USSR / General and Special Zoology. Insects. Insects and Arachnids. Biological Method of Controlling Insects and Arachnids. P

Abs Jour: Ref Zhur-Biol., No 21, 1958, 96613.

Author : Talalayev, Ye. V.
Inst : Not given.
Title : Reproduction of Epizootic Septicemia in Caterpillars of the Siberian Silkworm.

Orig Pub: Entomol. obozreniye, 1957, 36, No 4, 845-859.

Abstract: A section of young cedar plantings was artificially infested with spores of Bacillus dendrolimus. Siberian silkworm caterpillars of the IV-V generations were released on the section in the summer of 1954, and caterpillars of the V-VI generations were released in the spring of 1955 (a flight year). These experiments demon-

Card 1/3

USSR / General and Special Zoology. Insects. Insects and Arachnids. Biological Method of Controlling Insects and Arachnids. P

Abs Jour: Ref Zhur-Biol,, No 21, 1958, 96613.

Abstract: of secondary infestation of the larvae. The location of the cocoons in the upper stratum of the crowns was chiefly responsible for that. -- B. M. Gershenzon.

Card 3/3

TALALAYEV, Ye. V. (Irkutsk)

Bacteriological method for controlling the tent caterpillar Dendrolimus sibiricus. Zashch. rast. ot vred. i bol. 6 no.6: 20-22 Je '61. (MIRA 16:4)

1. Zaveduyushchiy kafedroy fiziologii i mikrobiologii Irkutskogo universiteta.

(Tent caterpillars—Biological control)
(Bacillus Dendrolimus)

TALALAYEV, Ye.V., kand.biolog.nauk

Let's exterminate the larch spinner (Dendrolimus sibiriens).
Priroda 51 no.2:79-83 F '62. (MIRA 15:2)

1. Irkutskiy gosudarstvennyy universitet.
(Tent caterpillars)

TALALAYEVA, A. V.

"Reaction of the Stroma of Stomach and Duodenum in Ulcerous Diseases." Cand Med Sci, First Moscow Medical Inst, Moscow, 1953. (RZhBiol, No 3, Oct 54)

Survey of Scientific and Technical Dissertations Defended at USSR Higher Educational Institutions (10)

SO: Sum. No. 481, 5 May 55

2697. TALALAEVA A. V. Moscow *A malignant leiomyoma of the stomach with multiple metastases (Russian text)* Arkh. Patol. 1957, 19/1 (78–82) Illus. 4

A 52-year-old man developed nausea, epigastric pain, weight loss and weakness 9 yr. prior to death. Four years after the onset of these symptoms a tumour in the greater curvature of the stomach was diagnosed roentgenologically and a gastric resection was performed. At that time a metastatic nodule was found in the omentum. For several years the patient's condition remained satisfactory, but eventually he developed progressive cachexia and jaundice, and finally he expired. Autopsy revealed metastatic leiomyosarcoma in the liver, kidneys, adrenals, lungs, heart, retroperitoneal and omental lymph nodes, and in the skeletal system. The author points out that leiomyosarcoma of the stomach is a rare neoplasm constituting not

2697

over 0.5–2% of all primary cancers of the stomach. Of 380 gastric sarcomas reported in the world literature until 1936 only 9.5% had been diagnosed as leiomyosarcomas.

Wilson – Dearborn, Mich.

BAYANDINA, S.A.; ISAYEVA, L.A.; TALALAYEVA, A.V.; MALYUGINA, Z.N.; KONOPLEVA, A.V.

Clinical picture and outcome of acute disseminated lupus erythematosus. Pediatriia 37 no.1:76-83 Ja '59. (MIRA 12:1)

1. Iz kliniki detskikh bolezney (dir. - deystvitel'nyy chlen AMN SSSR prof. Yu.F. Domborvskaya) i kafedry patologicheskoy anatomii (zav. - chlen-korrespondent AMN SSSR prof. A.I. Strukov) I Moskovskogo ordena Lenina meditsinskogo instituta.

(LUPUS ERYTHEMATOSUS, DISSEMINATED, in inf. & child acute, clin. picture & outcome (Rus))

GUTKINA, A.V.; TALALAEVA, A.V.

Fluorescence cytological method for detecting cancer cells in the lymph nodes. Vop. onk. 6 no.4:74-79 Ap '60. (MIRA 14:3)
(LYMPHATICS--CANCER)

VASILENKO, N. V., nauchnyy sotrud.; TALALAYEVA, A. V., kand. med. nauk

Cancer of the larynx in a 13-year-old boy. Vest. otorin. no.4: 93-95 '61. (MIRA 15:2)

1. Iz otdeleniya bolezney ukha, gorla i nosa (zav. - prof. D. I. Zimont[deceased]) patologoanatomicheskogo otdela (zav. - kandidat meditsinskikh nauk Z. V. Gol'bert,) Onkologicheskogo instituta imeni P. A. Gertsena, (nauchnyy rukovoditel' - deystvitel'nyy chlen AMN SSSR prof. A. I. Savitskiy), Moskva.

(LARYNX--CANCER)

SILINA, I.G.; TALALAYEVA, A.V.

Pseudotumor of the costal cartilage (Tietze syndrome). Vop. onk. 7 no.2:54-60 '61. (MIRA 14:5)
(RIBS—DISEASES)

ASNIN, D. I.; TALALAYEVA, A. V. (Moskva)

Lysis of hyphae of Actinomyces in tissues of patients with actinomycosis. Arkh. pat. no.9:47-50 '61. (MIRA 15:6)

1. Iz otdela bor'by s aktinomikozom Instituta meditsinskoy parazitologii i tropicheskoy meditsiny imeni Ye. I. Martsinovskogo (dir. - deystvitel'nyy chlen AMN SSSR prof. P. G. Sergiyev) i patologoanatomicheskogo otdeleniya (zav. - kandidat meditsinskikh nauk Z. V. Gol'bert) Gosudarstvennogo onkologicheskogo instituta imeni P. A. Gertsena (dir. - prof. A. N. Novikov)

(ACTINOMYCOSIS)

