KOCHESHKOV, K.A.

Studies in the field of organolithium compounds. Probl. fiz.khim. no.1:156-163 '58. (MIRA 15:11)

1. Laboratoriya sinteza i stroyeniya metallorganicheskikh soyedineniy Nauchno-issledovatel'skogo fiziko-khimicheskogo instituta im. Karpova.
(Lithium organic compounds)

SOV/48-22-9-27/40

AUTHORS: Rodionov, A. N., Shigorin, D. N., Talalayeva, T. V., Kocheshkov, K. A.

TITLE: Infrared Absorption Spectra of Organolithium Compounds (Infrakrasnyye spektry pogloshcheniya litiyorganicheskikh soyedineniy) Intermolecular Lithium Binding (Mezhmolekulyarnaya litiyevaya svyaz')

PERIODICAL: Izvestiya Akademii nauk SSSR. Seriya fizicheskaya, 1958, Vol 22, Nr 9, pp 1110 - 1113 (USSR)

ABSTRACT: In this paper a report is given on the discovery and the investigation of the intermolecular lithium binding $-\overset{-\delta}{C} - \overset{+\delta}{Li} \ldots \overset{-\delta}{C} - \overset{+\delta}{Li} \ldots$ and $-\overset{-\delta}{O} - \overset{+\delta}{Li} \ldots \overset{-\delta}{O} - \overset{+\delta}{Li} \ldots$ which were based upon the study of the infrared spectra of compounds of the type R - Li and R - O - Li. The intermolecular lithium binding $-\overset{+\delta}{Li} \ldots \overset{-\delta}{C} -$ must be granted special importance because it can be formed without cooperation of the acceptor-donor interaction. The required compounds were synthetized and purified according to the method developed by Kocheshkov et al. (Refs 9,10). The spectra

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were recorded of vapors, solutions and powder in vaseline oil (Figs 1,2). A comparison of the spectra and the analysis of the nature of the oscillation of the molecules permit to determine the frequencies of the valence oscillations of free and of C-Li groups taking part in the formation of the lithium binding (Table 2). The intermolecular lithium binding $-\overset{-\delta}{C} \ldots \overset{+\delta}{Li}$ - is stable ($\frac{\Delta\nu}{\nu_0}$ = 12 - 19%) notwithstanding the fact that it is produced without cooperation of the acceptor-donor interaction. Even more stable is the binding $\overset{+\delta}{Li} \ldots \overset{-\delta}{O}$ -. As was mentioned before, the $-\overset{+\delta}{Li} \ldots \overset{-\delta}{C}-$ binding is formed without the cooperation of the acceptor-donor interaction. in this connection the problem of the nature of this bond arises. It is known that the electrostatic interaction is unable to explain completely the formation and the properties of such molecular compounds. The explanation of this phenomenon can probably be sought in the particular

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nature of the lithium atoms. It is possible that in the case under review the nature of the lithium bond can principally be explained by the immediate interaction of the electron from the lithium atom, which is in a p-state together with the "free part of the electron density" of the carbon atom and partly also by the dipole interaction. There are 2 figures, 2 tables, and 14 references, 11 of which are Soviet.

ASSOCIATION: Fiziko-khimicheskiy institut im.L.Ya.Karpova (Institute of Physical Chemistry imeni L.Ya.Karpov)

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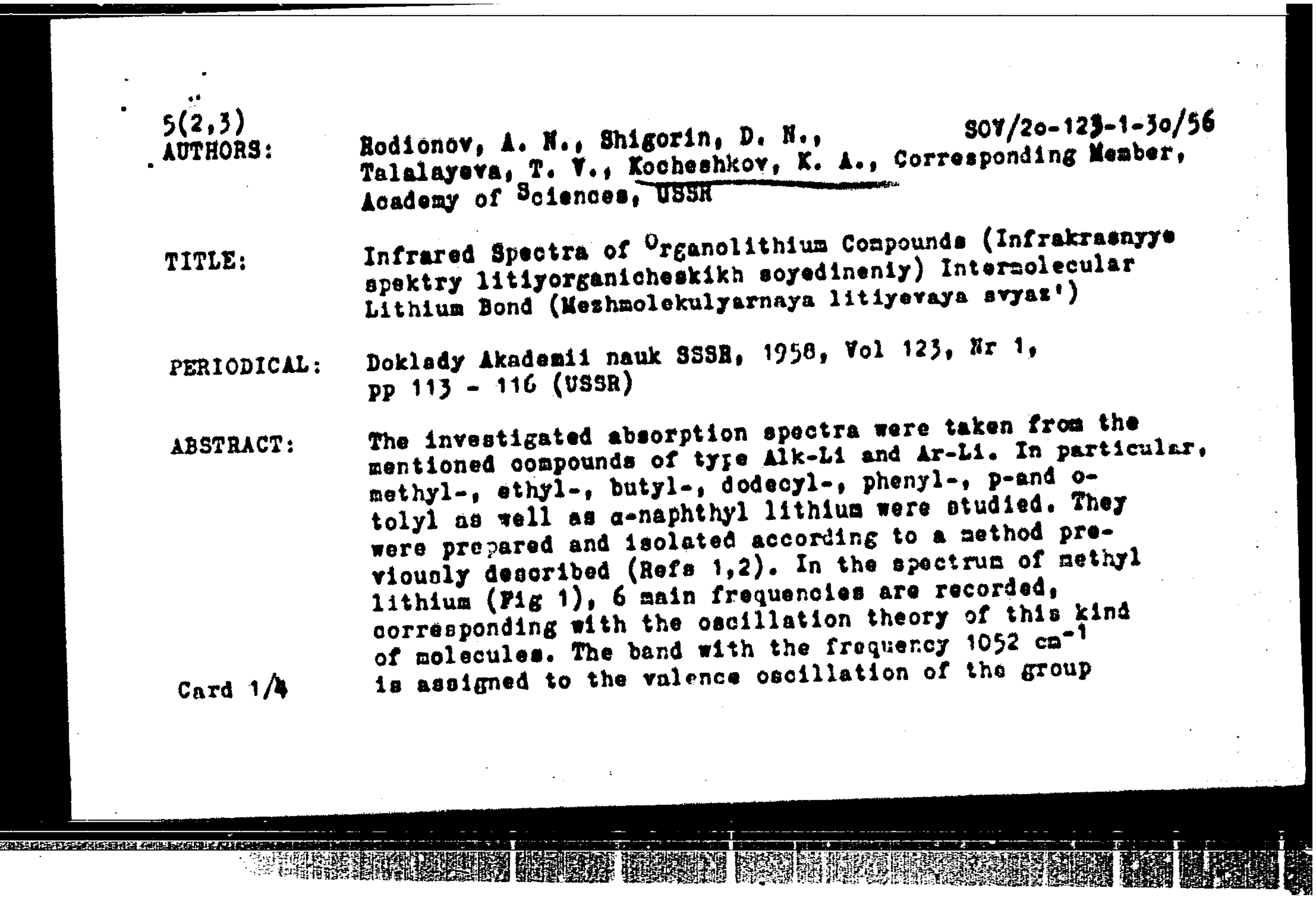

5(2,3)

SOV/20-123-1-30/56

AUTHORS: Rodionov, A. N., Shigorin, D. N., Talalayeva, T. V., Kocheshkov, K. A., Corresponding Member, Academy of Sciences, USSR

TITLE: Infrared Spectra of Organolithium Compounds (Infrakrasnyye spektry litiyorganicheskikh soyedineniy) Intermolecular Lithium Bond (Mezhmolekulyarnaya litiyevaya svyaz')

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol 123, Nr 1, pp 113 - 116 (USSR)

ABSTRACT: The investigated absorption spectra were taken from the mentioned compounds of type Alk-Li and Ar-Li. In particular, methyl-, ethyl-, butyl-, dodecyl-, phenyl-, p-and o-tolyl as well as α-naphthyl lithium were studied. They were prepared and isolated according to a method previously described (Refs 1,2). In the spectrum of methyl lithium (Fig 1), 6 main frequencies are recorded, corresponding with the oscillation theory of this kind of molecules. The band with the frequency 1052 cm^{-1} is assigned to the valence oscillation of the group

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$\overset{-\delta}{C} - \overset{+\delta}{Li}$. The accuracy of this assignment is in accordance with the spectral analysis of ethyl-, butyl-, and dodecyl lithium. Thus, the frequency of the valence oscillation, being ∼1050 cm^{-1}, is specific for the respective series of compounds. Further proof of this fact is presented. The variation of the mentioned frequency of the C-Li group on the transition from the vaporous state to the solid and to solutions is apparently related to the fact that the C-Li groups in crystals and solutions take part in some intermolecular reactions. This in particular is shifting the C-Li-band in the direction of the long waves. Thus, the spectra show definitely that the molecules of the organolithium compounds in crystals and solutions are associated under complex formation (in conformity with the references 3-8). If in the crystals the existence of chains is possible, in solutions with non-polar solvents the formation of associates under reduction of the entire dipole interaction is more favorable. This can be attained by

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the formation of various cycles as well as by variation of character and length of the chain. It is possible that different types of associates are existing in the solutions which are passing into one another on dilution, heating and under the influence of light in an atmosphere of nitrogen(in accordance with the results of cryoscopy ,References 4, 6-8). In the solutions of ethyl lithium in hexane, cyclohexane, and cyclohexene the portion of those molecules which do not take part in the association is larger than the portion of molecules associated . The type of association in the mentioned solvents is different from that in aromatic hydrocarbons. The spectra are given in figure 3. Extent and character of association of the molecules R-Li have to depend in the respective solutions to a considerable extent upon the length of the carbon chain. With a prolongation of the chain the probability of the formation of cyclic associates might decrease, whereas the possibility of a formation of the linear complexes must increase.

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An exception is methyl lithium. Apparently, the variation of the character and degree of association of the R-Li molecules greatly affects the dipole moment, according to the nature of the compound, the concentration and the temperature. It can be assumed that the dipole moment of ethyl lithium is approaching the dipole moment of a free molecule in dilute hexane solutions (as confirmed by common studies with V.N. Vasil'yeva). The authors have found that benzene does not participate directly in the association of ethyl lithium. According to the results the authors concluded that associations of organolithium compounds by an intermolecular lithium linkage are existing. Finally, cases of such interactions are discussed. There are 3 figures and 10 references, 3 of which are Soviet.

SUBMITTED: July 5, 1958

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SOV/20-123-2-24/50

5(2), 5(4)

AUTHORS: Panov, Ye. M., Kocheshkov, K. A., Corresponding Member, AS USSR

TITLE: The Reaction of Direct Lead Introduction (Reaktsiya plyumbirovaniya)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol 123, Nr 2, pp 295-297 (USSR)

ABSTRACT: Althoug the reaction of the direct introduction of metal atoms into an organic molecule (for Hg Ref 1, for Au Ref 2, and for Tl Ref 3) has been known already for a long time the "leading", i.e. the direct lead introduction has hitherto not been described. The authors investigated the leading as an interaction between salts of organic acids of the 4-valent lead and thiophene. The use of lead tetra-isobutyrate (Ref 5) seemed to be especially well suited for this purpose due to several favorable properties. The leading was observed under the following circumstances: After a smooth dissolution of the lead tetra-isobutyrate in an excess of thiophene a sample taken after several days' standing at room temperature did not show a reaction typical of the presence of 4-valent lead in the hydrolysis. This shows that the lead tetra-isobutyrate is gradually

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removed. The di-α-thienyl-lead-diisobutyrate can be isolated and identified under the conditions mentioned in the experimental part. It is a white crystalline substance. The probable reactions of its formation are given: first an unstable thienyl-lead-triisobutyrate is formed by a direct reaction of "leading" (I) which further on disproportionates (II). The analysis, the determination of the number of acid groups, and the transformation into the di-α-thienyl-lead-bismono-chloro acetate prove the proposed formula of the compound (II). The place of entrance "α" which is characteristic of thiophene in its metallization by salts of other metals is also proved in the case of lead. Here the process is slowed down considerably as compared to the rapid mercurisation and thalliation. In the first footnote on page 295 the authors point out that R. Criegee et al. (Ref 6) had overlooked the discovery and publication of the method of synthesizing the $ArPbX_3$ class by the authors (Ref 7). There are 9 references, 5 of which are Soviet.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physical and Chemical Institute imeni L. Ya. Karpov)

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5(3) SOV/20-123-4-29/53

AUTHORS: Abramova, L. V., Sheverdina, N. I., Kocheshkov, K. A., Corresponding Member, Academy of Sciences, USSR

TITLE: Investigations in the Field of Radiation Chemistry of Organometallic Compounds (Issledovaniya v oblasti radiatsionnoy khimii metalloorganicheskikh soyedineniy) Gamma Radiation in the Reaction of Metallic Tin With Halogen Alkyls (Gamma-izlucheniya v reaktsii mezhdu metallicheskim olovom i galoidnymi alkilami)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol 123, Nr 4, pp 681 - 684 (USSR)

ABSTRACT: The problems mentioned above are more or less completely unknown. The authors have investigated these problems systematically and studied the interaction reaction of halogen alkyls and aryls with various metals. The reaction mentioned in the subtitle is expressed by the general equation $2RBr+Sn \rightarrow R_2SnBr_2$. This reaction probably takes place according to a more complex mechanism (see below) and does not take place at normal temperatures; it only begins at 200° (Ref 1) or 300-350° (Ref 2)

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(Footnote: With the exception of Kakhut, 1860). Due to the unfavorable conditions of the reaction the final product is impurified by amounts of up to 25% R_3SnX and similar impurities. Heavy explosions also occurred. Besides, the said reaction is restricted by low alkyls (methyl, ethyl) (Ref 5) and there are still other difficulties. Therefore, the organic salts of Di-n-butyl tin (e.g. maleate, or laurate, which have the best effect in the stabilization of chloro-vinyl synthetics) were produced by the authors in an indirect way. The disproportionation of tetraalkyl tin compounds according to reference 6 was made use of: $(C_4H_9)_3Sn+SnCl_4 \longrightarrow 2(C_4H_9)_2SnCl$. Although the yields are close to the quantitative ones the production of tetrabutyl tin was necessary first. It was therefore of interest to find a new way of directly producing dihaloid-alkyl tin at normal pressure and temperature using new energy sources. For this reason the γ-radiation was used. Experimentally, this was successful. The yields went up to 55 mol/eV, as related to the halogen alkyl. The reaction mechanism is assumed to be one of chain

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Investigations in the Field of Radiation Chemistry of Organometallic Compounds. Gamma Radiation in the Reaction of Metallic Tin With Halogen Alkyls SOV/20-123-4-29/53

character with the formation of free radicals $R^{\bullet}$ and furthermore with an intermediate formation of an organo-tin radical. By comparing their results with those to be found in publications the authors arrived at the following conclusions: 1) Alkyl chlorides and tin do not yield any organo-tin compounds without catalyst in any type of reaction (the reactions proceed in other directions). 2) Alkyl bromides form such compounds with tin under γ-radiation and on heating (with the exception of low radicals). Ultraviolet light does not have any effect. 3) The alkyl iodides, however, yield organo-tin compounds under all influences mentioned above. There are 1 table and 8 references, 3 of which are Soviet.

