods rendering
possible the domination of thermonuclear energy are already
clarified in principle. But for the time being it cannot be
estimated how much time, work and invention will be necessary
to overcome serious difficulties on the way towards practical
utilization of these principles. I have no doubt that in the
long run the thermonuclear reaction will be the basis for
power economy. The sources of thermonuclear fuels is virtually

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Academicians on the Future of Thermonuclear Energy

SOV/29-59-1-3/26

inexhaustible in sea water, for instance, unlike uranium, thorium, and the like. Their wide distribution excludes any struggle among nations for their deposits. The very serious problems actually arising in connection with the harmful effect of radioactive waste in modern reactors will substantially lose their importance with the use of thermonuclear reactors. There are 2 figures.

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SOV/107-59-1-3/51
AUTHORS: Nesmeyanov, A.N., and Kotl'nikov, V.A., Academicians
TITLE: Soviet Scientists Speak (Govoryat sovetskiye uchenyye)
PERIODICAL: Radio, 1959, Nr 1, p 6 (USSR)
ABSTRACT: The authors state that the flight of an interplanetary rocket towards the moon is proceeding according to a program calculated with the aid of electronic computers. The rocket concerned has a useful pay load of more than 360 kg.

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5(3)

SOV/62-59-1-8/38

AUTHORS: Nesmeyanov, A. N., Reutov, O. A., Loseva, A. S.,
Khorlina, M. Ya.

TITLE: Synthesis of Organo-Mercury Compounds From Hydrazones
(Sintez rtutnoorganicheskikh soyedineniy iz gidrazonov)
Communication 2. Interaction of Hydrazones of the Aldehydes
and Ketones of the Alicyclic and Aromatic Series With
Mercury (II) Acetate (Soobshcheniye 2. Vzaimodeystviye gidra-
zonov al'degidov i ketonov alitsiklicheskogo i aromatches-
kogo ryadov s uksusnokisloy rtut'yu)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,
1959, Nr 1, pp 50 - 61 (USSR)

ABSTRACT: In the present paper the authors have shown that the hydra-
zones of aldehydes and ketones of the alicyclic and aromatic
series (hydrazones of cyclohexanone, 4-methyl cyclohexanone,
cyclopentanone, camphor, benzophenone and o-nitro-benzalde-
hyde) react with mercury (II) acetate in water, methanol
and absolute benzene and separate nitrogen, mercury (I)
acetate and metallic mercury, and form organo-mercury com-
pounds. In most cases the reaction under the action of

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Synthesis of Organo-Mercury Compounds From Hydrazones. SOV/62-59-1-8/38
Communication 2. Interaction of Hydrazones of the Aldehydes and Ketones
of the Alicyclic and Aromatic Series With Mercury (II) Acetate

the solvent takes place in the way mentioned in Ref 1 .
The reaction of hydrazones of cyclohexanone and 4-methyl
cyclohexanone with mercury (II) acetate in water and in
the presence of catalytic quantities of copper acetate is
very peculiar. As a result of this interaction organo-
mercury compounds with a double bond are formed. Organo-
mercury compounds are listed in the table which were
synthesized by way of hydrazones of the alicyclic and aro-
matic series. The structure of the organo-mercury compounds
obtained was confirmed by decomposition with concentrated
alkali or concentrated hydrochloric acid (Ref 1). The
hydrazones used in this paper were synthesized according to
methods already described: hydrazone of cyclohexanone
(Ref 2), of 4-methyl cyclohexanone (Ref 3), of camphor
(Ref 4), of benzophenone (Ref 5) and o-nitro-benzaldehyde
(Ref 6). There are 1 table and 14 references, 2 of which
are Soviet.

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Synthesis of Organo-Mercury Compounds From Hydrazones. SOV/62-59-1-8/38
Communication 2. Interaction of Hydrazones of the Aldehydes and Ketones
of the Alicyclic and Aromatic Series With Mercury (II) Acetate

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

SUBMITTED: April 8, 1957

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SOV/62-59-1-28/38

5(3)

AUTHORS:

Nesmeyanov, A. N., Sazonova, V. A., Drozd, V. N.