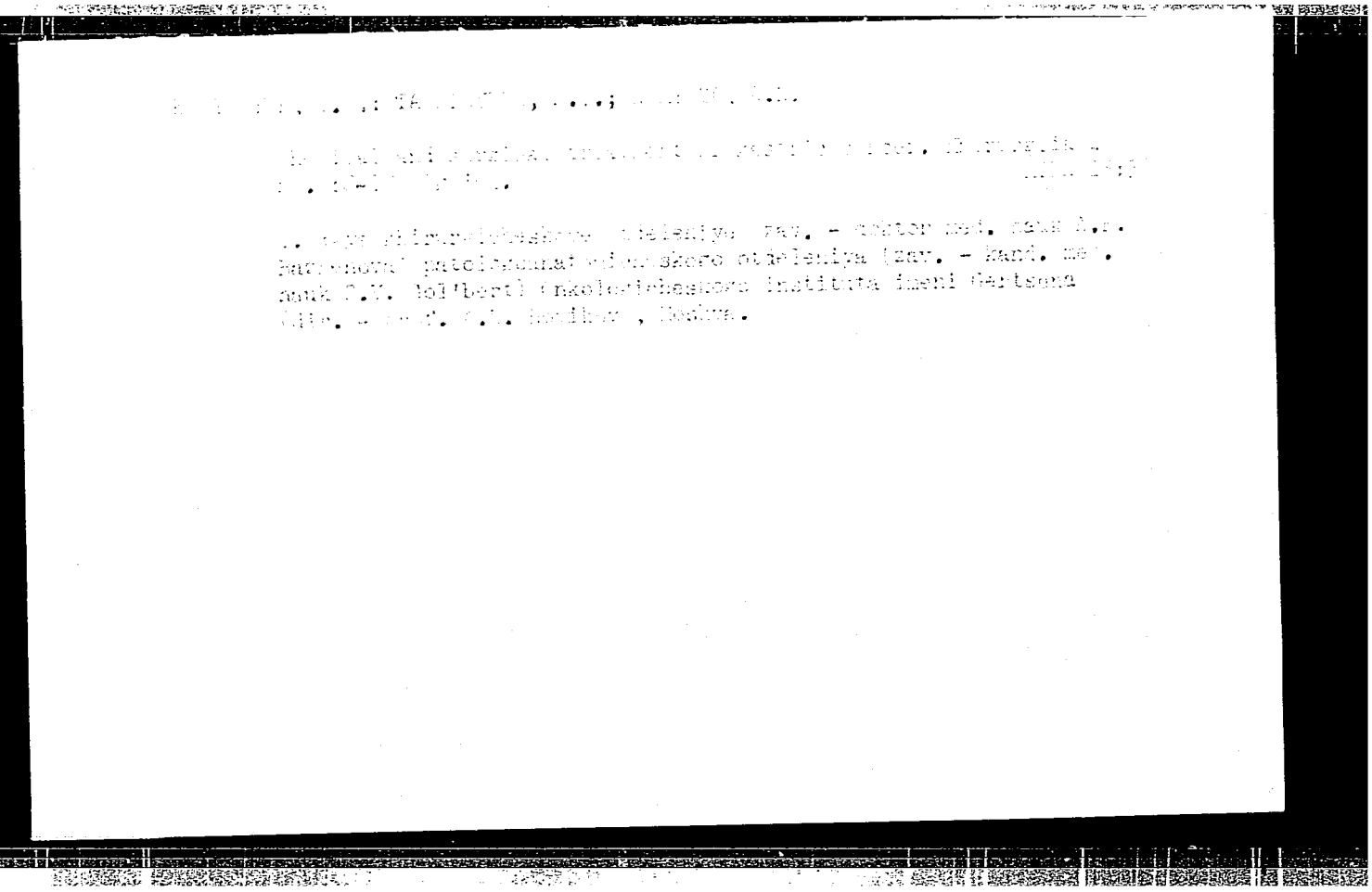
TALALAYEVA, A. V., kand. med. nauk; FILATOVA, A. M.

Sarcomas of the parametrium. Akush. i gin. 38 no.3:78-81 My-Je '62. (MIRA 15:6)

1. Iz ginekologicheskogo otdeleniya (zav. - prof. L. A. Novikova) i patologoanatomicheskogo otdeleniya (zav. - kandidat meditsinskikh nauk Z. V. Gol'bert) Gosudarstvennogo onkologicheskogo instituta imeni P. A. Gertsena (dir. - prof. A. N. Novikov)

(UTERUS--CANCER)

DANIYEL GUBER



TALALAYEVA, A.V. (Moskva); ASNIN, D.I. (Moskva)

Diagnosis of actinomycosis in tissues. Arkh. pat. no.11:71-74 '64. (MIRA 18:11)

1. Otdel bor'by s aktinomikozom Instituta meditsinskoy parazitologii i tropicheskoy meditsiny imeni Ye. I. Martsinovskogo (direktor - deystvitel'nyy chlen AMN SSSR prof. P.G. Sergiyev) i patologo-anatomicheskoye otdeleniye (zav. - kand. med. nauk Z.V. Gol'bert) Gosudarstvennogo onkologicheskogo instituta imeni P.A. Gertsena (Direktor - prof. A.N. Novikov).

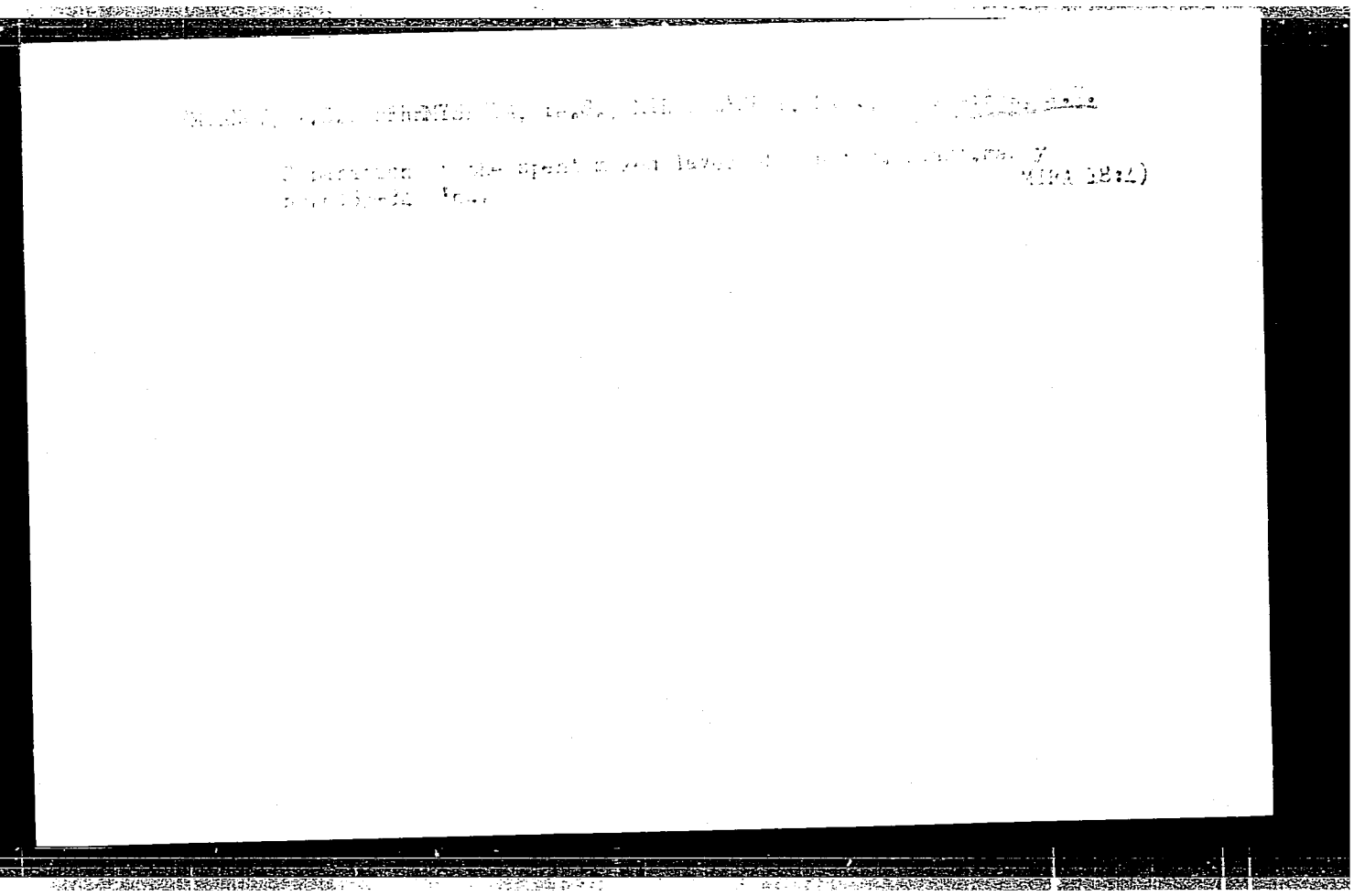
TALALAYEVA, A.V.; KAMILOV, Kh.