ASSOCIATION: Nauchno-issledovatel'skiy fiziko-khimicheskiy institut im. L. Ya. Karpova (Scientific Physico-Chemical Research Institute imeni L. Ya. Karpov)

SUBMITTED: August 5, 1958

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5(3), 5(4)

SOV/62-59-1-10/38

AUTHORS: Nad', M. M., Talalayeva, T. V., Kazennikova, G. V., Kocheshkov, K. A.

TITLE: Fluorinated Styrenes (Ftorirovannyye stiroly) Communication I. 2,4-Difluoro Styrene (Soobshcheniye 1. 2,4-Diftorstirol)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 1, pp 65 - 70 (USSR)

ABSTRACT: In the present paper the authors synthesized 2,4-difluoro styrene for the first time. 2,4-difluoro-phenyl lithium was also obtained for the first time from 2,4-dibromo benzene and n-butyl lithium at low temperatures. The initial m-difluoro benzene was obtained from hydrochloric m-phenyl diamine. The synthesis was performed in several ways (Scheme). The following variants proved to be the most favorable: a) m-difluoro benzene (I) was condensed with acetyl chloride in the presence of aluminum chloride in carbon disulfide at 35°. The yield of 2,4-difluoro-aceto phenone (II) amounted to 80-85%.(II) was reduced by the effect of sodium boron hydride solution of 10-15% in aqueous alcohol under very soft conditions at temperatures below 50°. The yield

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Fluorinated Styrenes. Communication I.2,4-Difluoro Styrene SOV/62-59-1-10/38

of 2,4-difluoro phenyl-methyl carbinol (III) amounted to 85%, which was dehydrogenated by sulfuric acid potassium (Ref 11). The yield of 2,4—difluoro styrene (IV) amounted to ~70% in that case. The compound represents a mobile, colorless and pungent liquid. Boiling point 50-51°(28 mm). b) 2,4-difluoro phenyl-methyl carbinol (III) was synthesized by way of lithium and organo-magnesium compounds; 2,4-difluoro-phenyl lithium (VI) was obtained by the effect of ether solution of 2,4-difluoro-bromo benzene on the ether solution of n-butyl lithium at ~-70°. A large quantity of acetaldehyde was added to the transparent 2,4-difluoro-phenyl lithium solution at -65 - -70°. The yield of 2,4-difluoro phenyl-methyl carbinol (III) amounted to 97%. The authors tried to synthesize directly 2,4-difluoro styrene by the condensation of vinyl bromide with 2,4-difluoro phenyl magnesium bromide in the presence of cobalt chloride (in nitrogen) (Ref 17). The yield of styrene (IV) was small: ~ 5 - 7%(as dibromide). There are 1 figure and 19 references, 1 of which is Soviet.

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Copies-Chem Inst [illegible]

5(3), 5(4) SOV/62-59-1-11/38

AUTHORS: Nad', M. M., Talalayeva, T. V., Kazennikova, G. V., Kocheshkov, K. A.

TITLE: Fluorinated Styrenes (Ftorirovannyye stiroly) Communication II. 2,4-Difluoro-β-Fluoro Styrene and 2,4-Difluoro-β,β-Difluoro Styrene (Soobshcheniye 2. 2,4-Diftor-β-ftorstirol i 2,4-diftor-β,β-diftorstirol)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 1, pp 71 - 75 (USSR)

ABSTRACT: In the present paper the authors described the synthesis of styrenes which were fluorinated both in the side chain and nucleus. 2,4-difluro-β-fluoro styrene and 2,4-difluoro-β,β-difluoro styrene were synthesized for the first time (Diagram). 2,4-difluoro-β-fluoro styrene was obtained on the basis of 2,4-difluoro-ω,ω-difluoro-aceto phenone (VI). This ketone was obtained in two ways by using m-difluoro benzene and 2,4-difluoro-bromo benzene as initial compounds. The condensation in difluoro acetic acid with 2,4-difluoro-phenyl lithium (V) at ~ -70° proved to be the most favorable.

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Fluorinated Styrenes. Communication II. 2,4-Difluoro-β-Fluoro Styrene and 2,4-Difluoro-β,β-Difluoro Styrene SOV/62-59-1-11/38

2,4-difluoro-ω,ω -difluoro-aceto phenone was therein obtained in a yield of 50%. Furthermore, (VI) was reduced with sodium boron hydride in which 2,4-difluoro-phenyl difluoro-methyl carbinol (VII) was formed in a yield of 90%. The hydroxyl group of (VII) was substituted by chlorine under the influence of thionyl chloride in pyridine. The yield of 2,4-difluoro-α-chloro-β,β-difluoro benzene (VIII) amounted to≈80%. Under the influence of zinc dust upon compound (VIII) 2,4-difluoro-β-fluoro styrene (IX) was synthesized in acetamide in a yield of 82%. 2,4-difluoro-β,β-difluoro styrene (XIII) was synthesized in a similar way. The yield amounted to 40%. The 2,4-difluoro-aceto phenone and m-difluoro benzene used in the synthesis were obtained according to the method described in Communication 1. Difluoro acetic acid and difluoro chloro acetic acid were separated from corresponding sodium salts in a yield of 70-80%. There is 1 figure.

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SOV/62-59-2-14/40

5(3), 5(4)

AUTHORS: Nad', M. M., Talalayeva, T. V., Kazennikova, G. V., Kocheshkov, K. A.

TITLE: Fluorinated Styrenes (Ftorirovannyye stiroly). Communication 3. Side-Chain Fluorinated Styrenes (Soobshcheniye 3. Stiroly, ftorirovannyye v bokovoy tsepi)

PERIODICAL: Izvestiya Akademii nauk SSSR, Otdeleniye khimicheskikh nauk, 1959, Nr 2, pp 272-277 (USSR)

ABSTRACT: In the present paper the authors present data concerning the synthesis of β-fluoro styrene, β,β-difluoro styrene, α,β-difluoro styrene and α-fluoro-β-chloro styrene. β-fluoro styrene and α-fluoro-βchloro styrene are described for the first time. The synthesis methods of β,β-difluoro styrene and α,β-difluoro styrene devised by the authors deviate from the conventional methods described in publications. For the synthesis of ω,ω-difluoro-acetophenone phenyl lithium was condensed with difluoroacetic acid at -70°. The yield was 70%. Besides dichloro-acetophenone was fluorinated in dry glycerin under the influence of potassium fluoride. Difluoro-acetophenone was obtained in a yield of ~35%. This was reduced under the influence of sodium

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SOV/62-59-2-14/40

Fluorinated Styrenes. Communication 3. Side-Chain Fluorinated Styrenes

boron hydride to difluoromethyl-phenyl-carbinol (yield 95%). Furthermore chlorine was substituted for the hydroxyl group of the carbinol by means of thionyl-chloride in pyridine which yielded α-chloro-β,β-difluoroethylbenzene (73%). By the action of zinc in acetamide chlorine and fluorine atoms were separated from this compound, with β-fluoro styrene being formed in a 60-65% yield. β,β-difluoro styrene was obtained in the following way: difluoro-chloro-acetic acid was condensed with phenyl lithium at -70°. The ω,ω,ω-difluoro-chloro-acetophenone was formed (50%). This was reduced by means of sodium boron hydride to difluoro-chloro-methyl-phenyl carbinol (yield 90-92%). By the action of thionyl chloride in pyridine the α,β-dichloro-β,β-difluoro ethyl benzene (78%) was obtained. By the action of zinc in acetamide 2 chlorine atoms were split off and β,β-difluoro styrene was formed in a 60-65% yield. By the influence of alcoholic KOH-solution hydrogen fluoride was split off and α-chloro-β-fluoro styrene (60%) with a small impurity of β,β-difluoro styrene was formed. α,β-difluoro styrene was synthesized as follows: From difluoro acetophenone α,α-dichloro-β,β-difluoro-ethyl benzene (85%) was obtained in the usual manner. By

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Fluorinated Styrenes. Communication 3. Side-Chain Fluorinated Styrenes

fluorination with antimony trifluoride the α-chloro-α,β,β-trifluoro benzene (30-40%) was obtained. By the action of zinc in acetamide β-difluoro styrene (45-50%) was formed at 125° after 40 minutes. α-fluoro-β-chloro styrene: α,α,β,β-tetrachloroethyl benzene was obtained by means of phosphorus pentachloride from dichloro acetophenone (37-40%). This was fluorinated with antimony trifluoride to α,α-difluoro-β,β-dichloro-ethyl benzene (46-49%). By the action of zinc in acetymide α-fluoro-β-chloro styrene was obtained in a yield of ~80%. There are 5 references.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-Chemical Institute imeni L. Ya. Karpov)

SUBMITTED: April 19, 1957

Card 3/3

KOCHESHKOV, K.A.; KARGIN, V.A.; TALALAYEVA, T.V.; SOGOLOVA, T.I.;
PALEYEV, O.A.

Macromolecular polymers of ethylene obtained from mixtures of lithium organic compounds with titanium tetrachloride. Vysokom. soed. 1 no.1:152-156 Ja '59. (MIRA 12:9)

1. Fiziko-khimicheskiy institut im. L.Ya.Karpova.
(Ethylene) (Lithium organic compounds) (Titanium chloride)

5 (3)

AUTHORS: Talalayeva, T. V., Kazennikova, G. V., Kocheshkov, K. A. SOV/79-29-5-39/75

TITLE: Fluorinated Styrenes (Ftorirovannyye stiroly). IV. 2,5-Difluoro-styrene and 2,5-~~Difluoro-β-fluoro-styrene~~ (IV. 2,5-Diftorstirol i 2,5-diftor-β-ftorstirol)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 5, pp 1593-1595 (USSR)

ABSTRACT: The method of synthesizing styrene derivatives with two fluorine atoms on the nucleus was devised by the authors on the basis of 2,4-difluoro-styrene (Ref 1). For the production of the compounds mentioned in the title 1,4-difluoro-benzene was used as initial substance. This was obtained from the hydrochloride of p-phenylene diamine by bis-diazotization at -15° in concentrated nitrous acid, conversion into bis-diazonium-boron fluoride at the same temperature, and thermal decomposition of the latter compound. In contrast with the statements of other authors (Ref 2) with respect to difficulties in the bis-diazotization of the hydrochloride of p-phenylene diamine, this reaction could be performed in large doses, if the low temperature mentioned was maintained.

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Fluorinated Styrenes. IV. 2,5-Difluoro-styrene and 2,5-Difluoro-β-fluoro-styrene

SOV/79-29-5-39/75

Bromination of 1,4-difluoro-benzene offers a low yield of 2,5-difluoro-bromo-benzene. Besides, 2,5-difluoro-1,4-dibromo-benzene is formed. From 2,5-difluoro-bromo-benzene the 2,5-difluoro-phenyl-lithium was obtained in nearly quantitative yield with n-butyl-lithium (or ethyl-lithium) in ether solution at -70°. By condensation with acetaldehyde (at -70°) 2,5-difluoro-phenyl-methyl carbinol was formed. By ordinary dehydrogenation 2,5-difluoro-styrene was obtained in the presence of potassium bisulfate. The condensation of 1,4-difluoro-benzene with acetyl chloride in carbon disulfide under the influence of aluminum trichloride is not possible. The preparation of the second compound mentioned in the title was based on 2,5-difluoro-phenyl-lithium, the formation of which was described earlier. It was condensed at -70° with difluoro acetic acid. The 2,5-difluoro-ω,ω-difluoro-acetophenone obtained was reduced with sodium-boron hydride to give 2,5-difluoro-phenyl-difluoro-methyl-carbinol. The carbinol was transformed by means of thionyl chloride into 2,5-difluoro-β,β-difluoro-α-chloroethylbenzene, and this was reduced by zinc in acetamide to form 2,5-difluoro-β-fluoro-

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Fluorinated Styrenes. IV. 2,5-Difluoro-styrene and 2,5-Difluoro-β-fluoro-styrene SOV/79-28-5-39/75

styrene. The experimental describes the reactions and the physical data of the compounds obtained. There are 5 references, 2 of which are Soviet.