TITLE:

Organo-Boron Heterocyclic Compounds (Bororganicheskiye geterotsiklicheskiye soyedineniya)

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 1, pp 163 - 166 (USSR)

ABSTRACT:

In the present communication the authors report that the reaction $RMgX$ with potassium fluoborate earlier investigated (Ref 2) was extended to oxygen-containing heterocyclic compounds (furan, sylvan) and triheterocyclyl boron compounds in the form of complexes were synthesized with pyridine. Tetra-(2-furyl) and tetra-5(2-methylfuryl)boron anions were obtained in the form of different salts. The presence of furan and sylvan nuclei in these anions was confirmed by decomposition of organo-boron compounds with alkali. Therein 2-chloro-mercuri furan and 2-methyl-5-chloro-mercuri furan were formed. Tetra-5-(2-methylfuryl)boron potassium separates ions of cesium, rubidium and quaternary ammonium salts. Pyridine salts of the type

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$$[C_5H_5NH^+]B^-Ar_4$$
 proved to be appropriate for the transition to

Organo-Boron Heterocyclic Compounds

SOV/62-59-1-28/38

triheterocyclyl boron compounds. The heating of pyridine salts in alcohol is sufficient for the synthesis of tri-substituted boron compounds in the form of pyridinates. In an exchange reaction between tetra-(2-selenyl)boron potassium and pyridine chlorine hydrate the pyridinate of triselenyl boron is immediately formed. There are 2 references, 1 of which is Soviet.

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

SUBMITTED: May 30, 1958

Card 2/2

5(3)

AUTHORS:

Nesmeyanov, A. N., Borisov, A. Ye.,
~~Nevikova, N. V.~~

SOV/62-59-2-11/40

TITLE:

Exchange Reactions of the Isopropenyl Compounds of Mercury,
Thallium and Tin (Reaktsii obmena izopropenil'nykh
soyedineniy rtuti, talliya i olova)

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,
1959, Nr 2, pp 259-262 (USSR)

ABSTRACT:

In the present paper the reactions of the double exchange of isopropenyl compounds of mercury and thallium as previously described (Ref 1) with salts of heavy metals were investigated. On fusion of diisopropenyl thallium bromide with tin bromide at 200-220° the diisopropenyl tin dibromide with a melting point of 100-101° was obtained. This readily reacts with mercury bromide and forms isopropenyl mercury bromide. This yields in alkali diisopropenyl mercury. In acetone this reaction proceeds in a more complex manner. It essentially resembles one of the variations of the interaction of symmetric organic mercury compounds with stannous salts. From the reaction products of diisopropenyl mercury with thallium tribromide at room temperature in ether the diisopropenyl

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Exchange Reactions of the Isopropenyl Compounds
of Mercury, Thallium and Tin

SOV/62-59-2-11/40

thallium bromide was obtained. This is decomposed at 190-194°. The interaction of diisopropenyl mercury with tin dibromide yields in various solvents isopropenyl mercury bromide, diisopropenyl tin dibromide, tetraisopropenyl tin and metallic mercury. There are 3 Soviet references.

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

SUBMITTED: May 24, 1957

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5(3)

AUTHORS:

~~Nesmeyanov, A. N.~~, Borisov, A. Ye.,
Novikova, N. V., Osipova, M. A.

SOV/62-59-2-12/40

TITLE:

Synthesis of Organo-Tin Compounds From Organomercurials and Stannous Salts in Inert Solvents (Sintez olovoorganicheskikh soyedineniy iz rtutnoorganicheskikh soyedineniy i soley dvalentnogo olova v inertnykh rastvoritelyakh)

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 2, pp 263-266 (USSR)

ABSTRACT:

In the present paper the interaction of organomercurials with stannous salts in an inert solvent not containing any mobile hydrogen atom was investigated. It was proved that in this connection no side reaction takes place in which $(RO)_2SnX_2$ is formed such as with the application of alcohol and acetone as solvent. From the reaction of dipropenyl mercury with stannous bromide dipropenyl tin was obtained. In the case of diisopropenyl mercury, diisopropenyl tin dibromide, tetraisopropenyl tin and isopropenyl mercury bromide were precipitated. The reaction of diphenyl mercury, di-p- and di-o-toluene mercury, di- α -naphthyl mercury and

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Synthesis of Organo-Tin Compounds From Organo-
mercurials and Stannous Salts in Inert Solvents

SOV/62-59-2-12/40

diethyl mercury with stannous chloride as well as diphenyl
mercury with stannous bromide yielded normal reaction products.
There are 3 Soviet references.