Chemodectomas of the stomach. Vop. onk. 11 no.6:3-9 '65.
(MIRA 18:8)

1. Iz patologoanatomicheskogo otdeleniya (zav. - kand.med.nauk Z.V. Gol'bert) i III khirurgicheskogo otdeleniya (zav. - doktor med.nauk A.P.Bazhenova) Gosudarstvennogo onkologicheskogo instituta imeni Gertsena (dir. - prof. A.N.Novikov), Moskva.

PEREMYSLOVA, Ye.S.; TALALAYEVA, A.V.

Studying the performance of a mixed layer of ion exchangers with one colored component in the mixture. Plast. massy no.3:67-69 '64. (MIRA 17:3)



[illegible]

[illegible] by the method of the filtrate. Plast. massy no.6:17-18 '65.
(MIRA 18:8)

L 28713-65 EWT(m)/EWG(m)/T/EWP(t)/EWP(b) IJP(c) JD/RWH

ACCESSION NR: AT5004072 S/3127/63/000/05-/0058/0062

AUTHOR: Sinyakova, S. I., Dudareva, A. G., Markova, I. V., Talalayeva, I. N.

TITLE: Determination of zinc, cadmium, lead, and copper impurities in indium and its salts

SOURCE: USSR. Gosudarstvennyy komitet po khimii. Metody analiza khimicheskikh reaktivov i preparatov, no. 5/6, 1963. Polyarograficheskoye opredeleniye ul'tramikroprimesey s nakopleniyem ihk na statsionamykh rtutnykh ili tverdykh elektrodakh s posleduyushchim rastvoreniyem (Polarographic determination of ultramicro-impurities with their accumulation on stationary mercury or solid electrodes and subsequent dissolution), 58-62

TOPIC TAGS: indium analysis, indium refining, zinc determination, cadmium determination, lead determination, copper determination, amalgam polarography, mercury cathode

ABSTRACT: The method is based on the separation of indium by extraction with diisopropyl ether from a solution of hydrobromic acid followed by a determination of the impurities by the amalgam polarographic technique with their electrolytic accumulation on a stationary mercury cathode. The apparatus, reagents, and solutions employed are listed, and the determination procedure is described. The content of the impurities present in indium as determined by the method of additions is calculated by means of the formula

Card 1/2

L 28713-65

ACCESSION NR: AT5004072

$$\% = \frac{C \cdot h_1 \cdot v_1 \times 100 \times 10^{-6}}{(h_2 - h_1) v_2 \cdot g}$$

where h_1 is the depth of the anode peak of the investigated solution, in mm; h_2 is the depth of the anode peak after the introduction of a standard solution of the impurity, in mm; C is the concentration of the impurity due to the addition, in μg/ml; v_1 is the volume of the solution being analyzed, in ml; v_2 is the volume of the solution after the introduction of the addition, in ml; and g is the weight of the sample in grams. The accuracy of the method varies between ± 3% and ± 15% depending upon the content of impurities. Orig. art. has: 3 figures, 1 table, and 1 formula.

ASSOCIATION: GEOKhI

SUBMITTED: 00Dec62 ENCL: 00 SUB CODE: IC, MM

NO REF SOV: 003 OTHER: 001

Card 2/2

S/075/63/018/003/003/006
E071/E436

AUTHORS: Sinyakova, S.I., Dudareva, A.G., Markova, I.V., Talalayeva, I.N.

TITLE: Determination of copper, lead, cadmium and zinc impurities in particular pure indium and its salts by the method of amalgam polarography with a stationary electrode

PERIODICAL: Zhurnal analiticheskoy khimii, v.18, no.3, 1963, 377-384

TEXT: A method of amalgam polarography with a stationary electrode (mercury drop) was developed for the determination of zinc, cadmium, lead and copper impurities at concentrations down to 10^{-6}% in metallic indium and its salts. The method is based on the extraction of indium (as bromide) with di-isopropyl ether from 5 M HBr. After concentrating the impurities in the mercury drop by electrolysis at a controlled potential from potassium (sodium) hydroxide and HCl solutions, they are determined from the curves of anodic dissolution of the metals from the amalgam at a continuously changing potential. Since indium is not completely removed by the extraction, the effect of additions of complexone III, sodium

Card 1/2

acetate and sodium tartrate on the shift of the indium wave to more negative potentials was investigated by the method of oscillographic polarography. The method was tested on a number of samples of metallic indium and indium iodide with satisfactory results. The maximum error does not exceed ± 15%. There are 6 figures and 4 tables.

ASSOCIATIONS: Institut geokhimii i analiticheskoy khimii im. V.I.Vernadskogo AN SSSR (Institute of Geochemistry and Analytical Chemistry imeni V.I.Vernadskiy AS USSR)
Moskovskiy institut tonkoy khimicheskoy tekhnologii im. M.V.Lomonosova (Moscow Institute of Fine Chemical Technology imeni M.V.Lomonosov)

SUBMITTED: June 26, 1962

SOV/48-23-8-21/25

24(3)
AUTHORS: Mitsuk, V. Ye., Koz'minykh, M. D., Talalayeva, I. V.