ASSOCIATION: Fiziko-khimicheskiy institut imeni L. Ya. Karpova
(Institute of Physical Chemistry imeni L. Ya. Karpov)

SUBMITTED: April 2, 1958

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SOV/79-29-7-32/83

5 (3).

AUTHORS: Lodochnikova, V. I., Panov, Ye. M., Kocheshkov, K. A.

TITLE: β-Naphthyl Derivatives of the Class $ArPbX_3$ (β-Naftil'nyye proizvodnyye klassa $ArPbX_3$)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 7, pp 2253-2255 (USSR)

ABSTRACT: As was proved by M. M. Nad' and K. A. Kocheshkov (Ref 1), organo-lead compounds of the class Ar_2PbX_2 are formed according to the scheme $2\ Ar_2Hg + Pb(OOCCH_3)_4 \longrightarrow Ar_2Pb(OOCCH_3)_2 + 2\ ArHgOOCCH_3$. Among the compounds synthesized by this method only di-β-naphthyl-lead diacetate which contained a β-naphthyl group were described in publications. Recently (Ref 2) the authors found that the same initial reagents, of a molar ratio, lead to the compounds $ArPbX_3$, which were identical with the representatives of this class (Ref 3) obtained by another method. It was of interest to synthesize the salts $\beta\text{-}C_{10}H_7Pb(OOCR)_3$ according to di-β-naphthyl mercury in order

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β-Naphthyl Derivatives of the Class $ArPbX_3$

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to obtain more complete data on the β-naphthyl compounds of lead. In the present paper the triacetate and tripropionate of β-naphthyl lead as well as β-naphthyl plumbic acid were synthesized. It was shown that the latter may serve as an intermediate in the substitution of an organic acid residue by another one. The compounds $ArPbX_3$ are the first stage of arylation of the salts of organic acids of tetravalent lead according to the above scheme; further they are bound to enter the reaction with Ar_2Hg under the formation of Ar_2PbX_2. Ar_2PbX_2 is thus formed in two stages. The triacetate of β-naphthyl lead with di-β-naphthyl mercury yields the diacetate of di-β-naphthyl lead. The same reaction was observed by R. Crigee, P. Dimroth, R. Schempf (Ref 4) in the formation of the diacetate of diphenyl lead. The compounds $\beta\text{-}C_{10}H_7Pb(OOCR)_3$ are formed more slowly. They form crystals more difficultly than the corresponding α-naphthyl derivatives which were described earlier by the authors (Ref 5). Acetates are the most convenient lead salts. There are 7 references, 5 of which are

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β-Naphthyl Derivatives of the Class $ArPbX_3$ SOV/79-29-7-32/83

Soviet.

ASSOCIATION: Fiziko-khimicheskiy institut imeni L. Ya. Karpova i Sverdlovskiy gosudarstvennyy meditsinskiy institut. (Physicochemical Institute imeni L. Ya. Karpov and Sverdlovsk State Medical Institute)

SUBMITTED: June 12, 1958

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SOV/20-124-3-31/67

5(3)

AUTHORS: Sheverdina, N. I., Abramova, L. V., Kocheshkov, K. A., Corresponding Member, Academy of Sciences, USSR

TITLE: Crystalline Mixed Organic Zinc Compounds (Kristallicheskiye smeshannyye tsinkorganicheskiye soyedineniya)

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 124, Nr 3, pp 602-605 (USSR)

ABSTRACT: On the dissolution of R_2Zn in ether (R = organic radical) and the addition of an equivalent quantity of zinc halide (also dissolved in ether), the compound RZnX (X = halogen) is formed. This compound is precipitated by the addition of dioxane, and the composition of the crystalline complex compound $RZnX.C_4H_8O_2$ is investigated by means of elementary analysis. The same compound is obtained from the direct reaction of the alkyl halide with zinc, dissolution in ether, and precipitation with dioxane. In the same way, zinc aryl compounds are treated, in an ether solution, with equivalent quantities of zinc iodide, crystalline complex compounds of the formula $ArZnX.(C_2H_5)_2O$ being formed in this process (Ar = aryl radical). The paper gives a detailed recipe for the

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Crystalline Mixed Organic Zinc Compounds SOV/20-124-3-31/67

preparation of 1) $C_2H_5ZnJC_4H_8O_2$ from zinc diethyl and zinc iodide, 2) the same compound from zinc and ethyl iodide, 3) the compound $C_6H_5ZnJ(C_2H_5)_2O$ from zinc diphenyl and zinc iodide. The reactions of these compounds with benzoyl chloride, with the formation of ethyl-phenyl ketone and benzophenone, respectively, are also given. There are 7 references, 2 of which are Soviet.

ASSOCIATION: Nauchno-issledovatel'skiy fiziko-khimicheskiy institut im. L. Ya. Karpova
(Physico-Chemical Scientific Research Institute imeni L. Ya. Karpov)

SUBMITTED: August 20, 1958

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SOV/20-125-2-30/64

5(2, 3)

AUTHORS: Sheverdina, N. I., Paleyeva, I. Ye., Delinskaya, Ye. D., Kocheshkov, K. A., Corresponding Member AS USSR

TITLE: Crystalline Cadmium-organic Compounds of the RCdX-Class in the Aliphatic Series (Kristallicheskiye kadmiyorganicheskiye soyedineniya klassa RCdX v alifaticheskom ryadu)

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 125, Nr 2, pp 348-350 (USSR)

ABSTRACT: Solutions in ether of the compounds mentioned in the title, obtained from exchange reactions of cadmium salts and Grignard's reagent, are fairly extensively used as an excellent reagent for ketone production (Ref 1). When dissolved in ether, the cadmium-organic compounds are considered as dialkyl compounds (Ref 2). However, cadmium-organic compounds of a mixed type had never been isolated in an individual crystalline state. The authors were the first to succeed in effecting this isolation after the reaction between dialkyl cadmium and the cadmium salts on the equation $R_2Cd + CdX_2 \longrightarrow 2RCdX$ (I). The reaction occurs in an

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Crystalline Cadmium-organic Compounds of the RCdX-Class in the Aliphatic Series

analogous way in the aromatic series as well. For this purpose dehydrated cadmium halogenides in absolute ether were employed. Contrary to an analogous reaction, described by the authors on an earlier occasion (sinc-organic compounds, Ref 3), they had in this case - due to the ether insolubility of the cadmium halogenides - to employ the appropriate suspensions. The mixed cadmium-organic compounds (obtained for the first time) are white, finely crystalline powders that do not melt, but which soften above 100°. They are energetically decomposed by water and alcohol. Atmospheric oxygen oxidizes them, but does not cause their spontaneous ignition. With the exception of n-butyl-cadmium-bromide, which is soluble in ether, all the compounds of the ethyl series are insoluble in aromatic hydrocarbons, hexane, and ether. Unlike in the RZnX (Ref 3), no stable complexes (e. g. with ether or dioxane) of the compounds concerned have been observed so far. The interaction of the individual cadmium-organic compounds described with the halogen anhydrides of the acids occurs on the equation

SOV/20-129-3-37/63

5(2,4)

AUTHORS: Rodionov, A. N., Vasil'yeva, V. N., Talalayeva, T. V., Shigorin, D. N., Gur'yanova, Ye. N., Kocheshkov, K. A., Corresponding Member, AS USSR

TITLE: Intermolecular Lithium Bond. Its Influence Upon the Vibration Spectra of Molecules and Upon the Dipole Moments (Mezhmolekulyarnaya litiyevaya svyaz', yeye vliyaniye na kolebatel'nyye spektry molekul i dipol'nyye momenty)

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 129, Nr 3, pp 598-601 (USSR)

ABSTRACT: In an earlier paper (Ref 1) the authors proved the formation of a bond referred to in the title $-\overset{-\delta}{C}H_2-\overset{+\delta}{Li}\ldots\overset{-\delta}{C}H_2-\overset{+\delta}{Li}$ (I) and R-O-Li...O-Li (II). The lithium bond like the hydrogen bond is a secondary chemical bond (Ref 2). Type (I) was closely investigated on the basis of infrared absorption spectra. In the work under review, infrared spectra of Alk-Li compounds with a varying length of the radical chain were solved in benzene and investigated at various concentrations. The aim was to clarify

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the dependence of the intermolecular space, of the stability of the lithium bond and also of the magnitude of the frequency displacement of the groups C-Li on the length and on the structure of the carbon radical. Table 1 as well as figures 1 and 2 illustrate the results obtained. As may be observed therefrom, the value of the displacement of the said groups actually decreases with increasing chain length. Thus also the stability of the lithium bond in the complexes decreases. The investigation of the solutions of ethyl, n-butyl, and n-amyl lithium in benzene showed a linear course of the dependence of the dielectric constant on the concentration in the case of lower concentrations. This course diverges from the straight line at an increase of concentration (0.4-3.0 mole %). The dipole moment of ethyl lithium in benzene remains constant between 0.08-0.4 mole% and amounts to 0.87 D. The variation of the dipole moment in the complex, connected with the formation of lithium, goes back on the whole to the action of this bond upon the type of orientation of the dipoles with respect to one another. Therefore, the formation of cyclic complexes and especially the type

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of the "quadrupoles" must decrease the dipole moment. This apparently takes place in the ethyl lithium solutions in benzene. It follows from the above that alkyl lithium molecules are associated both in benzene and in hexane solutions. The character of the associate depends both on the nature of the solvent and on the radical composition. The lithium bond considerably influences the frequency variations of the vibrations of the C-Li groups and also the dipole moments of the complexes; these variations here depend on the radical length, on the concentration of the solutions, and also on the nature of the solvent. There are 2 figures, 1 table, and 3 references, 2 of which are Soviet.

ASSOCIATION: Nauchno-issledovatel'skiy fiziko-khimicheskiy institut im. L. Ya. Karpova (Scientific Physico-chemical Research Institute imeni L. Ya. Karpov)

SUBMITTED: December 29, 1958

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5 (2, 3) SOV/20-128-2-27/59

AUTHORS: Sheverdina, N. I., Abramova, L. V., Kocheshkov, K. A., Corresponding Member AS USSR

TITLE: Organozinc Compounds of the Ar_2Zn Class and Their Dioxanates

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 128, Nr 2, pp 320-322 (USSR)

ABSTRACT: The authors proved for the first time that zincorganic compounds of the RZnX class (X - halogen) may be isolated as complexes in purely crystalline state with ether or dioxane (Ref 1) (S. Gvozdov, Ref 4, could not isolate C_2H_5ZnJ purely; this was done by the authors). All halogen salts of Zn produce dioxanates according to data of publications (Ref 2), whereas an etherate $ZnX_2 \cdot 2$ eth. has hitherto been known only for zinc iodide. It was now investigated whether the zinc aryls produce such complexes as well. The zinc diaryls described in the present paper did not yield corresponding etherates. With 1,4-dioxane, the following complexes could, however, be isolated: $C_6(H_5)_2Zn \cdot C_4H_8O_2$; $(p\text{-}CH_3C_6H_4)_2Zn \cdot C_4H_8O_2$; $(\alpha\text{-}C_{10}H_7)_2ZnC_4H_8O_2$. These dioxanates are white crystalline substances, soluble in ether and dioxane, insoluble in benzene and petroleum ether. The perfection of the method of preparing the initial zinc

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Organozinc Compounds of the Ar_2Zn Class and Their Dioxanates

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diaryls (Ref 5) became necessary in connection with the successful production of dioxanates (as well as of the compounds of the ArZnX class, Ref 1). This method (heating of diphenyl mercury with metallic zinc without solvent) which is too vigorous was improved by K. A. Kocheshkov, A. N. Nesmeyanov, and V. I. Potrosov (Ref 3). They carried out the reaction in boiling xylene. In this way the synthesis could be used for a series of organozinc compounds with one substituent in the nucleus. This method has the disadvantage that the success of the synthesis depends on the state of the zinc. So-called "zinc wool" should be preferred. The authors proceeded from solid lithium aryls to avoid vacuum distillation (Ref 6). The latter produced by the method of T. V. Talalayeva and K. A. Kocheshkov (Ref 7) (exchange reaction X - M) practically contain no diaryls, or only little quantities of it. The isolation of pure diaryl zinc by crystallization is therefore obtained without distillation. Diphenyl zinc (yield 83%), di-o-tolyl zinc (71%), di-p-tolyl zinc (45%), and di-α-naphthyl zinc (46%) were produced in this way, the two first ones for the first time. White crystalline precipitations

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Organozinc Compounds of the Ar_2Zn Class and Their Dioxanates

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of corresponding dioxanates are separated in the dissolution of diaryl zinc in dioxane and in the distillation of the major part of the solvent. There are 7 references, 4 of which are Soviet.