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

SUBMITTED: May 24, 1957

Card 2/2

Н. Е. Смирнов, А. М.

2(0)
AUTHOR: Shcherbakov, E. M., Deputy Chairman of the Organization Committee of the VIII Mendeleev Congress, Corresponding Member of the AS USSR

TITLE: VIII. Mendeleev Congress of General and Applied Chemistry (VIII. Mendeleevskiy s'ezd po obshchey i prikladnoy khimii)

ETHNICAL: Khimicheskaya promyshlennost', 1959, Nr 4, 99 1-10 (USSR)

ABSTRACT: From March 16 to 25, 1959, the eighth traditional congress of Russian chemists took place in Moscow. The congress was organized by the Academy of Sciences of the USSR, by the Vsesoyuznyy Khimicheskoye Obshchestvo (USSR Chemical Society) and the All-Union Chemicalists Society (All-Union Chemicalists Society, Ministry of Chemical Industry) and by the Council of Ministers of the USSR of Chemistry and by the Ministerstvo vyzhshchego obrasovaniya SSR (Ministry of Higher Education of the USSR).

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... contribution of the Chairman of the State Committee of the Council of Ministers of the USSR of Chemistry E. M. Shcherbakov given about the "Problems of Scientific Technical Progress of the Chemical Industry" and by the Academician G. I. Zhuravskiy on the "Fundamental Problems of the Polymer Chemistry". In the plenary meetings the following contributions were given: Academician A. I. Zhuravskiy - "The Periodic System of the Elements of D. I. Mendeleev and Organic Chemistry"; Academician K. L. Sasnov - "Fundamental Problems of Chemical Kinetics"; Academician I. I. Priglas - "Modern State of the Periodic System of D. I. Mendeleev"; Academician A. F. Konovalov - "Fundamental Problems of Radiochemistry"; Academician V. A. Engel'gryn - "Fundamental Problems of Biochemistry"; Academician G. G. Sokolov - "Chemical Problems of the Agriculture of the USSR"; Director of the Institute of Scientific Research Institute of Chemical Machine Construction (I. V. Eklolov) - "Main Problems of the Chemical Apparatus and Machine Construction"; Corresponding Member of the AS USSR I. F. Svirkin - "Present State of the Periodic System of Elements"; Academician A. P. Aleksandrov - "Chemical Aspects in the Application of Atomic Energy"; Director of the Institute of Chemistry of the Academy of Sciences of the Chinese People's Republic - "State of the Periodic System of the Elements in the Chinese People's Republic"; K. K. Kuznetsov, Russian scientist, Chinese People's Republic of the "Chemistry of Cyclic Compounds"; Academician I. Zhuravskiy - "Kinetics of the Hydrolysis of the Crystalline Hydrates"; Academician E. E. Eklolov - "Investigation of the Structure of Some Macromolecules by Means of Radioactive Isotopes"; Academician G. G. Sokolov - "Main Problems of the Chemical Apparatus and Machine Construction"; F. K. Kuznetsov - "Quantitative Ratio in Frontal Gas Chromatography"; E. E. Eklolov, Professor of the London University - "Interaction with Respect to Nitrogen and Oxygen"; R. P. Hall, President of the Faraday Society and Professor at Oxford University - "The Tunnel Effect in Reactions with the Action of Hydrogen Isotopes"; Academician A. P. Aleksandrov - "Chemical Aspects of the Kinetics of the Nitration Process";

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SOV/30-59-4-2/51

AUTHOR: Nesmeyanov, A. N.