TITLE: Measurement of an Electric Field in Plasma of Ultrahigh Frequency

PERIODICAL: Izvestiya Akademii nauk SSSR. Seriya fizicheskaya, 1959, Vol 23, Nr 8, pp 1031-1035 (USSR)

ABSTRACT: In the introduction it is pointed out that the linear Stark effect cannot be investigated in the space of the positive column of a plasma since then fields within the range of 10^3 v/cm would be necessary for a noticeable effect. In the plasma of microwaves, however, such electric fields occur, and the amplitude of the electric field is reported to be 10^4 v/cm for a frequency of 10^{10} cycles. Conditions are described for a Holzmark effect so small that the contours of the Balmer lines represent the Stark effect. It is further shown that measurement of the electric field in microwave plasma is possible by the quantum mechanic theory of the Stark effect introduced by D. I. Blokhintsev. In part I of this article the Stark contour in the alternating field is investigated, and

Card 1/2

formula (1) by Epstein-Schwarzschild is given for line splitting. The line splitting in a static and alternating field is discussed and exemplified in the diagrams of figure 1. The theoretical structure of the alternating field is shown in the diagram of figure 2, and it is indicated that the voltage amplitude of the electric field may be determined by measuring the half width. The methods of measurement are discussed in part II. The results obtained by means of an arrangement, which has already been discussed in a previous paper (Ref 3) where the half width was found by photography, are compared to results determined by means of a photoelectronic multiplier. The diagram of figure 3 shows the comparison. In part III of the present paper the measurement of the electric field is described, and the above methods of measurement and the block scheme of the experimental arrangement are discussed. The measurement of the half width is explained by figure 5. The experimentally determined function of the electric field of high-frequency discharge in deuterium is shown in the diagram of figure 6. There are 6 figures and 3 Soviet references.

SOKOLOV, A.; TALAYEVA, M.; MITIN, P.; MIROPOL'SKIY, I.; OCHKIN, V.; GOL'FMAN, B.; STROMOV, V.; BORISOV, V.

Exchange of practices. Mias. ind. SSSR 33 no.4:33-40 '62. (MIRA 17:2)

1. Vsesoyuznyy nauchno-issledovatel'skiy institut myasnoy promyshlennosti (for Sokolov, Talayeva, Ochkin). 2. Gomel'skiy myasokombinat (for Mitin, Miropol'skiy). 3. Brestskiy myasotrest (for Gol'fman). 4. Kislovodskiy myasokombinat (for Stromov). 5. Rizhskiy zavod "Kompressor" (for Borisov).

TALALAYEVA, O. D.

The complex-forming reactions of ions of bivalent copper with ions of citric acid. O. D. Talalaeva and A. S. Tikhonov (Voronezy State Univ.). *Zhur. Obshchei Khim.* 23, 2067–74(1953).—Photometric, soly., and visual titration methods show that in solns. of $CuSO_4$ and citric acid at pH 2–3 the ion $Cu(H_3C_6H_5O_7)^+$ exists. At pH 3–5 $[Cu(H_3C_6H_5O_7)(HC_6H_5O_7)]^-$ is formed with dissocn. const. 10^{-4}. At pH 7–11.5 the stable ion is $[Cu(OH)(C_6H_5O_7)]^{--}$, $K = 4.5 \times 10^{-11}$, and above pH 12 the ion is $[Cu(OH)_2(C_6H_5O_7)_2]^{4-}$, $K = 1.7 \times 10^{-15}$. H. M. Leicester

SOV/137-58-12-25510

Translation from Referativnyy zhurnal Metallurgiya, 1958, Nr 12, p 201 (USSR)

AUTHORS Kuznetsova, Ye T., Talalayeva, O. D., Tikhonov, A. S.

TITLE Rapid Method for the Analysis of a Cadmium Alloy Using Sodium Versenate (Uskorennyy metod analiza kadmiyevogo splava s primeneniyem trilona B)

PERIODICAL Sb tr Voronezhsk otd Vses khim. o-va im D. I Mendeleyeva, 1957 Nr 1, pp 151-154

ABSTRACT The analysis of the Cd-Sn-Pb alloy is based on the initial separation of Sn in the form of metastannic acid from a nitric-acid solution followed by the volumetric determination of Cd and Pb jointly and of Pb separately in separate portions of the solution. 0.5 g of the alloy are dissolved in 15 cc of HNO_3 (1 : 1), Sn is filtered off, and the filtrate is diluted to 250 cc. 10 cc of 10% KNa-tartarate solution and one drop of methyl red are added to 50 cc of the solution, whereupon it is neutralized with NH_4OH. 10 cc of an ammoniacal buffer solution (mixture of 350 cc of 25% NH_4OH and 54 g NH_4Cl in 1 liter of water), 10 cc of 10% NaCN, solid chromogen black and 100 cc of water are added, and the whole is titrated with sodium versenate (I). The Pb content is calculated according to the