ASSOCIATION: Nauchno-issledovatel'skiy fiziko-khimicheskiy institut im. L. Ya. Karpova (Scientific Physicochemical Research Institute imeni L. Ya. Karpov)

SUBMITTED: June 16, 1959

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5 (2,3,4) SOV/20-128-4-26/65

AUTHORS: Rodionov, A. N., Talalayeva, T. V., Shigorin, D. N., Kocheshkov, K. A., Corresponding Member AS USSR

TITLE: The Infrared Spectra and Structure of Aromatic Organolithium Compounds

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 128, Nr 4, pp 728 - 731 (USSR)

ABSTRACT: There are very few experimental data on the compounds mentioned in the title (Refs 1,2). To clarify the structure of these substances, the infrared absorption spectra of phenyl-, o- and p-tolyl-, mesityl-, p-diphenyl-, p-chlorophenyl-, p-bromophenyl-, p-iodophenyl-, as well as α- and β-naphthyl lithium were measured. These aromatic compounds are crystalline substances, and not soluble either in hexane or benzene. Therefore, the spectra of their powders were measured in vaseline- and fluorated oil. Table 1 shows that in these spectra several new bands appear which are in a certain connection with the C—Li bond. The data in table 1, as well as a comparison with spectra of aliphatic compounds previously described by the authors (Ref 5), lead to the conclusion that the band in the range of

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The Infrared Spectra and Structure of Aromatic Organolithium Compounds

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1045-1060 cm^{-1} is apparently connected with a free C-Li bond or, at least, with one poorly participating in the association. The lower frequencies (870, 970 cm^{-1}), however, may be related with the C-Li bonds participating in the association. These frequencies characteristic of the vibrations of the C-Li groups in the spectra of aromatic and aliphatic organolithium compounds, as well as their close position, speak much in favor of a covalent character of the said bond in the two classes of compounds mentioned. Therefore, the assumption of an ionic character of the C-Li bond in aromatic organolithium compounds found in publications is incorrect. The authors investigate the dependence on aromatic compounds responsible for the complex formation of aliphatic compounds of this type (formation of an intermolecular lithium bond and dipole interaction). In the present paper, they study not only the effect of the purely steric factor on the strength of the lithium bond but also that of the change in the general polarity of molecules. For this purpose, they introduce other polar groups or atoms into the organic rest of the molecule. On comparison of the spectra of phenyl-, o- and p-tolyl-, biphenyl- and mesityl lithium, it

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appears that the degree and type of association of these substances are different. The CH_3-group in orthoposition has little effect on the degree and character of association. The same group in paraposition (p-tolyl lithium), however, changes the spectrum considerably (Fig 1). A complication of the nonpolar substituent in paraposition equals an extension of the carbon rest. This reduces the degree of association. The screening effect becomes most distinct in the spectrum of mesityl lithium. The symmetrically arranged CH_3-groups render the association rather difficult. Therefore, only the band of the free C-Li group at about 1052 cm^{-1} is more or less distinctly visible. Figure 2 shows the spectra of p-chloro-, p-bromo-, and p-iodophenyl lithium. 2 dipoles each - C-Li and C-Hal - are present in every case. They increase the general polarity of the molecule. This brings about an intensification of the dipole interaction between the molecules. The p-chloro-phenyl lithium is most intensely and completely associated. The spectra of α- and β-naphthyl lithium are different from all other spectra dis-

The Infrared Spectra and Structure of Aromatic Organolithium Compounds SOV/20-128-4-26/65

cussed. The band is most intensive at 943 cm^{-1} while little intensive bands are present at 1050 cm^{-1}. In crystals, these two substances are apparently in a mainly associated state. There are 2 figures, 1 table, and 5 references, 3 of which are Soviet.

ASSOCIATION: Nauchno-issledovatel'skiy fiziko-khimicheskiy institut im. L. Ya. Karpova (Scientific Physicochemical Research Institute imeni L. Ya. Karpov)

SUBMITTED: June 16, 1959

Card 4/4

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SOV/20-129-1-30/64

~~5(2,3)~~ 5.3830

AUTHORS: Glushkova, V. P., Delinskaya, Ye. L., Kocheshkov, K. A., Corresponding Member, AS USSR

TITLE: Metallization of Polymers

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 129, Nr 1, pp 109 - 112 (USSR)

ABSTRACT: The introduction of metallic atoms into polymers (called "metallization") may play a certain role in the investigation of the structure of polymers (or copolymers) as well as in the change of their properties. In the present paper the authors describe a few reactions involving mercury and thallium. The thiophene ring takes up thallium very readily. Thallium-triisobutyrate (Ref 1) was used as reagent. Metallization of polymers is difficult. Higher polymers are solid substances. In solutions they can be metallized by only a few solvents, which cannot be easily metallized themselves nor react otherwise with the metallizing agent. Investigations were carried out of: 1) The introduction of thallium into poly-α-vinylthiophene in benzene; 2) introduction of Hg into the same compound in benzene; and 3) introduction of Hg into polystyrene in nitrobenzene (also in polyvinylfurane into α position). Mercury diisobutyrate was used as the metallizing agent in mecurization.

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Metallization of Polymers

Reaction (1) is completed within 15 minutes (1). Reaction (2) needs several minutes. The two reaction products are yellowish powders insoluble in benzene and other organic solvents. Poly-α-vinylthiophene is easily combinable with lithium (according to I. M. Viktorova). The choice of experimental conditions and the solvent is more difficult in the case of reaction (3). Thus R. N. Smirnov (Ref 2) obtained only 50-60% of the theoretical mercury content by mercurization of styrene in acetic acid. Nitrobenzene is a suitable medium. The final product is a yellowish powder. It can be dissolved in nitrobenzene if a small quantity of isobutyric acid is added. The number of atoms of the absorbed metal was: reaction (1): 0.94-1.0 of thallium per 1 member of polyvinylthiophene; reaction (2): 1 mercury atom per 1 member of polyvinylthiophene; reaction (3): 0.96 atoms per 1 aromatic nucleus. The position attained by mercury was not proved by the authors. Probably, it is the para position. Mercury atoms can be substituted by halogens in the polystyrene molecule by means of the effect of bromine. O. A. Paleyev is mentioned in the text. There are 2 Soviet references.

ASSOCIATION: Nauchno-issledovatel'skiy fiziko-khimicheskiy institut im. L. Ya. Karpova (Scientific Physico-chemical Research Institute imeni L. Ya. Karpov)

Card 2/2

87118

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B023/B064

24.2500 2209, 1144 only

AUTHORS: Vasil'yeva, V. N., Talalayeva, T. V., Gur'yanova, Ye. N., and ~~Kocheshkov, K. A.~~

TITLE: Dipole Moments of Organolithium Compounds of the Aliphatic Series

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, No. 9, pp. 1549-1552

TEXT: On the basis of published data (Refs. 1, 2, 3, 4, 5, 6), the authors measured the dipole moments of ethyl lithium, n-propyl lithium, n-butyl lithium, n-amyl lithium, and n-dodecyl lithium in hexane. Measurements were carried out at concentrations as low as possible, for which an association was unlikely, and concentration values at which association was determined by means of the cryoscopic method. Since all these compounds are extremely unstable, their syntheses, the preparation of the solutions and the measurements of the dipole moments were carried out in pure argon atmosphere. The authors describe the preparation of the solutions and the determination of their concentration by means of titration. The dipole

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Dipole Moments of Organolithium Compounds of the Aliphatic Series

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moments were measured at 25°C with the help of the pulsation method. The concentration of the solutions was 0.094-0.66 mole%. Tables 1 and 2 show the results. Table 3 shows the results of the measurements made at 0.6-7.5 mole%. The dipole moment μ was determined by the formula $\mu = 0.0127\cdot10^{-18}\sqrt{(P_{\infty}-P_E)T}$ (P_E = electron polarization of the substance). It was 1.1 D for ethyl lithium concentrations of 0.12-0.62 mole%, for butyl lithium concentrations of 0.13-0.36 mole%, and for amyl lithium concentrations of 0.13-0.66 mole%. From the linear dependence of the dielectric constant of the solution on concentration (Table 1), and the constancy of the dipole moment value of all three compounds, it is concluded that in this range of concentration monomeric molecules are concerned, and that the value of the dipole moment for the compounds mentioned refers to the moment of the monomer. A deviation from the linear dependence is found when measuring the dielectric constant of alkyl lithium solutions in hexane at higher temperatures. The greatest deviation is observed in the range of concentration of from 0.62 to 3.27 mole%. This deviation and the reduction of the dipole moments is, in the authors' opinion, caused by the association of the molecules and the formation of

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Dipole Moments of Organolithium Compounds of the Aliphatic Series

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complexes. This is in agreement with the published data (Refs. 3,4, and 5). If the chain of the aliphatic radical is extended from ethyl to amyl, the degree of association of the alkyl lithium compounds decreases. This dependence will be subject of further investigations. The behavior of the alkyl lithium compounds in benzene solutions differs from the behavior of these compounds in hexane. The authors measured the dipole moment of ethyl lithium in benzene at 25°C and obtained 0.87 D in the concentration range of from 0.094-0.49 mole%. Apparently, lithium forms stable complexes in benzene solutions also in the case of comparatively low concentrations. There are 3 tables and 6 references: 3 Soviet, 2 US, and 1 German.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-chemical Institute imeni L. Ya. Karpov)

SUBMITTED: March 7, 1959

Legend to Tables 1 and 3: c - concentration of the dissolved substance in mole%; ε - dielectric constant of the solution; d - density of the solution. 1) determination in hexane at 25°C, 2) ethyl lithium, 3) n-amyl lithium,

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5.3831
5.3100

AUTHORS: Shigorin, D. N., Rodionov, A. N., Talalayeva, T. V., Kocheshkov, K. A., Corresponding Member AS USSR

TITLE: An Investigation of the Nature of Secondary Chemical Bonds

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 133, No. 1, pp. 178 - 181

TEXT: The authors defined the formation of secondary (less strong) chemical bonds as an additional interaction of the valence electrons caused by a change in the energy-state of the electrons in the total system of chemical bonds of the molecule. The formation of secondary bonds thus does not depend solely on the nature of the atom entering into the molecule, but also on the properties of the molecular system and on the distribution of electron density in the molecule. The authors investigated the infrared spectra of lithium-organic compounds and acetylene derivatives. The infrared spectrum of R-Li and Ar-Li compounds shows a characteristic frequency of the valence oscillations of the free C-Li group at 1050 - 1100 cm^{-1}. Measurement of the dipole moments of R-Li

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An Investigation of the Nature of Secondary Chemical Bonds

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B004/B007

compounds in hexane gave the electric moment of 1.1 - 1.2 D for C-Li. The existence of oscillation frequencies and the low dipole moment indicate the covalence-character of the C-Li bond. In benzene- and hexane solutions of lithium-organic compounds as well as on their crystals, additional bonds were found, which lack in the vapor spectra, and which are due to complex formation. Like the compounds of Be, B, and Al, also the lithium-organic compounds form complexes by way of a secondary Li-bond. This is explained by means of the properties which these elements have in common: free energetically low p-orbits; the possibility of changing the energy state of the valence electrons in the direction s → p with only little energy. In this way, polycentric molecular electron orbits can be formed. These elements form chemical bonds not only by means of their valence electrons, but also by ceding free orbits to electrons which participate in the primary bond of other molecules. In the dimeric complex of lithium-organic compounds every C-atom of the carbon bridge with 2 Li-atoms is able to form a tricentral orbit (two electrons in the field of three nuclei). This orbit is more stable than the usual C-Li bond. For the initiation of the polymerization of ethylene and its derivatives under participation of R-Li or $Al(R)_3$, the formation of a complex[1](I) is

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An Investigation of the Nature of Secondary Chemical Bonds

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assumed on the basis of these conceptions. Together with V. I. Smirnova, the authors proved the formation of radicals in the reaction of $TiCl_4$ with R-Li by means of electron paramagnetic resonance. The formation of complex (I) is proved by the colored complexes of ethyl lithium with styrene, α- and β-methyl styrene and other unsaturated compounds, which are characterized by an intense absorption band of the C=C bond. The authors discuss the formation of secondary bonds under participation of undivided electron pairs in the complexes R-Li...X ($X = O<$, $N\lessgtr$, etc.) the σ,π-conjunction $\overset{+\delta}{Li}\overset{\sigma}{—}\overset{-\delta}{C}-C\overset{\pi}{=}C-$ in the compounds of benzyl lithium and fluorenyl lithium as well as the participation of the O-Li group, O-Al group etc. in secondary bonds in acetyl acetonates under formation of quasiaromatic rings with participation of π-electrons. Accordingly, there exist various types of secondary chemical bonds, which manifests itself in the physical properties and in the reactivity of the compounds. There are 13 references: 10 Soviet, 1 British, and 2 German.

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An Investigation of the Nature of Secondary Chemical Bonds

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ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-chemical Institute imeni L. Ya. Karpov)

SUBMITTED: March 23, 1960

Card 4/4

SHEVERDINA, N.I.; ABRAMOVA, L.V.; KOCHESHKOV, K.A.

Complexes of the series of aromatic organozinc compounds of the class ArZnX. Dokl.AN SSSR 134 no.4:853-855 O '60. (MIRA 13:9)

1. Fiziko-khimicheskiy institut im. L.Ya.Karpova. 2. Chlen-korrespondent AN SSSR (for Kocheshkov).
(Zinc compounds)

20946

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B117/B208

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1273
1374

AUTHORS: also Kocheshkov, K. A., Panov, Ye. M., and Sorokina, R. S.