TITLE: The Opening Address of the President of the Academy of Sciences of the USSR, Academician A. N. Nesmeyanov (Vstupitel'noye slovo Prezidenta Akademii nauk SSSR akademika A. N. Nesmeyanova)

PERIODICAL: Vestnik Akademii nauk SSSR, 1959, Nr 4, pp 5-9 (USSR)

ABSTRACT: Since the Plenary Meeting of 1958 the following Members of the Academy of Sciences USSR have died: the following Corresponding Members, Academy of Sciences, USSR: V. Z. Vlastov, expert in the field of mechanics; N. S. Koshlyakov, mathematician; A. D. Udalt'sev, historian; S. I. Arkhangel'skiy, historian; N. N. Slavyanov, hydrogeologist; O. N. Podvyat'skaya, dermatologist; S. D. L'vov, plant physiologist; V. A. Prakhonskiy, hydrogeologist and geologist; the Academicians: S. N. Sergeev Tsenskiy, writer; L. A. Orbeli, physiologist. The permanent staff of the scientific institutions of the AS USSR increased by 45.7% from January 1st, 1956 until January 1st, 1959 and amounts at present to 165 Academicians and 353 Corresponding Members, Academy of Sciences, USSR. In the course of the past years more than 4000 young experts were admitted to the AS USSR. among them were 3360 with university education. 922 persons

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SOV/50-59-4-2/81

The Opening Address of the President of the Academy of Sciences of the USSR,
Academician A. N. Nesmeyanov

were awarded the degree of a "Senior Scientific Worker".
Members of the Academy defended 132 Doctors' and Candidates' dissertations. During the past three years the AS USSR has quantitatively and qualitatively very much developed. Among other things, in the field of physical and mathematical sciences 11 new institutes were founded, in the field of chemical sciences 11 new institutions, in the field of biological sciences 8 institutes as well as many others. On January 1st, 1959 all scientific institutions, including the branches, comprised 136 institutes, 25 independent laboratories, sections, scientific councils, 13 institute departments as well as a large number of scientific research stations, botanical gardens, museums, and expedition bases. The financial means of the AS USSR covered by the budget increased considerably. The lack of workrooms is, however, still an unsolved problem in spite of the considerable monetary aid by the Government. The number of scientific works published has highly increased as well. In conclusion, A. N. Nesmeyanov states that in the past everything has been done to promote the quantitative development of the Academy; this principle will be maintained in future. Now,

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SOV/30-59-4-2/51

The Opening Address of the President of the Academy of Sciences of the USSR,
Academician A. N. Nesmeyanov

~~when~~ the Academy has grown so important, it is its main task
to use the results of science for the benefit of the country,
economy and civilization to a continuously increasing extent.

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5(3)

SOV/62-59-4-11/42

AUTHORS:

Nesmeyanov, A. N., Borisov, A. Ye., Novikova, N. V.

TITLE:

On the Possibility of a Synthesis of Organic Tin Compounds by the Reduction of Organic Thallium Compounds With Salts of Divalent Tin (O vozmozhnosti sinteza olovoorganicheskikh soyedineniy vosstanovleniyem talliyorganicheskikh soyedineniy solyami divalentnogo olova)

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 4, pp 644-646 (USSR)

ABSTRACT:

In the present work the interaction of cis- and trans-di-propenylthallium bromide, diisopropenylthallium bromide, di- α -naphthylthallium bromide with tin bromide and the interaction of diphenylthallium chloride and di-p-tolylthallium chloride with tin chloride upon heating of the reaction products ground to a powder, without solvents, was investigated. The yield of reaction products was between 50% and 85%. A stereo isomer mixture of dipropenyl tin bromide, diisopropenyl tin dibromide, diphenyl tin dichloride, di-p-tolyl tin dichloride and di- α -naphthyl tin dibromide appears to have thus been obtained. This reaction was also investigated in various solvents. A re-

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SOV/62-59-4-11/42

On the Possibility of a Synthesis of Organic Tin Compounds by the Reduction of Organic Thallium Compounds With Salts of Divalent Tin

action of diisopropenyl thallium bromide with tin bromide in acetone can be effected only with difficulty. It does not react in benzene and ligroin solutions even when heated. On the other hand, cis-cis-dipropenyl thallium bromide reacts with tin bromide in benzene at 50° to form diproponyl tin dibromide and thallium dibromide. This reaction is similar to the reaction investigated (Ref 3) between organo-mercury compounds and divalent tin salts and is effected with relative ease. This reaction can be used as a method of synthesizing organic tin compounds of the type R_2SnX_2 . There are 6 references, 4 of which are Soviet.