Card 1/2

Rapid Method for the Analysis of a Cadmium Alloy Using Sodium Versenate

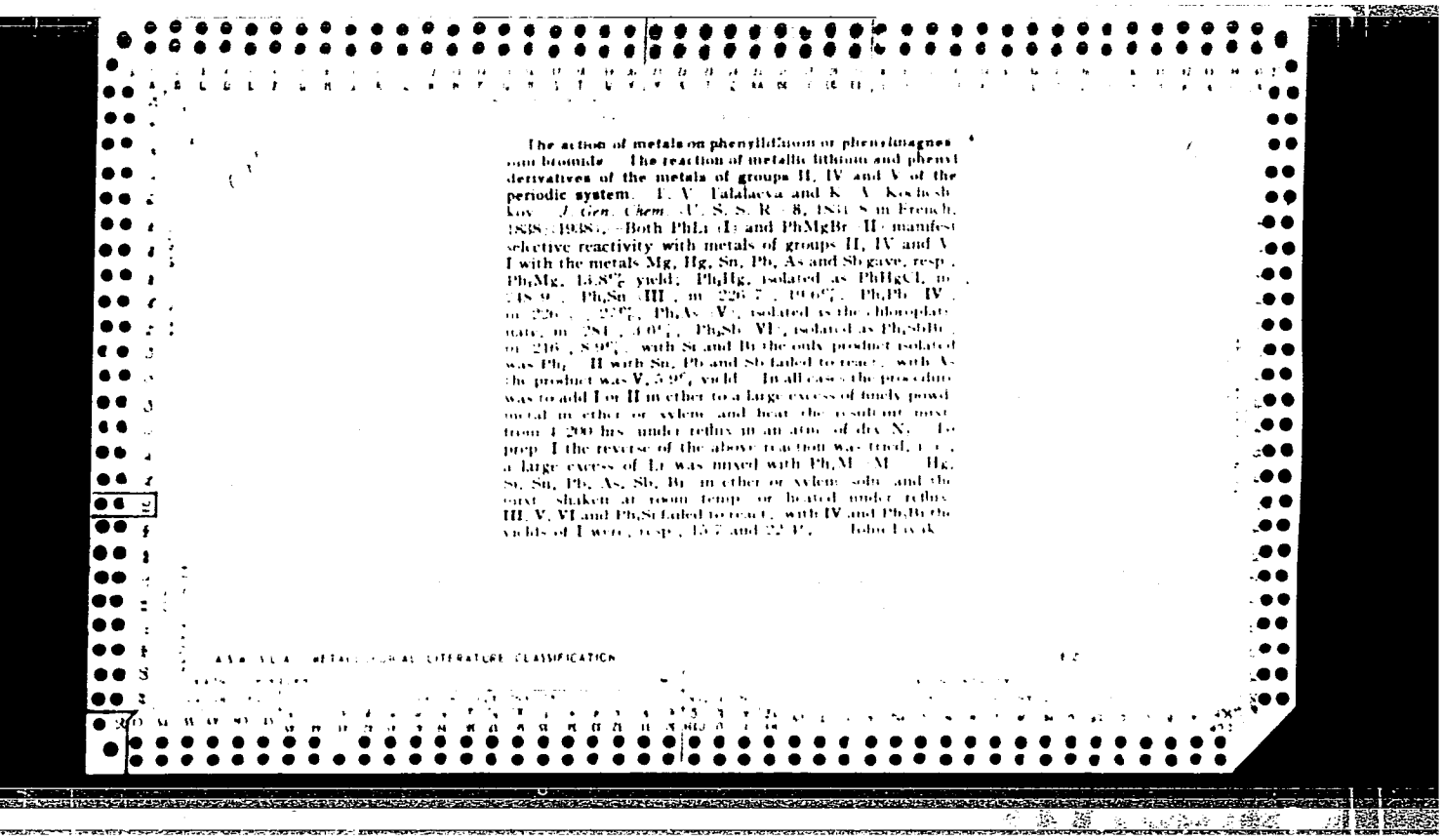
formula %Pb=5 V M 207 21 · 100/1000 D, where V is the volume of I used in the titration of Pb, M is the molarity of I, and D is the weight of the specimen of the alloy. To another 50 cc portion of the solution are added an excess of I solution and one drop of methyl red; it is neutralized with NH_4OH, 10 cc of the ammoniacal buffer and chromogen black are added, and the excess I is titrated with a solution of $MgSO_4$ until the color changes from blue-green to blue. In this way the sum total of Pb and Cd is determined. Cd is calculated by the following formula: %Cd = 5 [(V1M1 - V2M2)-VM1 · 112.41 · 100/1000D], where V_1 is the volume of I taken in excess, M_1 is the molarity of I, V_2 is the volume ["molarity" in Russ Text; Transl Note] of the $MgSO_4$ solution used for the back titration, and M_2 is the molarity of $MgSO_4$. Results are adduced for the analysis of the following alloys: (in %) Sn 46 5, Cd 17 3, and Pb 35.5 with an error for Cd from -0.29 to +0 36% and for Pb from -0 49 to +0.13%

Z. G.

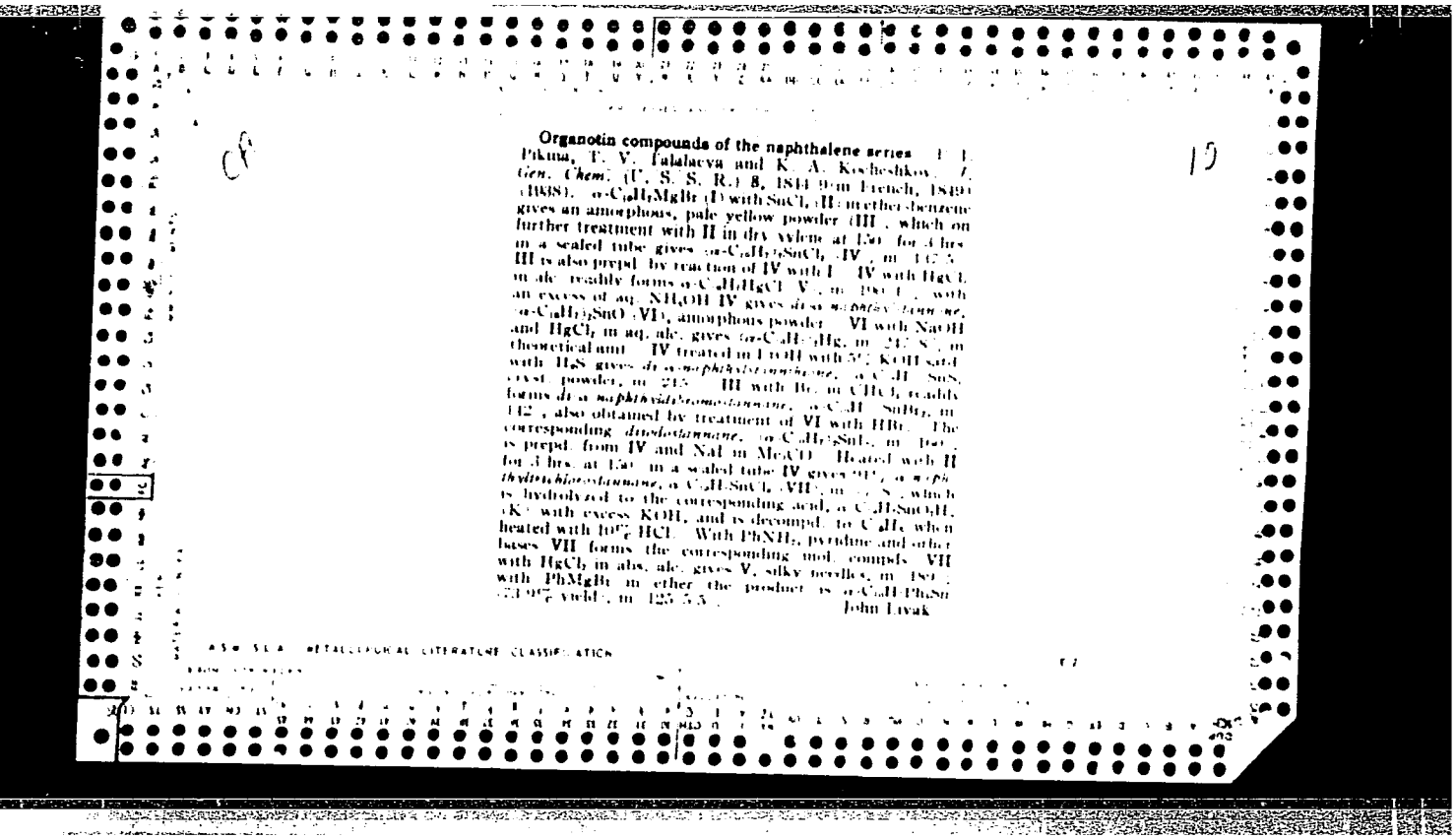
TIKHONOV, A.S.; VITUSHENKO, N.K.; TALALAYEVA, O.D.; YAKSHOVA, I.I.