TITLE: Organolithium vinyl benzenes halogenated in their side chains, and their reactions

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, no. 3, 1961, 532

TEXT: In the present "Letter to the Editor", the authors report that they have been able to obtain organolithium vinyl benzenes halogenated in their side chain at low temperature. The synthesis was achieved by an exchange reaction $CX_2 = CXC_6H_4Br + C_4H_9Li \longrightarrow CX_2 = CXC_6H_2Li + C_4H_9Br$ (X being either F or Cl) in ether, and some of their reactions have been studied. This was exemplified by the following novel conversions of ArLi: 1) carbonization of ArLi gives ArCOOH (Ar denotes $CClF = CFC_6H_4-$), melting point 165°-166°C. Found: C 49.49; 49.59; H 2.26; 2.32; Cl 16.16; 16.39 %. Calculated: C 49.43; H 2.29; Cl 16.25 %. 2) Reaction of ArLi with $HgBr_2$ yields ArHgBr, melting point 221°-223°C. Found: Hg 44.80 %; the sum of Cl and Br 24.96;

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Organolithium vinyl benzenes halogenated... B117/B208

25.18. Calculated: Hg 44.18 %; the sum of Cl and Br 25.40. 3) Reaction of ArLi with $(C_6H_5)_3SnCl$ gives $ArSn(C_2H_5)_3$, boiling point 170°C (4 mm). Found: Sn 31.16; 31.15; Cl 9.76; 9.90 %. Calculated: Sn 31.28; Cl 9.36 %. 4) From the reaction with acetaldehyde a corresponding divinyl benzene results, which is halogenated in one of the vinyl groups. Low temperatures (about -70°C) were necessary for carrying out the afore-mentioned reactions, as well as reactions with halides of other elements or elemental-organic compounds. This new type of aryl lithium is capable of all the manifold reactions of organolithium compounds. The resultant monomers are polymerisable. It is pointed out that a rise of temperature or retardation of the reaction during the synthesis of the new ArLi type yield polycondensation products of the $(-CX=CXC_6H_4-)$ type which are of special interest to the authors. [Abstracter's note: This is a full translation from the original].

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-chemical Institute imeni L. Ya. Karpov)

SUBMITTED: January 19, 1961

Card 2/2

ZAYTSEVA, N.A.; PANOV, Ye.M.; KOCHESHKOV, K.A.

Synthesis of fluorinated ketones by use of organolithium compounds and N, N-dialkylamides of fluorinated acids. Izv.AN SSSR.Otd.khim. nauk no.5:831-835 My '61. (MIRA 14:5)

1. Fiziko-khimicheskiy institut im. L.Ya.Karpova.
(Ketones) (Lithium organic compounds) (Amides)

KAZENNIKOVA, G.V.; TALALAYEVA, T.V.; ZIMIN, A.V.; SIMONOV, A.P.; KOCHESHKOV, K.A.

Synthesis of side chain fluorinated vinylnaphthalenes. Izv.AN SSSR, Otd.khim.nauk no.5:835-838 My '61. (MIRA 14:5)

1. Fiziko-khimicheskiy institut im. L.Ya.Karpova.
(Naphthalene)

25061
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B118/B220

53660

AUTHORS: Kazennikova, G. V., Talalayeva, T. V., Zimin, A. V., Simonov, A. P., and Kocheshkov, K. A.

TITLE: Fluorinated styrenes. Report 5. ω, β, β-Trifluoro-styrenes

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 6, 1961, 1063 - 1065

TEXT: In the present study, ω, β, β-trifluoro-styrenes were synthesized by condensation of tetrafluoro-ethylene with organometallic compounds of the aromatic series:

$$RLi + CF_2{=}CF_2 \longrightarrow RCF{=}CF_2 + LiF.$$

It has been found that the yield in ω, β, β-trifluoro-styrene amounts to 25-15 % when the phenyl lithium solution is added to the tetrafluoro-ethylene at -75°C; at lower temperatures (down to -120°C), the yield does not increase. It may, however, be increased up to 35-40 % if an excess of pure tetrafluoro-ethylene is allowed to pass rapidly through a dilute ether

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B110/B220

Fluorinated styrenes. Report...

[illegible]ation of phenyl lithium for [illegible] to 2 hr. Concentrated solutions of the latter (or a longer passage of tetrafluoro-ethylene) reduces the yield to [illegible] %. The condensation of tetrafluoro-ethylene with organolithium compounds at low temperatures may be used generally for the synthesis of perfluoro-vinyl compounds. Depending on the radical RLi, the yield usually amounts to 4[illegible]–55 % and sometimes to 15–30 %. The corresponding difluoro-stilbene forms as a by-product. The monomeric α, β, β-trifluoro-styrenes obtained are stable in sealed ampullae in argon atmosphere over a small amount of copper powder from - 25° to - 35°C. The formation of the dimer is insignificant. α, β, β-trifluoro-p-methyl styrene (40%), α, β, β-trifluoro-o methyl styrene (55%), α, β, β-trifluoro-p-chloro-styrene (15%), α, β, β-trifluoro-m-methyl styrene (44%), α, β, β-trifluoro-p-bromo-styrene (5-10%), α-perfluoro-vinyl naphthalene ([illegible]%) were synthesized by this method. Tetrafluoro-ethylene with tetramethylene dilithium, pentamethylene dilithium, and decamethylene dilithium gives the unsaturated compounds $CF_2=CF(CH_2)_nCF=CF_2$ (5%). With butyl lithium, only the compound $p\text{-}C_4H_9CF=CF_2$ was obtained. The infrared spectra of the

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B118/B220

Fluorinated styrenes. Report...

compounds obtained were taken. The styrenes were analyzed by the method of A. V. Zimin et al. (Dokl. AN SSSR, 126, 784 (1959)). There are 1 table and 8 references: 2 Soviet-bloc and 6 non-Soviet-bloc. The 3 references to English-language publications read as follows: 1) P. Tarrant, D. A. Warner, J. Amer. Chem. Soc. 76, 1674 (1954); pat. USA 2904484 (1957); 2) S. Dixon, J. Organ. Chem. 21, 400 (1956); 3) D. I. Livingston, P. M. Kamath, R. S. Corley, J. Polymer. Sci. 20, 485 (1956); W. G. Barb, J. Polymer Sci. 37, 515 (1959).

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-chemical Institute imeni L. Ya. Karpov)

SUBMITTED: April 1, 1960

Card 3/3

25042
S/062/61/000/006/004/010
B118/B220

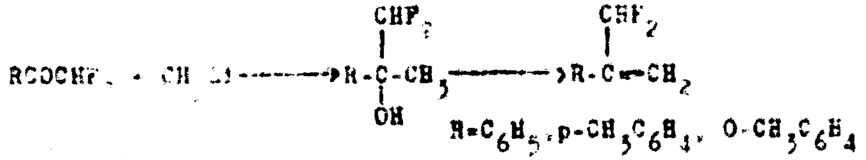
5.3600

AUTHORS: Kazennikova, G. V., Talalayeva, T. V., Zimin, A. V., and Kocheshkov, K. A.

TITLE: Fluorinated styrenes. Report 6. α-Difluoro-methyl styrenes and α-trifluoro-methyl styrenes

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 6, 1961, 1066 - 1069

TEXT. The present paper deals with the synthesis of α difluoro-methyl styrene, α-difluoro-methyl-p-methyl styrene, α-difluoro-methyl-o-methyl styrene, α-trifluoro-methyl styrene, and α-trifluoro-methyl-p-fluoro-styrene according to the equation:



$$RCOCHF_2 + CH_3Li \longrightarrow R-\underset{OH}{\overset{CHF_2}{C}}-CH_3 \longrightarrow R-\overset{CHF_2}{C}=CH_2$$

$R=C_6H_5, p-CH_3C_6H_4, O-CH_3C_6H_4$

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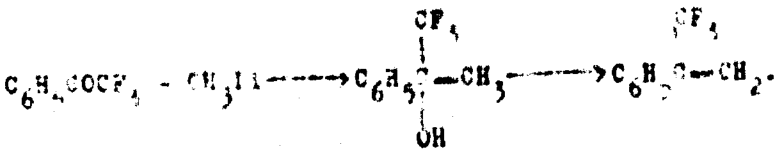
B110/B220

Fluorinated styrenes. Report...


$$C_6H_5COCF_3 - CH_3Li \longrightarrow C_6H_5\underset{OH}{\overset{CF_3}{C}}-CH_3 \longrightarrow C_6H_5\overset{CF_3}{C}=CH_2.$$

Starting from phenyl magnesium bromide and p-fluoro-phenyl magnesium bromide, α-trifluoro-methyl styrene and α-trifluoro-methyl-p-fluoro-styrene were obtained by using trifluoro-acetone (via the carbinol stage). The most convenient method proved to be the use of methyl lithium and of ω-difluoro-aceto-phenones or ω-trifluoro-acetophenones which are easily accessible for synthesis and obtained from RLi and fluorinated acids (or their diethyl amides). The condensation of methyl lithium with fluorinated acetophenones is effected at temperatures between -20 and -25°C in ether, resulting in tertiary carbinols with yields between 60 and 95%. The dehydration of the carbinols is effected by phosphorus pentoxide (yield of 65 - 85%). Moreover, p-chloro-styrene was synthesized. There are 10 references: 4 Soviet-bloc and 6-non-Soviet-bloc. The references to

Card 2/3

25042
S/062/61/000/006/004/010
B118/B220

Fluorinated styrenes. Report...

English-language publications read as follows: 1) P. Tarrant, R. E. Taylor, J. Organ. Chem. 24, 238(1958). 2) K. T. D..shard, R.Levine, J. Amer. Chem. Soc. 78, 2268(1956); 77, 3656(1955); J. D. ?ark, R. E. Noble, I. R. Lacher, J. Organ. Chem. 23, 1396(1956); D. A. Rausch, A. M. Lovelace, L. E. Coleman, J. Organ. Chem. 21, 1328 (1956). A. M. Lovelace, J. Amer. Chem. Soc. 79, 4983(1957); 3) T. Mc.Groth, R. Levine, J. Amer. Chem. Soc. 77, 3656(1955).

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-chemical Institute imeni L. Ya. Karpov)

SUBMITTED: June 1, 1960

Card 3/3

TALALAYEVA, T.V.; RODIONOV, A.N.; KOCHESHKOV, K.A.

Solutions of aromatic organolithium compounds in ethers. Izv.AN SSSR.Otd.khim.nauk no.11:1990-1996 N '61. (MIRA 14:11)

1. Fiziko-khimicheskiy institut im. L.Ya.Karpova.
(Lithium organic compounds)

30170
S/062/61/000/012/011/012
B117/B147

5 3700

AUTHORS: Kocheshkov, K. A., Panov, Ye. M., and Zemlyanskiy, N. N.

TITLE: Stepwise formation of the elementoxane chain in the presence of diazo alkanes

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 12, 1961, 2255

TEXT: In the present "Letter to the Editor", the authors report on the reaction of elemental organic compounds with diazo alkane. They point out that the usually practiced hydrolysis, e.g., of $R_2Sn(OOCR)_2$, results in a mixture of organic tin compounds. In the case examined, an increase of the elementoxane chain takes place whereby, during the individual stages, pure products are isolated and the RCOO end groups are preserved, such as for $(n\text{-}C_4H_9)_2Sn(OOCCH_3)_2$. Monomer (boiling point 142° - 145°C (100 mm Hg)) ⟶ dimer (melting point 58° - 60°C) ⟶ tetramer (melting point 138° - 139°C) ⟶ octamer (decomposition at above 200°C), etc. The

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Stepwise formation of the...

reaction is shown by the example of two elements (Sn, Pb). The authors concluded, however, that the reaction may be extended to other elemental organic compounds comprising at least two saponifiable groups in the element (e.g., $R_2Si(OOCR)_2$ or $RTl(OOCR)_2$, etc.). With diazomethane: (a) $2R_2SnX_2$ (I) $\longrightarrow$ $X(R)_2Sn-O-Sn(R)_2X$ (II). (II) is $C_{20}H_{42}O_5Sn_2$ having a molecular weight of 591. (b) $2X(R)_2Sn-O-Sn(R)_2X$ (II) $\longrightarrow$ $X(R)_2Sn-[O(R)_2Sn]_3-X$ (III). (III) is $C_{36}H_{78}O_7Sn_4$, molecular weight 1109. (c) $2X(R)_2Sn-[O(R)_2Sn]_3-X$ (III) $\longrightarrow$ $X(R)_2Sn-[O(R)_2Sn]_7-X$ (IV). (IV) is $C_{68}H_{150}O_{11}Sn_8$, molecular weight 2156. In each case, $R = n-C_4H_9$ and $X = OOCCH_3$. (d) $2R_2PbX_2$ (I) $\longrightarrow$ $X(R)_2Pb-O-Pb(R)_2X$ (II). In this case, $R = C_6H_5$ and $X = OOCCH(CH_3)_2$. (II) is $C_{32}H_{34}O_5Pb_2$ decomposition at 240°C. (II) was also obtained with diazoethane and diazobutane. [Abstracter's note: Essentially complete translation.] There is 1 Soviet reference. X

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2

[illegible] Inst. im. L. Ya. Karpova

S/020/61/136/002/024/034
B016/B060

AUTHORS: Rodionov, A. N., Talalayeva, T. V., Shigorin, D. N., and Kocheshkov, K. A., Corresponding Member AS USSR

TITLE: Study of the Structure of Complexes of Organolithium Compounds With Ethers by Infrared Spectra

PERIODICAL: Doklady Akademii nauk SSSR, 1961, Vol. 136, No. 2, pp. 369-372

TEXT: The authors wanted to clarify the effect of ethers upon the structure and the character of complexes of organolithium compounds with the ethers. For this purpose they took infrared absorption spectra in the two-beam spectrometer type Н-800 (N-800) featuring a NaCl prism. The following compounds were examined: methyl-, ethyl-, n-butyl, phenyl-, o-, m-, and p-tolyl, p-Cl- and p-Br-phenyl-, mesityl-, and fluorenyl lithium as well as the ethers: $(C_2H_5)_2O$, $(n\text{-}C_3H_7)_2O$, $(iso\text{-}C_3H_7)_2O$, $(n\text{-}C_4H_9)_2O$, and $(iso\text{-}C_5H_{11})_2O$. Table 1 gives the vibration frequencies

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Study of the Structure of Complexes of Organolithium Compounds With Ethers by Infrared Spectra