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

SUBMITTED: July 12, 1957

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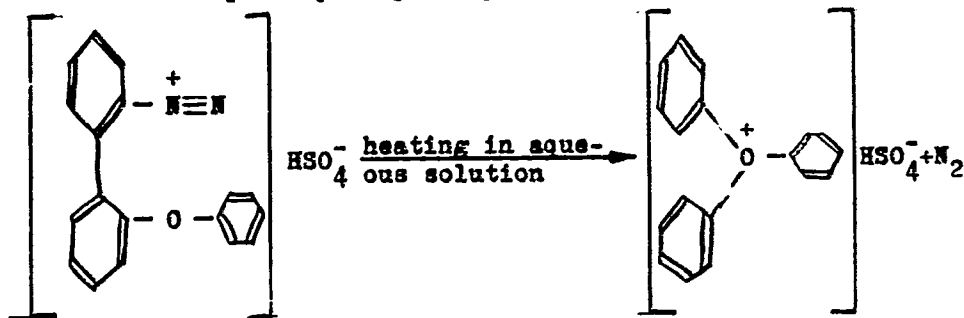
SOV/62-59-4-12/42

AUTHORS: Nesmeyanov, A. N., Tolstaya, T. P.

TITLE: Salts of o,o'-Diphenylene Phenyl Oxonium (Sol'i o,o'-difenilen-feniloksoniya)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 4, pp 647-651 (USSR)

ABSTRACT: In the present work the o,o'-diphenylene phenyl oxonium sulphate has been synthesized for the first time, by heating the aqueous solution of o-phenoxy-o'-phenoxy-diazonium sulphate:



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Salts of o,o'-Diphenylene Phenyl Oxonium

SOV/62-59-4-12/42

By an exchange reaction a number of salts of this cation have been obtained: picrate, rhodanide, trichromate, borofluoride, tetraphenyl borate, chloroplatinate, ferric cyanide, ferrous cyanide, nitroprusside, permanganate and iodide. All oxonium salts are difficultly soluble in water. They have been obtained by an addition of aqueous inorganic salt solutions to the above-mentioned oxonium sulphate solution. The thermal decomposition of o,o'-diphenylene phenyl oxonium iodide causes a breaking of the cycle and the formation of o-phenoxy-o'-iodide diphenyl. This is considered a proof of the structure of the salts described. There are 1 figure and 9 references, 4 of which are Soviet.

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

SUBMITTED: July 16, 1957

Card 2/2

5(3)
AUTHORS: Freydlina, R. Kh., Semenov, N. A., Nesmeyanov, A. N. SOV/62-59-4-13/42

TITLE: Synthesis of Aromatic Compounds of the Types $\text{ArCH}_2\text{CH}=\text{CCl}_2$ and $\text{Ar}'(\text{CH}_2\text{CH}=\text{CCl}_2)_2$ (Sintez aromaticheskikh soyedineniy tipa $\text{ArCH}_2\text{CH}=\text{CCl}_2$ i $\text{Ar}'(\text{CH}_2\text{CH}=\text{CCl}_2)_2$)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 4, pp 652-656 (USSR)

ABSTRACT: It has already been shown (Refs 1 and 2) that 1,1,1-trichloropropene and 1,1,3-trichloropropene-1 condense with benzene and some other aromatics in the presence of aluminum chloride to form compounds having the structure $\text{ArCH}_2\text{CH}=\text{CCl}_2$. In the present work the synthesis of substances of this type was continued and some of their conversions were investigated. In addition, aromatic compounds containing γ,γ -dichloroallyl groups were synthesized. As the condensation in the presence of aluminum chloride is very violent and accompanied by saponification it was attempted to effect the reaction in the presence of other Friedel-Crafts catalysts (SnCl_4 , ZnCl_2 , SbCl_5). The reaction