Studying the formation reaction of hydroxides of certain metals by physicochemical analysis. Zhur.neorg.khim. 2 no.9:2196-2201 S '57. (MIRA 10:12)

(Hydroxides)

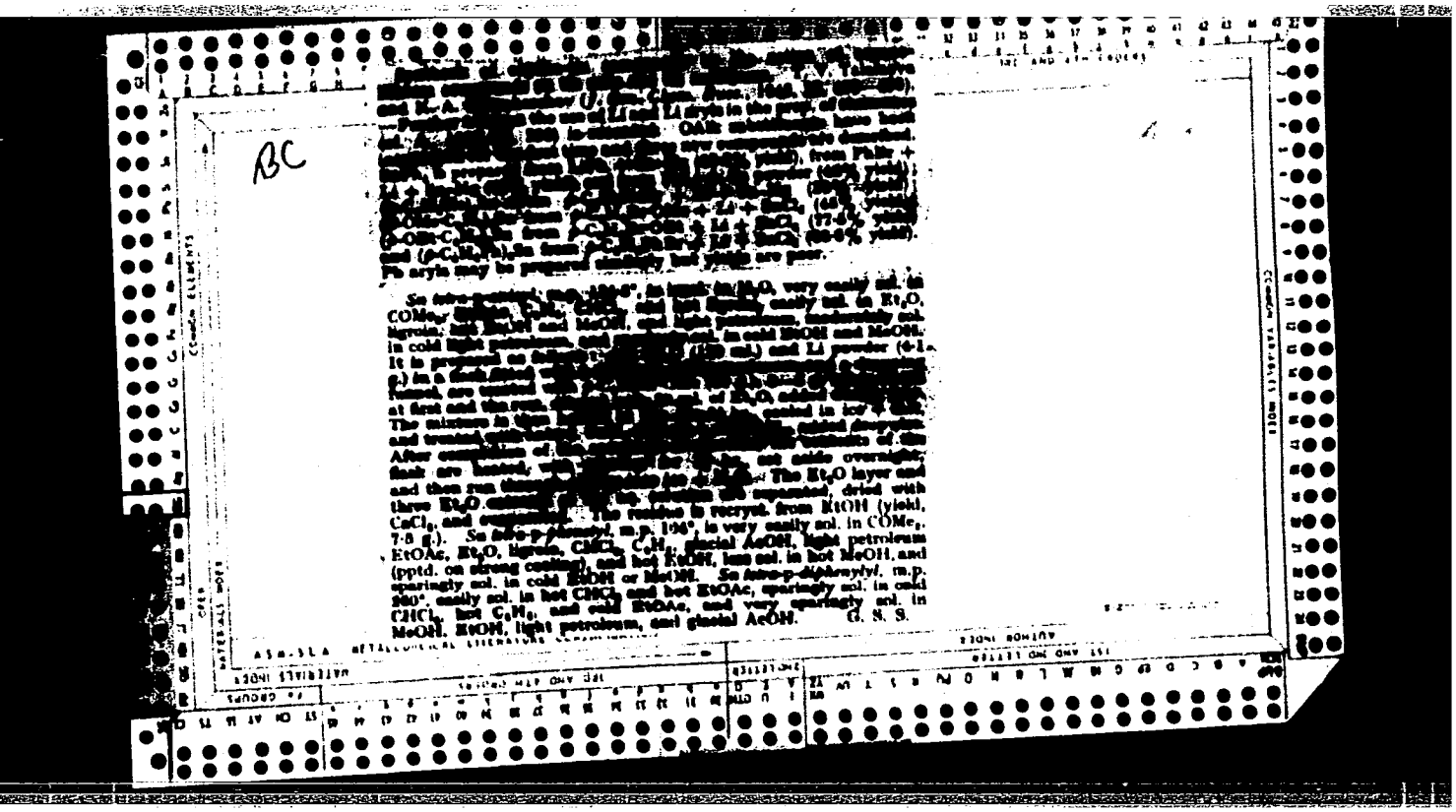


The action of metals on phenyllithium or phenylmagnesium bromide. The reaction of metallic lithium and phenyl derivatives of the metals of groups II, IV and V of the periodic system. I. V. Talalaeva and K. V. Kocheshkov. *J. Gen. Chem.* (U. S. S. R.) 8, 1881-5 in French. 1885-1938.—Both PhLi (I) and PhMgBr (II) manifest selective reactivity with metals of groups II, IV and V. I with the metals Mg, Hg, Sn, Pb, As and Sb gave, resp., Ph_2Mg, 13.8% yield; Ph_2Hg, isolated as PhHgCl, m. 248°; Ph_3Sn (III), m. 226.7°, 19.6%; Ph_4Pb (IV), m. 226°, 22%; Ph_3As (V), isolated as the chloroplatinate, m. 284°, 4.0%; Ph_3Sb (VI), isolated as Ph_3SbBr_2, m. 216°, 8.9%; with Si and Bi the only product isolated was Ph_2. II with Sn, Pb and Sb failed to react; with As the product was V, 5.9% yield. In all cases the procedure was to add I or II in ether to a large excess of finely powd. metal in ether or xylene and heat the resulting mixt. from 1-200 hrs. under reflux in an atm. of dry N_2. To prep. I the reverse of the above reaction was used, i. e., a large excess of Li was mixed with Ph_2M (M = Hg, Sn, Sn, Pb, As, Sb, Bi) in ether or xylene, sealed and the mixt. shaken at room temp. or heated under reflux. III, V, VI and Ph_2Si failed to react, with IV and Ph_2Bi the yields of I were, resp., 15.7 and 22.4%. John Lovik