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B016/B060

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(cm^{-1}) of the C-Li bond in fresh solutions of the mentioned organolithium compounds in the five ethers. Some of the former were synthesized directly in the respective ethers. The authors compared the spectra with the data obtained from their previous studies (Ref. 1) and in this manner assigned the absorption bands to the vibrations of the C-Li...O groups. The conclusion is drawn from an analysis of the data in Table 1 that almost all of the fresh solutions of the 11 substances mentioned display a similar spectrum in the same ether. The replacement of one ether by another has a remarkable effect upon the position of the C-Li...O group bands (Fig. 1 B). The analysis of the spectra proves that the more complicated the radicals used in the ethers, the farther the C-Li...O bands will be shifted in the region of shorter waves. It is inferred from results obtained that during the dissolution of organolithium compounds in ethers the primary complexes are deformed and decompose due to an acceptor-donor interaction and a dipole interaction with the ether. Subsequently, new complexes according to the acceptor-donor type

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Study of the Structure of Complexes of Organolithium Compounds With Ethers by Infrared Spectra

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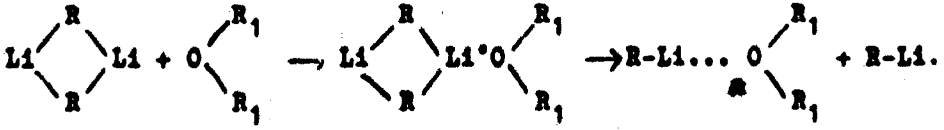

are formed (depending on the structure of the radicals of the two components) between the molecules of the ether and the organolithium compound. In this connection, the polarity of the C-Li bond is increased with increasing stability of the new complexes. In the authors' opinion, this is bound to express itself in a change both of the reactivity of the organolithium compound and its stability in the solution. This circumstance is believed to be the cause of the high activity of ethyl lithium in many reactions in the ethereal medium as well as of the poor stability of this substance in the same medium. There are 2 figures, 1 table, and 8 references: 4 Soviet, 3 German, and 1 British.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physicochemical Institute imeni L. Ya. Karpov)

SUBMITTED: September 14, 1960

Card 3/3

S/020/61/136/003/018/027
B016/B052

AUTHORS: Simonov, A. P., Shigorin, D. N., Talalayeva, T. V., and Kocheshkov, K. A., Corresponding Member AS USSR

TITLE: Examination of the Structure of Lithium Alcoholates by the Method of Infrared Absorption Spectra. O—Li...O Bond

PERIODICAL: Doklady Akademii nauk SSSR, 1961, Vol. 136, No. 3, pp. 634-637

TEXT: The authors examined the structure of R—O—Li bonds: tert.-C_4H_9OLi, CH_3OLi, C_2H_5OLi, n-C_3H_7OLi, and n-C_4H_9OLi. By measuring various properties of tert.-C_4H_9OLi (under the collaboration of V. N. Vasil'yeva, V. A. Dubovitskiy, and O. V. Nogina) the authors found that the O—Li bond of tert.-C_4H_9OLi is of a co-valent character, and the latter associates already in weak solutions. This was proven by infrared spectra in crystallized state and in solutions (Table 1). In hexane, CCl_4, cyclohexane, dioxan, di- and triethyl amine, these spectra hardly differed from those of the crystallized sample. Therefrom, and from the

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Examination of the Structure of Lithium
Alcoholates by the Method of Infrared
Absorption Spectra. O—Li...O Bond

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B016/B052

indifference of tert.-C_4H_9OLi toward active solvents and temperatures between + 70 and -80°C the authors conclude that its complexes are very constant. They attempted to explain the existence of such solid complexes as follows: 1. three-center intermolecular electron orbits are formed due to the fact that the Li atom of a molecule gives the free p-orbit to those electrons which take part in the O—Li σ-bond of another molecule. Consequently, one pair of valence electrons takes part in the formation of two O—Li...O bonds (see scheme Ia); 2. an acceptor - donor interaction sets in during which the unshared pair of p-electrons of the oxygen atom uses the free p-orbit of lithium in another molecule and thus additionally intensifies the intermolecular bond (I b). From the luminescence spectra of tert.-C_4H_9OLi (crystals and solutions in hexane), the authors conclude that either one electron changes over from the multi-center molecular orbit of the ground state into the excited multi-center orbit, or that the system is excited by the passage of one electron of the unshared pair of the oxygen atom into the multi-center orbit. The four other alcoholates studied, were spectroscopically examined in crystallized state (paste in

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Examination of the Structure of Lithium
Alcoholates by the Method of Infrared
Absorption Spectra. O—Li...O Bond

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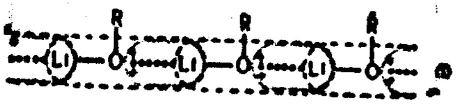
vaseline or fluorinated oils) (Table 2). Since tert.-C_4H_9OLi is closely associated, the authors conclude that lithium alcoholates and unbranched aliphatic radicals are even more closely associated. This explains their insolubility or low solubility in solvents in which tert.-C_4H_9OLi is easily soluble. The authors approximately assigned the bonds of the four latter alcoholates to the complex oscillations of the associated O—Li groups. A more accurate assignment, however, will become possible by further investigations. There are 2 tables and 21 references: 4 Soviet, 1 US, 3 British, and 2 German.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-chemical Institute imeni L. Ya. Karpov)

SUBMITTED: September 14, 1960



Card 3/3

GOL'DSHTEYN, I.P.; GUR'YANOVA, Ye.N.; DELINSKAYA, Ye.D.; KOCHESHKOV, K.A.

Dipole moments of organotin chlorides and their complex-forming ability. Dokl.AN SSSR 136 no.5:1079-1081 F '61. (MIRA 14:5)

1. Fiziko-khimicheskiy institut im. L.Ya.Karpova. 2. Chlen-korrespondent AN SSSR (for Kocheshkov).
(Tin organic compounds--Dipole moments)

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S/020/61/138/004/013/023
B103/B203

AUTHORS: Gol'dshteyn, I. P., Fayzi, N. Kh., Slovokhotova, N. A., Gur'yanova, Ye. N., Viktorova, I. M., and Kocheshkov, K. A., Corresponding Member AS USSR

TITLE: Complexes of diphenyl ethylene with tin tetrachloride and organo-tin chlorides

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 138, no. 4, 1961, 839-842

TEXT: The authors studied complexes of asymmetric diphenyl ethylene (DPE) with $SnCl_4$, $C_6H_5SnCl_3$, and $(C_6H_5)_2SnCl_2$. The catalytic activity of $SnCl_4$ is explained with the formation of π-complexes with monomers without ever clarifying the nature of these complexes. The authors studied them by (A) infrared spectra, (B) electron spectra, and (C) dielectric polarization. In previous papers (I. P. Gol'dshteyn et al., Ref. 4: DAN, 136, No. 5 (1961)) it had been found by method (C) that the mentioned compounds formed a series according to their capability of forming complexes with dioxane: $SnCl_4 > C_6H_5SnCl_3 > (C_6H_5)_2SnCl_2$. The authors tried to find out whether or

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not this series was also maintained in complexes with monomers. The following systems were studied: (a) $SnCl_4$ + DPE, (b) $C_6H_5SnCl_3$ + DPE, (c) $(C_6H_5)_2SnCl_2$ + DPE, (d) $SnCl_4$ + DPE + DPE-dimer, and (e) $C_6H_5SnCl_3$ + DPE + DPE-dimer. (A) The spectra were taken with a split-beam spectrophotometer H-800 (H-800) with fluorite cuvettes and Teflon insertions (20 μ). The mixtures were prepared in an airtight chamber in dry nitrogen and filled into cuvettes. $SnCl_4$ and $C_6H_5SnCl_3$ in DPE give green solutions with an absorption band 610 mμ and an intensive absorption below 500 mμ. (B) The electron spectra were taken with an CΦ-4 (SF-4) spectrophotometer in benzene solution. Results of (A): as compared with the spectra of pure DPE, the spectra of systems (a) and (b) show considerable changes: (1) The bands of the region 1612, 1420 - 1400, and 1335 cm^{-1} disappear, the intensity of the band 1578 cm^{-1} decreases strongly. They are all connected with the double bond in the molecule of diphenyl ethylene. The band 1615 cm^{-1} belongs to the stretching vibrations of the C = C double bond whose frequency is reduced owing to the conjunction with phenyl rings. The bands 1400 and 1330 cm^{-1} belong to the deformation vibrations of the methylene group on the double bond. The band 1578 cm^{-1} belongs to the vibrations of

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Complexes of diphenyl ethylene with tin...

the phenyl ring. Its intensity increases strongly due to the interaction with the conjugate double bonds. (2) New bands appear in the regions 1376, 1250, and 1220 cm^{-1}. (3) The band 1605 cm^{-1} of the benzene ring vibration is slightly shifted, and its intensity increases. Besides, the authors measured the spectrum of the solution of the DPE dimer in DPE to prove that the above-mentioned changes (1)-(3) are not connected with the appearance of the dimer in the above systems. This spectrum shows two additional bands which are absent in the spectrum of the monomer. The band 1665 cm^{-1} belongs to the stretching vibrations of the C = C bond in the dimer. The band 1785 cm^{-1} possibly belongs to the CH deformation vibrations on the double bond. None of these two bands appears in the spectra of systems (a) and (b). The authors consider this fact as a proof that the changes (1)-(3) in the infrared spectra are not caused by the dimer but by the intermediates of the interaction of DPE with the tin halides. Further spectral data suggest that the dimer also forms complexes with $SnCl_4$ and $C_6H_5SnCl_3$. (C) The authors measured the dipole moment of DPE in benzene solution with excess $SnCl_4$, and obtained the value 1D. Thus, it lies by 0.7-0.8 D higher than the dipole moment in benzene. For these reasons, the

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Complexes of diphenyl ethylene with tin... B103/B203

authors think that the band 480 mμ (contrary to statements made by A. C. Evans et al. (see below)) cannot be explained with carbonium ions. The absorption band in the region 610 mμ may be ascribed to the π-complex. According to A. N. Terenin et al. (Ref. 10: Optika i spektroskopiya, 3, 480 (1957); Izv. AN SSSR, OKhN, 1958, 1100), the frequency of the valency formation decreases by 115-195 cm^{-1} in the complex formation from cyclohexane and $SnCl_4$; besides, absorption bands appear in the region 1400-1340 and 1200 cm^{-1}; The band 1525 cm^{-1} in systems (d) and (e) is ascribed to the reduced (by 140 cm^{-1}) frequency of vibrations of the double bond in the π-complex of the dimer with the tin halides. In contrast to systems (a) and (b), the authors had not found any indications of a formation of π-complexes in system (c). The solutions of the latter in benzene are colorless, and no changes were observed in their infrared spectrum as compared with the spectra of components. Thus, the authors proved that the above-mentioned order was also maintained in the case of complexes with monomers. They conclude that $C_6H_5SnCl_3$ can also be a catalyst for the polymerization of olefins whereas this cannot be expected for $(C_6H_5)_2SnCl_2$. There are 3 figures, 1 table, and 10 references: 5 Soviet-bloc and 5 non-

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Complexes of diphenyl ethylene with tin... B103/B203

Soviet-bloc. The 4 references to English-language publications read as follows: Ref. 1: P. H. Plesh, Cationic Polimerisation and Related Complexes, London, 1953; Ref. 6: N. Sheppard, D. M. Simpson, Quart. Rev., 6, 1 (1952); Ref. 8: A. G. Evans et al., J. Chem. Soc., 2975, 1957, 105; 1956, 2757; 1955, 1524; Ref. 9: G. E. Coates, L. E. Sunou, J. Chem. Soc., 1942, 567.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-chemical Institute imeni L. Ya. Karpov)

SUBMITTED: December 23, 1960

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Card 5/5

GOL'DSHTEYN, I.P.; GUR'YANOVA, Ye.N.; KOCHESHKOV, K.A.