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SOV/62-59-4-13/42

Synthesis of Aromatic Compounds of the Types $\text{ArCH}_2\text{CH}=\text{CCl}_2$ and $\text{Ar}'(\text{CH}_2\text{CH}=\text{CCl}_2)_2$

was found to proceed smoothly in the presence of antimony pentachloride. The process can be controlled and the reaction mixture is homogeneous. The condensation of 1,1,3-trichloropropene-1 with toluene in the presence of SbCl_5 gave 3-(p-toluene)-1,1-dichloropropene-1 in a yield of 80%. The introduction of two γ,γ -dichloroallyl groups into the aromatic nucleus takes place in one or two stages. The interaction of equimolar quantities of naphthalene and 1,1,3-trichloropropene-1 in heptane in the presence of aluminum chloride or tin chloride gives mixtures of mono- or dialkylated products. The condensation of 3-(p-chlorophenyl)-1,1-dichloropropene-1 with 1,1,3-trichloropropene-1 in the presence of aluminum chloride gave a compound of the composition $\text{ClC}_6\text{H}_3(\text{CH}_2\text{CH}=\text{CCl}_2)_2$. The interaction of 3-phenyl-1,1,1,2-tetrachloropropane with 1,1,3-trichloropropane in the presence of SbCl_5 gave a compound $\text{p-CCl}_2=\text{CHCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{CHClCCl}_3$. Its structure was proved by oxidation. The interaction of benzene with 1,1,1,3-tetrachloropropane in the presence of SbCl_5 gave 3-phenyl-1,1-dichloro-

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Synthesis of Aromatic Compounds of the Types $\text{ArCH}_2\text{CH}=\text{CCl}_2$ and $\text{Ar}'(\text{CH}_2\text{CH}=\text{CCl}_2)_2$

propene-1 and 3-(p-phenylene)-bis-1,1-dichloropropene-1. The oxidation of 3-(p-chlorophenyl)-1,1-dichloropropene-1 with aqueous nitrogenous acid gave p-chlorocinnamic acid. There are 7 references, 6 of which are Soviet.

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

SUBMITTED: July 13, 1957 (initially) and April 14, 1958 (after revision)

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5(3)

SOV/62-59-4-14/42

AUTHORS:

Nesmeyanov, A. N., Freydlina, R. Kh., Petrova, R. G.,
Terent'yev, A. B.

TITLE:

Interaction of 1,1,1-Trichloropropene With Sulphene Chlorides
and Sulphur Dichloride (Vzaimodeystviye 1,1,1-trikhlorpropena s
sul'fenkhloridami i dvukhloristoy seroy)

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,
1959, Nr 4, pp 657-662 (USSR)

ABSTRACT:

In the present work the addition of phenyl-, benzil-, 2,4-di-
nitrophenyl-, 2-nitrophenyl sulphene chloride and sulphur di-
chloride to 1,1,1-trichloropropene was investigated. The addi-
tion of phenyl sulphene chloride to 1,1,1-trichloropropene gave
1,1,1,3-tetrachloroisopropylphenylsulphide as the main product.
The dehydrochlorination of 1,1,1,3-tetrachloroiso propyl phenyl
sulphide with alkali in ethyl Cellosolve gives a mixture the
composition of which depends mainly on the reaction conditions.
The investigation of the reactions of other sulphene chlorides
shows that 2,4-dinitro- and 2-nitrophenyl sulphene chlorides do
not associate with 1,1,1-trichloropropene under the assumed
conditions. The reaction of 1,1,1-trichloropropene with benzil

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Interaction of 1,1,1-Trichloropropene With Sulphene Chlorides and Sulphur Dichloride

sulphene chloride is more complicated and forms mainly a dehydrochlorinated adduct. The consideration of the reaction of 1,1,1-trichloropropene with sulphur dichloride, 2,4-dinitro- and 2-nitrophenyl sulphene chloride shows a similarity between the action of the $-CCl_3$ group having no double bond on the next double bond and the action of other acceptor groups having π -bonds. Sulphur dichloride reacts with 1,1,1-trichloropropene to form 1,1,1,3-tetrachloroisopropyl sulphene chloride. There are 6 references, 4 of which are Soviet.

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

SUBMITTED: July 13, 1957

Card 2/2

54(3)

AUTHORS:

Freydlina, R. Kh., Kost, V. N.,
Vasil'yeva, T. T., Nesmeyanov, A. N.