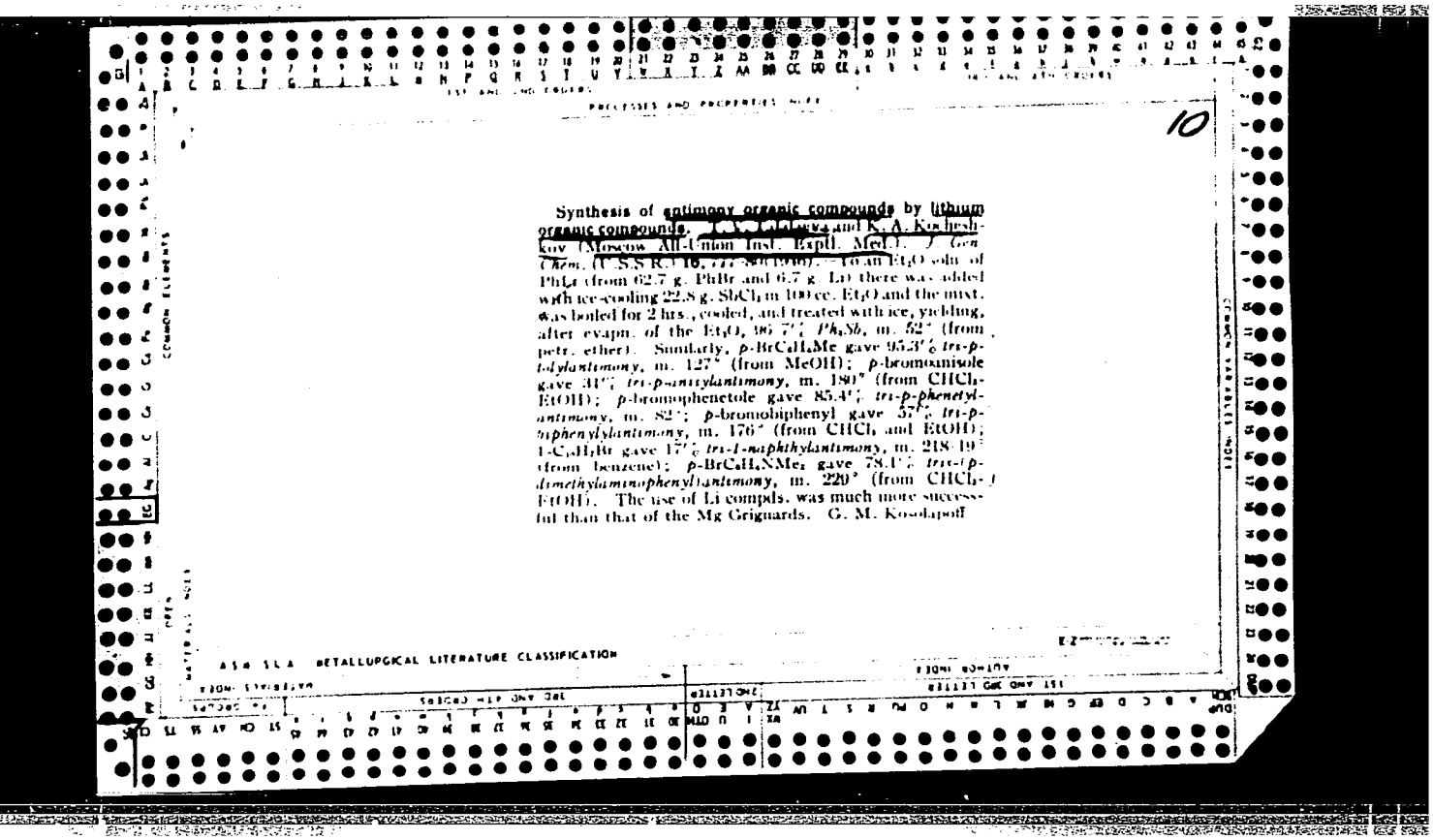


Organotin compounds of the naphthalene series. I. I. Pikina, T. V. Talalaeva and K. A. Kocheshkov. *J. Gen. Chem.* (U. S. S. R.) **8**, 1814-9 (in French, 1938). α-$C_{10}H_7MgBr$ (I) with $SnCl_4$ (II) in ether-benzene gives an amorphous, pale yellow powder (III), which on further treatment with II in dry xylene at 130° for 4 hrs. in a sealed tube gives α-$C_{10}H_7SnCl_3$ (IV), m. 142.5°. III is also prepd. by reaction of IV with I. IV with HgCl in alc. readily forms α-$C_{10}H_7HgCl$ (V), m. 190.5°; with an excess of aq. NH_4OH IV gives *di-α-naphthyltin oxide*, (α-$C_{10}H_7)_2SnO$ (VI), amorphous powder. VI with NaOH and $HgCl_2$ in aq. alc. gives (α-$C_{10}H_7)_2Hg$, m. 242.5°, m. theoretical amt. IV treated in EtOH with 5% KOH and with H_2S gives *di-α-naphthyltin sulfide*, α-$C_{10}H_7SnS$, crystl. powder, m. 245°. III with Br_2 in $CHCl_3$ readily forms *di-α-naphthyldibromotin*, α-$C_{10}H_7SnBr_3$, m. 142°, also obtained by treatment of VI with HBr. The corresponding *diodotin*, α-$C_{10}H_7SnI_3$, m. 160°, is prepd. from IV and NaI in MeCO. Heated with II for 3 hrs. at 130° in a sealed tube IV gives *α-naphthyltrichlorotin*, α-$C_{10}H_7SnCl_3$ (VII), m. 72°, which is hydrolyzed to the corresponding acid, α-$C_{10}H_7SnO_2H$, with excess KOH, and is decompd. to $C_{10}H_8$ when heated with 10% HCl. With $PhNH_2$, pyridine and other bases VII forms the corresponding mol. compds. VII with $HgCl_2$ in abs. alc. gives V, silky needles, m. 189°; with PhMgBr in ether the product is α-$C_{10}H_7PhSn$ (73.9% yield), m. 125.5°.