Molecular compounds of tin tetrachloride with organic sulfides.
Dokl.AN SSSR 138 no.5:1099-1102 Je '61. (MIRA 14:6)

1. Fiziko-khimicheskiy institut im. L.Ya.Karpova. 2. Chlen-korrespondent AN SSSR (for Kocheshkov).
(Tin organic compounds)

29017

S/020/61/140/004/018/023
B106/B110

5.3700

AUTHORS: Talalayeva, T. V., Rodionov, A. N., and Kocheshkov, K. A., Corresponding Member AS USSR

TITLE: Ternary complexes of methyl lithium

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 140, no. 4, 1961, 847-850

TEXT: Methyl lithium is very stable in diethyl ether and, thus, like the aromatic lithium compounds, phenyl lithium and tolyl lithium, which form ternary complexes of the composition $2RLi \cdot LiX \cdot 2(C_2H_5)_2O$ in ether solutions (Ref. 2: T. V. Talalayeva, K. A. Kocheshkov, DAN, 104, 260 (1955)). The authors investigated whether such ternary complexes also formed in the case of methyl lithium. Crystalline ternary complexes of the composition $CH_3Li \cdot LiX \cdot 2(C_2H_5)_2O$ (X = Br, I) could be isolated from ether solutions of methyl lithium which were obtained by reacting lithium with methyl chloride or iodide. These complexes are stable in nitrogen or argon atmosphere. Primarily the less soluble lithium iodide dietherate precipitates when lithium iodide exceeds methyl lithium. In case of lithium bromide excess

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Ternary complexes of methyl ...

in the solution, crystalline precipitates with increasing content of lithium bromide and ether are formed, e.g., $CH_3Li \cdot 2LiBr \cdot 3(C_2H_5)_2O$ or $CH_3Li \cdot 5LiBr \cdot 7(C_2H_5)_2O$. This behavior is similar to that of binary complexes of aliphatic lithium compounds with lithium halides ($RLi \cdot nLiX$, n from 1.4 to 6), which form in the reaction of alkyl halides and aliphatic RLi in hydrocarbon media. The monoetherate of methyl lithium, $CH_3Li \cdot (C_2H_5)_2O$, could be isolated from the above-mentioned ether solutions of methyl lithium. This compound contains small impurities of LiCl which are probably complex-bound. A fine powder with an IR spectrum characteristic of crystalline methyl lithium is obtained when methyl lithium is precipitated from ether solutions by excess n-pentane and the precipitate dried in vacuo at 100°C (Ref. 7: A. N. Rodionov, D. N. Shigorin, T. V. Talalayeva, K. A. Kocheshkov, DAN, 123, 113 (1958); Izv. AN SSSR, OKhN, 1958, 120; Izv. AN SSSR, ser. fiz., 22, 1110 (1958); T. L. Brown, M. T. Rogers, J. Am. Chem. Soc., 79, 1859 (1957)). This powder is, however, poorly soluble in ether even when heated (0.2-0.5 N solutions), and contains 8% lithium chloride impurities. Presumably, methyl lithium precipitates in highly associated form on destruction of the ether complex

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B106/B110

Ternary complexes of methyl ...

by n-pentane. Methylene dilithium, CH_2Li_2, a loose, fine precipitate of extreme inflammability in air, forms on pyrolysis of the resultant powder at 240°C according to Ref. 6 (K. Ziegler, K. Nagel, M. Patheiger, Zs. anorg u. allgem. Chem., 282, 345 (1955)). Methyl lithium and methylene dilithium were used to polymerize ethylene with $TiCl_4$ (1 : 1) (Ref. 9: K. A. Kocheshkov, V. A. Kargin, T. V. Talalayeva, T. I. Sogolova, O. A. Paleyev, Vysokomolek. soyed., 1, 152, (1959); J. Polym. Sci., 34, 121 (1959)). The IR spectrum of CH_3Li in the range 2000-650 cm^{-1} is not affected by formation of the ternary complex of CH_3Li with lithium halide and ether (Ref. 8: A. N. Rodionov, T. V. Talalayeva, D. N. Shigorin, K. A. Kocheshkov, DAN, 136, 369 (1960)). The capability of forming ternary complexes with ether and lithium bromide is not limited to aliphatic and aromatic RLi but becomes also evident in the case of lithium acetylides. When pure acetylene is introduced into an ether solution of RLi (R = CH_3, C_6H_5, $CH_3C_6H_4$) containing an equimolecular quantity of lithium bromide, lithium acetylide precipitates, which contains lithium bromide

Card 3/4

SIMONOV, A.P.; SHIGORIN, D.N.; TALALAYEVA, T.V.; KOCHESHKOV, K.A.

Infrared absorption spectra of some R - O - Li compounds.
Dokl. AN SSSR 141 no.3:665-667 N '61. (MIRA 14:11)

1. Fiziko khimicheskiy institut im. L.Ya. Karpova. 2. Chlen-korrespondent AN SSSR (for Kocheshkov).
(Lithium organic compounds—Spectra)

KOCHESHKOV, K.A.

(4)

KOCHESHKOV, Ksenofont A., Corresponding Member, Academy of Sciences USSR, CHEVERDINA, N. I., and PALEYEVA, I. E., all at Scientific Research Physico-Chemical Institute imeni L. Ya. Karpov - "Research in the realm of organometallic compounds of zinc and cadmium" (Morning session 28 Sep 62) [Only KOCHESHKOV is included in the List of Participants in the Colloquium. KOCHESKHKOV is also scheduled as President of the Morning session 25 Sep 62.]

REUTOV, Oleg A., Faculty of Chemistry, Moscow State University - "On the synthesis of optical active alkylmagnesium and alkyllithium compounds by means of mercuriorganic compounds" (Morning session, 25 Sep 62)

report to be submitted for the Intl, Colloquium on Organometallic Derivatives (CNRS) Paris France, 24-28 Sep 1962.

S/844/62/000/000/068/129
D204/D307

AUTHORS: Abramova, L. V., Sheverdina, N. I. and Kocheshkov, K. A.

TITLE: The preparation of organotin compounds under high energy irradiation

SOURCE: Trudy II Vsesoyuznogo soveshchaniya po radiatsionnoy khimii. Ed. by L. S. Polak. Moscow, Izd-vo AN SSSR, 1962, 394-397

TEXT: Compounds of the general formula R_2SnBr_2 (where R = n-propyl, n-butyl, n-hexyl, n-heptyl, n-octyl and n-nonyl) were synthesized by γ irradiation of powdered Sn with the corresponding alkyl bromide, at 90 - 100°C, in yields of 30 - 165 mol/100 ev with a dose of 18 - 20 Mr (37 - 74% of theoretical yields calculated w.r.t. RBr), since such compounds may be used to prepare R_2SnX_2 (where X = organic acid radical), used as stabilizers and catalysts in plastics technology. The yields of n-Bu_2SnBr_2 and n-Pr_2SnBr_2 increased with increasing dose of irradiation, to maxima of 74% at 18.3 and

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The preparation of ...

S/844/62/000/000/068/129
D204/D307

69 at 19.7 Mr for the butyl and propyl compounds respectively. The energy yields decreased with increasing dose. The compounds formed under a certain induction period. Experimental details are given of (a) above reactions, which involved the irradiation of premixed Sn powder and RBr in an ampoule, and (b) the preparation of n-Bu_2SnBr_2 in an apparatus in which n-BuBr circulated gradually into an irradiated ampoule containing the Sn, and the reaction product and unreacted bromide passed back into the flask holding the original n-Bu_2SnBr_2 to be raised to 300 - 400 mol/100 ev. There are 1 figure and 3 tables.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-Chemical Institute im. L. Ya. Karpova)

Card 2/2

SIMONOV, A.P.; SHIGORIN, D.N.; TALALAYEVA, T.V.; KOCHESHKOV, K.A.

Association of tert.C_4H_9OLi in the gaseous state. Izv.AN SSSR.-Otd.khim.nauk no.6:1126 '62. (MIRA 15:8)

1. Fisiko-khimicheskiy institut im. L.Ya.Karpova.
(Lithium butoxide—Spectra)

S/064/62/000/010/001/002
D214/D307

AUTHORS: Shaverdina, N.I., Abramova, L.V., Paleyeva, I.Ye. and Kocheshkov, K.A. Corresponding Member of the AS USSR

TITLE: Preparation of organic salts of di-*n*-butyltin

PERIODICAL: Khimicheskaya promyshlennost', no. 10, 1962, 7-8

TEXT: This paper reports a new method of preparing organic salts of di-*n*-butyltin, suitable for application on an industrial scale. The interaction of $SnCl_4$ with $n\text{-}C_4H_9\,MgCl$ in $(n\text{-}C_4H_9)_2O$ forms $(n\text{-}C_4H_9)_2\,SnCl_2$ which on treatment with 30% ethanolic NaOH gives a precipitate of $(n\text{-}C_4H_9)SnO$. A slow addition of this oxide (1.25 moles) to 2.5 moles of a warm organic acid (60-70°C) gives, after 2 hours, the organic salt (95-98% yields). In this way the dicaprylate, dilaurate, distearate, and dioleate of di-*n*-butyltin were prepared. The dimaleate and diacetate were obtained by adding 1 mole of the oxide to 1 mole of the corresponding anhydride dissolved in toluene (yields > 95%). There is 1 table.

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KOCHESHKOV, K.A.

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38767

S/190/62/004/006/016/026
B124/B138

15.8100

AUTHORS: Dokukina, A. F., Yegorova, Ye. I., Kazennikova, G. V., Kolom, M. M., Kocheshkov, K. A., Smirnova, Z. A., Talalayeva, T. V.

TITLE: Synthesis and polymerization (copolymerization) of fluoren-substituted styrenes. I. Copolymerization of fluoren-substituted styrenes with vinyl monomers

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4, no. 6, 1962, 885 - 888

TEXT: This paper describes the authors' experiments in the production and
characterization of the copolymers of α, β, β'-trifluoro styrene with 2,5-
dimethyl styrene and methyl methacrylate; o-, m- and p-methyl-α, β, β'-
trifluoro styrene with styrene, α, β-difluoro-β'-chloro styrene with
styrene, and 2,5-difluoro styrene. The emulsion used for copolymerization
consisted of 80 - 85 % water, 2.5 emulsifier (sodium stearate or oleate),
and 0.5 % persulfate initiator. The monomer mixture, which was added drop-
wise after heating to 80 - 90°C, contained azoisobutyric acid dinitrile
(0.5 %) as initiator. Eleven copolymers of the above monomers were ob-
tained. Their compositions and properties are given in Table 2. The best

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Synthesis and polymerization ... S/190/62/004/006/016/026
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resistance of the copolymers thus produced increases with the fluoro styrene content in the copolymer. An exception is that of α,β-difluoro-β'-chloro styrene with styrene, the heat resistance of which is 4°C higher than that of polystyrene produced under similar conditions. This is probably due to the low concentration of substituted styrene (16 mole%) in the copolymer, and to the extremely low molecular weight of the product ($[\eta] = 0.05$). There are 2 tables. The English-language references are: D. Livingstoun, J. Polymer Sci., 20, 485, 1956; M. Prober, J. Amer. Chem. Soc., 75, 968, 1953.

ASSOCIATION: Institut vysokomolekulyarnykh soyedineniy AN SSSR (Institute of High-molecular Compounds of the AS USSR)

SUBMITTED: April 11, 1961

Table 2: Copolymerization time, yield, composition and intrinsic viscosities of the copolymers. Legend: (A) length, hours; (B) copolymer yield, %; (C) composition of copolymer (mole%); (D) intrinsic viscosities of the benzene solutions of copolymers at 20°C; (E) copolymers of

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33932
S/079/62/032/001/009/016
D202/D302

5.3700

AUTHORS: Zemlyanskiy, N.N, Panov, Ye.M., and Kocheshkov, K.A.

TITLE: Synthesis of organostannic salts of organic acids

PERIODICAL: Zhurnal obshchey khimii, v. 32, no. 1, 1962, 291-293

TEXT: The authors describe a new method of preparing organostannic salts with organic acids by an exchange reaction between organic lead salts and organic halides of tin, stating that this reaction takes place easily with fairly high yields, e.g. $(Bu)_2SnBr_2 + Pb(000C.Ch_3)_2 \rightarrow (Bu)_2Sn(OOC.CH_3)_2 + PbBr_2$. The lead salts of liquid organic acids can be obtained by dissolving litharge in the corresponding acid and may be directly used for the reaction; organostannic salts of dicarboxylic acids can be obtained by direct action of the acid on tin tetraethyl. The starting Sn organic chlorides were obtained by usual methods. The authors synthesized 6 known and 3 new compounds and give full details of the procedure. 1) Triethyl tin acetate was obtained in 77.8 % yield by boiling lead acetate

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Synthesis of organostannic salts ...
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with triethyl tin chloride. 2) Tributyl tin acetate from lead acetate and tri-*n*-butyl tin chloride; yield - 84.5 %. 3) Triethyl tin methacrylate from PbO in methacrylic acid and triethyl tin chloride; yield - 58.7 %; 4) Tri-*n*-butyl tin methacrylate from PbO in methacrylic acid and tri-*n*-butyl tin chloride; yield - 99.1 %. 5) Di-*n*-butyl tin diacetate from lead acetate and di-*n*-butyl tin bromide, yield 85.4 %. 6) Triphenyl tin acetate from lead acetate and triphenyl tin chloride; yield 84.5 %. Physical constants determined for these products were in very good agreement with data given in literature. 7) Diethyl tin adipate was obtained by heating tetraethyl tin with adipic acid; yield - 90 %; m.p. 143-144°C. The compound is soluble in cold $CHCl_3$ and in hot benzene, toluene, tylene, dichloethane and CCl_4. 8) Diethyl tin azelate was obtained by heating tetraethyl tin and azelaic acid. The yield was 79.95 %, m.p. 121-124.5°C. Its solubility is similar to that of the adipate. 9) Diethyl tine sebacate was obtained in the same way from tetraethyl tin and a slight excess of sebacic acid. The yield was 64.9 %; m.p. 122-123°C. Its solubility is similar to that of the above compounds.

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S/079/62/032/001/011/016
D204/D302

AUTHORS: Gol'dshteyn, I.P., Gur'yanova, Ye.N., and
Kocheshkov, K.A.

TITLE: Polar properties of complexes of $SnCl_4$ with unsaturated compounds

PERIODICAL: Zhurnal obshchey khimii, v. 32, no. 1, 1962, 317-318

TEXT: Dipole moments of unsaturated organic compounds in benzene solutions with and without $SnCl_4$ were measured by dielectrometric titration to determine the nature of the bonds between the adducts, as such complexes are of interest in polymerization processes catalyzed by metal halides. Dipole moments of octene-1, styrol, stilbene and 1,1-diphenyl ethylene were only increased by 0.8-1D in the presence of 0.05-0.1 M $SnCl_4$, which formed π-complexes with the hydrocarbons, as opposed to a typical increase of 3-5 D in complexes of the donor-acceptor type. Complexes of $SnCl_4$ with thiophan and tetrahydrofuran (class I) showed marked increases ($\sim$ 2.2 and

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Polar properties of complexes of ...

S/079/62/032/001/011/016
D204/D302

3.7 D), whilst the dipole moments of those with furan and thiophen (class II) were only increased by $\sim$1.2 and 0.3 D. It was, therefore, concluded that complexes I are of the donor-acceptor type whilst complexes II utilize the π-electrons. Reduction in the basic properties of O and S in furan and thiophen is ascribed to the neighboring double bonds. Further work is in progress. There are 3 references: 2 Soviet-bloc and 1 non-Soviet-bloc. The reference to the English-language publication reads as follows: H. Plesh, Cationic polymerization and related complexes, London, 1953.