SOV/62-59-5-10/40

TITLE:

Synthesis of D,L- α -aminocarboxylic Acids From Compounds Con-
taining the $\text{CCl}_2=\text{CH}$ Group (Sintez D,L- α -aminokarbovoykh kislot
iz soyedineniy soderzhashchikh $\text{CCl}_2=\text{CH}$ -gruppu)

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,
1959, Nr 5, pp 826 - 830 (USSR)

ABSTRACT:

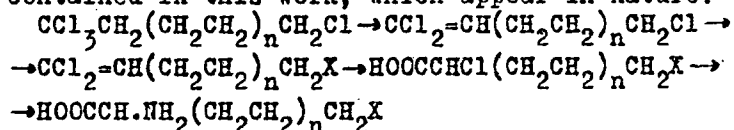
In this work the ammonolysis of some α -chlorocarboxylic acids was investigated which had been synthesized from tetrachloroalkanes by the effect of sulfuric acid or acetic acid in the presence of mercury acetate. This investigation was carried out in order to find a way of synthesizing amino acids and their analogues appearing in nature from tetrachloroalkanes. The synthesis is rather difficult and, in the case of chlorine derivatives, the yield is small according to data from publications. Two authors of this work and Petrov (Ref 7) succeeded in synthesizing D,L-proline and D,L-ornithine from α,δ -dichloro- and α -chloro- δ -phthalimidovalerianic acid; they showed that the yield does not depend on the nature of the halogen in α -position. In this work the initial products α -chlorodipinic, α -

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Synthesis of D,L- α -aminocarboxylic Acids From
Compounds Containing the $\text{CCl}_2=\text{CH}$ Group

SOV/62-59-5-10/40

chloropimelic, and α -chlorosuberic acid were obtained (Ref 2); α -chloroglutaric acid and α -chloro- β -(p-chlorophenyl)propionic acid (Ref 8) and α -chloro- ϵ -phthalimido-hexanic acid were obtained under the same conditions from 1,1-dichloro-6-phthalimido-hexene-1 and 1,1-dichloro-3-(p-chlorophenyl propene. The best method was that of the synthesis of α -chloro- β -phenylpropionic acid from chlorophenyldiazonium and acrylonitrile according to the Merrwein reaction (Ref 10) with subsequent hydrolysis of nitrile of α -chloro- β -phenylpropionic acid. Starting from the $\alpha,\alpha,\alpha,\omega$ -tetrachloroalkane mentioned, the following scheme is valid for the synthesis of the α -amino acids (phenylalaline, p-chlorophenylalanine, glutamic acid, α -amino-adipic acid, α -aminopimelic acid, α -aminosuberic acid, and lysine) contained in this work, which appear in nature:



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$n = 0, 1, 2, \dots$; $X = \text{C}_6\text{H}_5, \text{ClC}_6\text{H}_4, \text{COOH}, \text{C}_2\text{H}_2\text{COOH}, \text{C}_5\text{H}_4(\text{CO})_2\text{N}$

Synthesis of D,L- α -aminocarboxylic Acids From
Compounds Containing the $\text{CCl}_2\text{-CH}$ Group

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It was also shown that the synthesis of α -chloro- β -phenylpropionic acid can be carried out by the effect of chlorine on 1,1-dichloro-3-phenylpropene-1 in a formic acid medium with a yield of 63% of the theoretical yield, that is, without addition of mercury salts if anhydrous formic acid is used. There are 19 references, 10 of which are Soviet.

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

SUBMITTED: August 2, 1957

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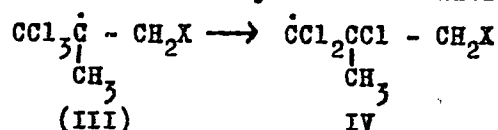
5 (3)

AUTHORS: Nesmeyanov, A. N., Freydina, R. Kh., SOV/62-59-6-12/36
Belyavskiy, A. B.

TITLE: Hetero- and Homolytical Rearrangements in the Chemical Transformation of 1,1,1-Trichloro-2-methylpropene (Getero- i gomoliticheskiye peregruppirovki pri khimicheskikh prevrashcheniyakh 1,1,1-trikhlor-2-metilpropena)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 6, pp 1028 - 1033 (USSR)

ABSTRACT: The addition of HBr to 1,1,1-trichloro-2-methylpropene in the presence of benzoyl peroxide was investigated. Two isomers are formed at the homolytical affiliation:



In the case of the electrophilic affiliation in an acetic acid medium an affiliation must have occurred because of the strongly inducing effect of the CCl_3 -group though this is in contra-

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