ASSOCIATION: Fiziko-khimicheskiy institut imeni Karpova (Physico-Chemical Institute imeni Karpov)

SUBMITTED: March 31, 1961

Card 2/2

RODIONOV, A.N.; SHIGORIN, D.N.; TALALAYEVA, T.V.; KOCHESHKOV, K.A.

Structure of complexes formed by aliphatic organolithium compounds. Dokl. AN SSSR 143 no.1:137-139 Mr '62.
(MIRA 15:2)

1. Chlen-korrespondent AN SSSR (for Kocheshkov).
(Lithium organic compounds)

S/020/62/143/003/018/029
B110/B138

AUTHORS: Panov, Ye. M., Zemlyanskiy, N. N., and Kocheshkov, K. A., Corresponding Member AS USSR

TITLE: Investigation of the element-oxane bond. Lead oxanes

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 143, no. 3, 1962, 603-605

TEXT: A method is described for the synthesis of compounds with lead oxane bond which may also be used for other elements. The compounds Ar_2PbX_2 and $ArPbX_3$ (where Ar is the aromatic radical and X is the residue of the organic acid) have low moisture resistance. When left standing in air, their melting point drops and impurities insoluble in organics appear. During recrystallisation, even with the freshly precipitated compound, some drops of acid must be added to prevent hydrolysis. From a solution of diphenyl lead diacetate in a mixture of acetone and water, 15-20% of the substance will gradually separate in the form of $(C_6H_5)_2Pb(OH)\cdot OCOCH_3$. Hydrolysis of $Ar_2Pb(OCOR)_2$ in the presence of diazoalkane produces the lead-oxane bond:

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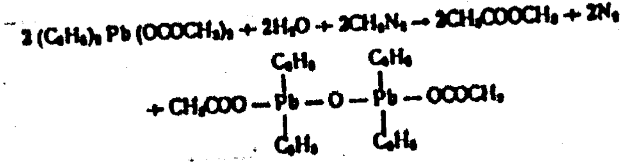
S/020/62/143/003/018/029
B110/B138

Investigation of the element- ...



$$2(C_6H_5)_2Pb(OOCCH_3)_2 + 2H_2O + 2CH_2N_2 \rightarrow 2CH_3COOCH_3 + 2N_2 + CH_3COO-\underset{C_6H_5}{\overset{C_6H_5}{Pb}}-O-\underset{C_6H_5}{\overset{C_6H_5}{Pb}}-OOCCH_3$$

After addition of water 1-2 ml ethereal diazoalkane to the acetone solution of $Ar_2Pb(OCOR)_2$, tetraphenyl diplumbo-oxane diacetate crystallizes out within a few minutes. Excess diazomethane produces almost quantitative yield. In the same way, tetraphenyl diplumbo-oxane was obtained with a yield of 72%. As the reaction does not take place with dry solvents, the hydrolysis of the organo lead salt is the first reaction phase. Diazoalkane does not participate in the synthesis of the final product, but only binds the acid formed during hydrolysis, thus preventing reaction reversal. When heating with organic acids, the lead-oxane bond is broken, and the initial product is re-formed. There are 5 references. The most important reference to English-language publications is: W. T. Reichle, J. Polym. Sci., 49, 521 (1961).

Card 2/3

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-Chemical Institute imeni L. Ya. Karpov)

SUBMITTED: December 30, 1961

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VASIL'YEVA, V.N.; KOCHESHKOV, K.A.; TALALAYEVA, T.V.; PANOV, Ye.M.;
KAZENNIKOVA, G.V.; SOROKINA, R.S.; PETRIY, O.P.

Dipole moments and structure of some fluorine-substituted styrenes. Dokl. AN SSSR 143 no.4:844-846 Ap '62. (MIRA 15:3)

1. Fiziko-khimicheskiy institut im. L.Ya.Karpova. 2. Chlen-korrespondent AN SSSR (for Kocheshkov).
(Styrene—Dipole moments) (Fluorine compounds)

SHEVERDINA, N.I.; PALEYEVA, I.Ye.; DELINSKAYA, Ye.D.; KOCHESHKOV, K.A.

New organocadmium compounds of the Ar_2Cd class, and their dioxanates. Dokl. AN SSSR 143 no.5:1123-1126 Ap 62.
(MIRA 15:4)

1. Fiziko-khimicheskiy institut im. L.Ya.Karpova. 2. Chlen-korrespondent AN SSSR (for Kocheshkov).
(Cadmium organic compounds) (Dioxanate)

S/020/62/144/003/020/030
B119/B101

AUTHORS: Gol'dshteyn, I. P., Gur'yanova, Ye. N., and Kocheshkov, K. A., Corresponding Member AS USSR

TITLE: Complexes of tin tetrachloride with unsaturated compounds containing heteroatoms

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 144, no. 3, 1962, 569-572

TEXT: The complex formation of $SnCl_4$ with furan, 2-methyl furan, thiophene, and diallyl sulfide was studied. The results were compared with those obtained applying $SnCl_4$ to analogous saturated compounds (tetrahydrofuran, tetrahydrothiophene, 2,5-dimethyl thiophane, and dipropyl sulfide). The change in the dielectric constant and in the density of $SnCl_4$ solutions in benzene and hexane (0.05 - 0.08 g-moles/liter) was measured with small amounts of the above-mentioned substances successively added. Where appropriate the method of cryoscopic titration was used. (Results

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Complexes of tin...

S/020/62/144/003/020/030
B119/B101

SUBMITTED: February 22, 1962

Card 3/3

GOL'DSHTEYN, I.P.; IL'ICHEVA, Z.F.; SLOVOKHOTOVA, N.A.; GUR'YANOVA, Ye.N.; KOCHESHKOV, K.A.

Spectroscopic investigation of complexes formed by thiophane and thiopene with tin tetrachloride. Dokl.AN SSSR 144 no.4: 788-791 Je '62. (MIRA 15:5)

1. Fiziko-khimicheskiy institut im. L.Ya.Karpova. 2. Chlen-korrespondent AN SSSR (for Kocheshkov).
(Thiophene--Spectra) (Tin chlorides)

40183
S/020/62/145/005/014/020
B106/B144

11 2214

AUTHORS: Panov, Ye. M., Sorokina, R. S., Zimin, A. V., and Kocheshkov, K. A., Corresponding Member AS USSR

TITLE: Fluorine-containing divinyl benzenes

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 145, no. 5, 1962, 1068-1070

TEXT: The synthesis of two hitherto unknown divinyl benzenes containing fluorine is described: p-α,β-difluoro-β-chlorovinyl styrene and bis-α,β-difluoro-β-chlorovinyl benzene. In both cases the initial material, p-lithium-α,β-difluoro-β-chlorostyrene, was produced as described earlier (Izv. AN SSSR, OKhN, 1961, 532) by a 20-30 min action of butyl lithium on p-bromo-α,β-difluoro-β-chlorostyrene in absolute ether at -70°C. This new organolithium compound gives all reactions of ordinary aromatic lithium compounds feasible at -70°C. Action of acetaldehyde at -70°C yields p-α,β-difluoro-β-chlorovinyl phenyl methyl carbinol (42% yield, b. p. 107 - 116°C (4 mm), n_D^{20} 1.5455, d_4^{20} 1.2800). This intermediate product is dehydrated in vacuo by heating with potassium bisulfate to 200°C.
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p-α,β-difluoro-β-chlorovinyl styrene (b. p. 66 - 69°C (2 mm), n_D^{20} 1.5650, d_4^{20} 1.2563) forms in 50% yield. Polymerization of this product (benzoyl peroxide as a starter, 2.5 hrs heating over a water bath) gave a solid, transparent product insoluble in organic solvents and swelling slightly in benzene and xylene. To produce bis-α,β-difluoro-β-chlorovinyl benzene, p-lithium-α,β-difluoro -β-chlorostyrene was mixed with trifluoro chloroethylene immediately after its production at -75°C. Data of the reaction product: b. p. 100 - 105°C (5 mm), n_D^{20} 1.5430, d_4^{20} 1.4240. This product polymerizes in the presence of benzoyl peroxide at 100°C at about the same rate as styrene with formation of a solid, transparent polymer which, unlike polystyrene, is not soluble on heating in aromatic hydrocarbons and swells in them only slightly. The polymer is stable on heating in air up to 210°C. The two compounds described exemplify the possible combinations of the groups $-CH{=}CH_2$, $-CF{=}CFCl$, $-C(CF_3){=}CH_2$, etc. synthesized by the authors in fluorine-containing divinyl benzenes. There is 1 figure.

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S/020/62/145/005/014/020
B106/B144

Fluorine containing divinyl ...

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-chemical Institute imeni L. Ya. Karpov)

SUBMITTED: May 11, 1962

Card 3/3

S/020/62/146/006/010/020
B106/B186

AUTHORS: Zemlyanskiy, N. N., Panov, Ye. M., Kocheshkov, K. A., Corresponding Member AS USSR

TITLE: Dialkyl tin

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 146, no. 6, 1962, 1335-1336

TEXT: As no reliable method has so far been worked out for the synthesis of tin dialkyls, the data published on these compounds differ greatly. Referring to a reaction made by G. Wittig, F. I. Meyer, G. Lange (Ann., 571, 167 (1951)) the authors of this article succeeded in synthesizing analytical-grade di-n-butyl tin and diethyl·tin by reacting a suspension of anhydrous $SnCl_2$ in a 1:4 mixture of ether and benzene with an ether solution of n-butyl lithium and with ethyl lithium, respectively (reaction temperature, -10°C; molar ratio between $SnCl_2$ and alkyl lithium = 1:2). Di-n-butyl tin is thus obtained in a yield of 63.7% and in the form of a dark cherry-red oil readily soluble in hexane, benzene, toluene, ether, chloroform, and carbon tetrachloride, but poorly soluble in alcohol and

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Dialkyl tin ..

S/020/62/146/006/010/020
B106/B186

acetone. Diethyl tin is obtained similarly in a yield of 40.8% in the form of a dark, cherry-red oil which is as soluble as di-n-butyl tin. Both tin dialkyls oxidize in air and more quickly in solution. In the case of di-n-butyl tin, a white product is formed, which, together with HCl, gives $(C_4H_9)_2SnCl_2$, m.p. 42-43°C. The oxidation of diethyl tin is more complex. Di-n-butyl tin reacting with bromine in CCl_4 gives $(C_4H_9)_2SnBr_2$, m. p. 18.5-19.5, in a quantitative yield. Di-n-butyl tin heated in a sealed ampoule with an argon atmosphere begins to precipitate metallic tin at 230°C. The tin dialkyls synthesized here are polymers. Their molecular weights were determined by cryoscopy and ebullioscopy and were found to be 1780 and 1633, respectively, for diethyl tin, and 1921 and 1745, for di-n-butyl tin. There is 1 table. The most important English-language references are: T. Harada, Sci. Papers Inst. Phys. Chem. Res. (Tokyo), 35, 290 (1939); S.F.A. Kettle, J. Chem. Soc., 1959, 2936.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-chemical Institute imeni L. Ya. Karpov)

SUBMITTED: July 9, 1962

Card 2/2

ZEMYLANSKIY, N.N.; PANOV, Ye.M.; KOCHESHKOV, K.A.

Dialkyltin. Dokl. AN SSSR 146 no.6:1335-1336 O '62.
(MIRA 15:10)

1. Fiziko-khimicheskiy institut im. L.Ya.Karpova. 2. Chlen-korrespondent AN SSSR (for Kocheshkov).
(Tin)

SHEVERDINA, N.I.; ABRAMOVA, L.V.; PALEYEVA, I.Ye.; KOCHESHKOV, K.A.

Preparation of organic salts of di-n-butyl tin. Khim.prom.
no.10:707-708 O '62. (MIRA 15:12)

1. Chlen-korrespondent AN SSSR (for Kocheshkov).
(Tin organic compounds)

SIMONOV, A.P.; SHIGORIN, D.N.; TALALAYEVA, T.V.; KOCHESHKOV, K.A.

Study of the lithium alcoholate structure by the method of infrared absorption spectra; O-Li...O bond. Isv. AN SSSR.Ser.fis. 26 no.10: 1246-1249 O '62. (MIRA 15:10)

(Lithium alcoholate—Spectra)

KOCHESHKOV, K.A., PALEYEV, O.A., SOKOLOVA, T.I., SHEVERDINA, N.I.,
TALALAYEVA, T.V., RODIONOV, A.N.

Nouveaux composants des catalyseurs de la polymerisation de l'ethylene dans des conditions habituelles et inhabituelles.

Report submitted for the International Symposium of Macromolecular Chemistry, Paris, 1-6 July 63

IOFFE, Saveliy Timofeyevich; NESMEYANOV, Aleksandr Nikolayevich;
KOCHESHKOV, K.A., otv. red.; OKHLOBYSTIN, O.Yu., red.;
DOROKHINA, I.N., tekhn. red.

[Methods of the chemistry of organometallic compounds; magnesium, beryllium, calcium, strontium, barium] Metody elementno-organicheskoi khimii; magnii, berillii, kal'tsii, strontsii, barii. Pod obshchei red. A.N.Nesmeianova i K.A. Kocheshkova. Moskva, Izd-vo AN SSSR, 1963. 561 p.
(MIRA 16:12)

1. Chlen-korrespondent AN SSSR (for Kocheshkov).
(Organometallic compounds)