John Livak



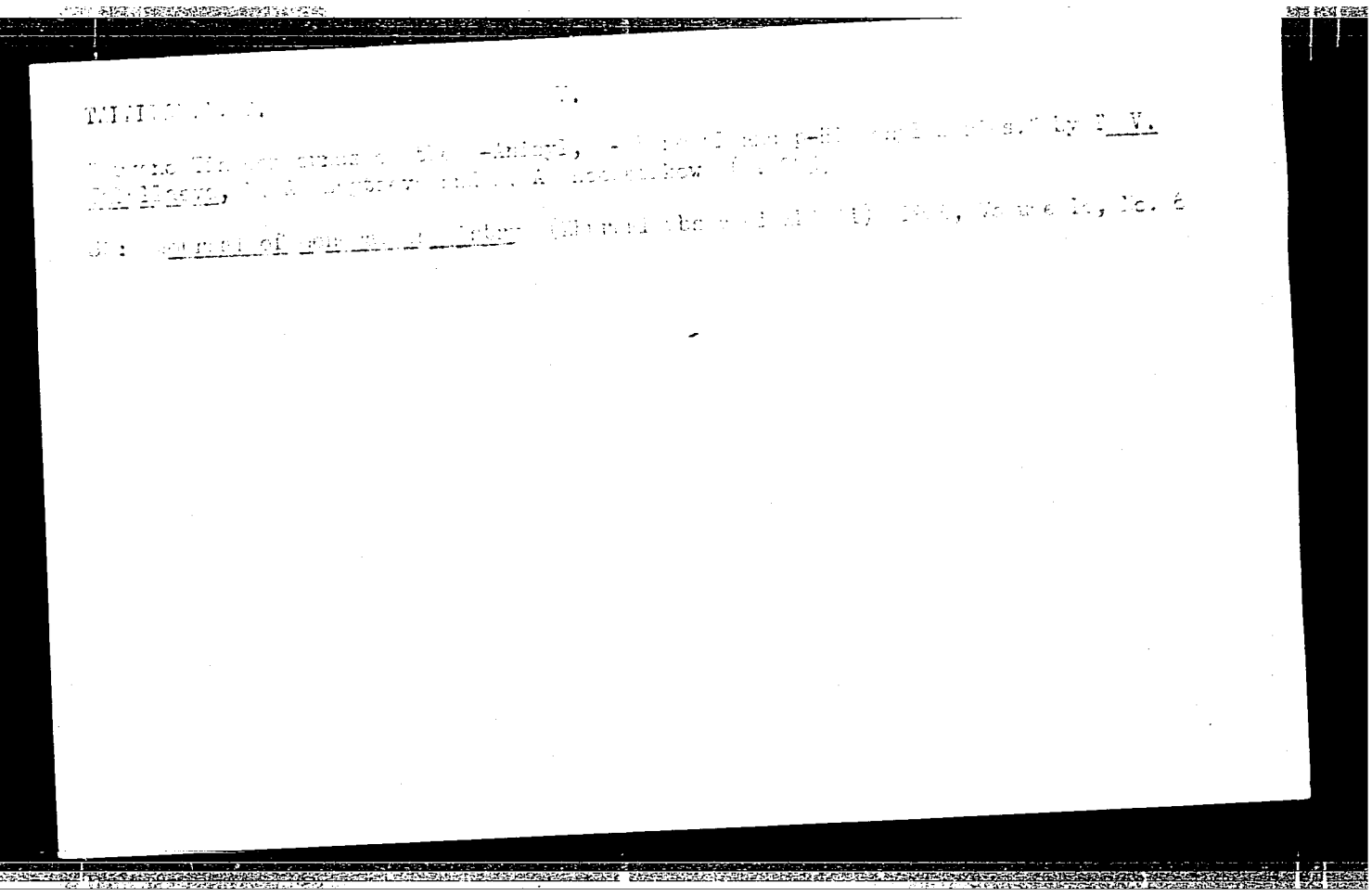
BC

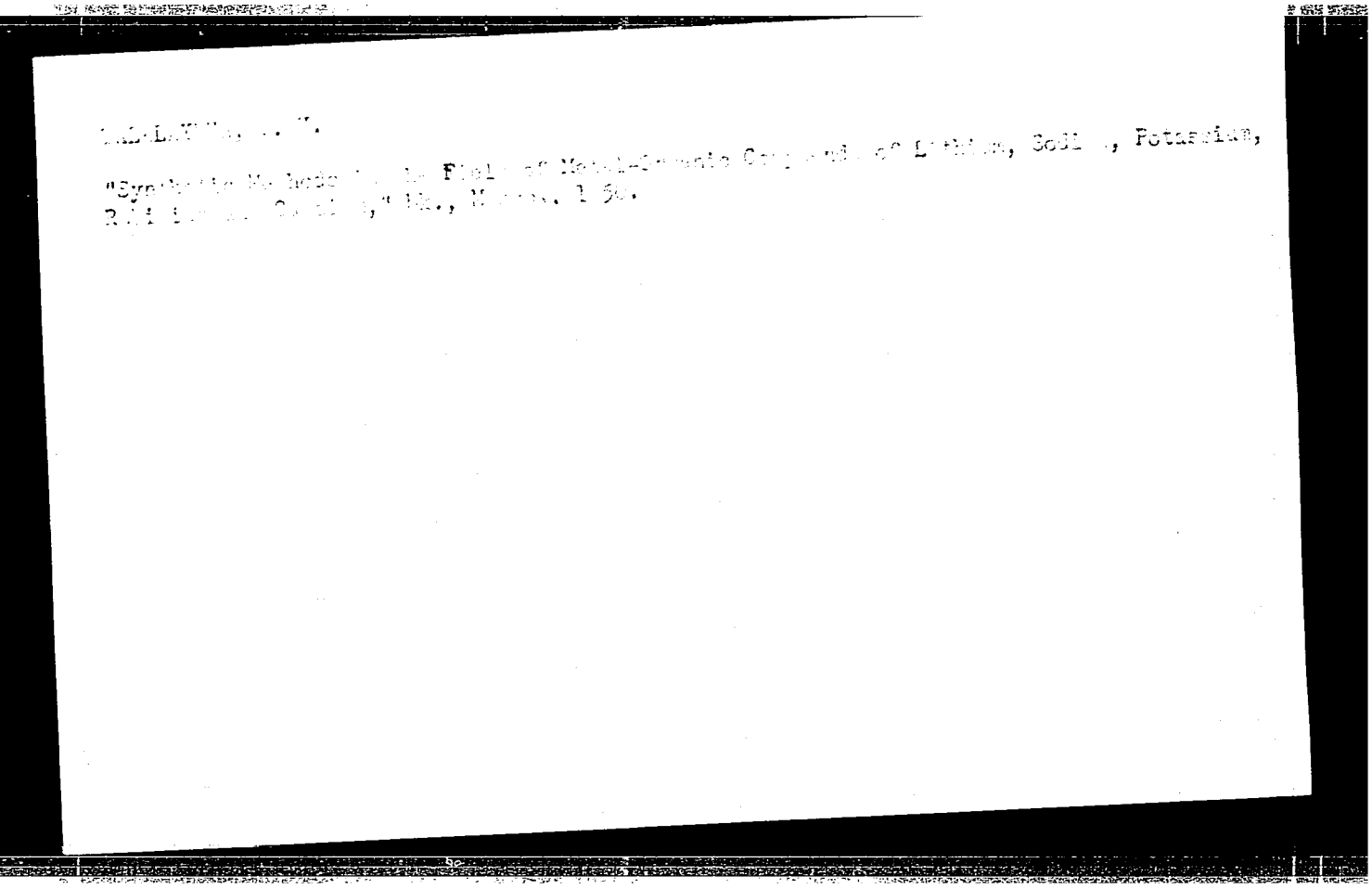


10

Synthesis of antimony organic compounds by lithium organic compounds. [illegible] and K. A. Kocheshkov (Moscow All-Union Inst. Exptl. Med.). *J. Gen. Chem. (U.S.S.R.)* 10, [illegible] (1940). To an Et_2O soln. of $PhLi$ (from 62.7 g. PhBr and 6.7 g. Li there was added with ice-cooling 22.8 g. $SbCl_3$ in 100 cc. Et_2O and the mixt. was boiled for 2 hrs., cooled, and treated with ice, yielding, after evapn. of the Et_2O, 86.7% Ph_3Sb, m. 52° (from petr. ether). Similarly, *p*-BrC$_6$H$_4$Me gave 95.3% *tri-p-tolylantimony*, m. 127° (from MeOH); *p*-bromoanisole gave 31% *tri-p-anisylantimony*, m. 180° (from $CHCl_3$-EtOH); *p*-bromophenetole gave 85.4% *tri-p-phenetylantimony*, m. 82°; *p*-bromobiphenyl gave 57% *tri-p-biphenylantimony*, m. 176° (from $CHCl_3$ and EtOH); 1-$C_{10}H_7Br$ gave 17% *tri-1-naphthylantimony*, m. 218-19° (from benzene); *p*-BrC$_6$H$_4$NMe$_2$ gave 78.1% *tri-(p-dimethylaminophenyl)antimony*, m. 220° (from $CHCl_3$-EtOH). The use of Li compds. was much more successful than that of the Mg Grignards. G. M. Kosolapoff

METALLURGICAL LITERATURE CLASSIFICATION





10

CA

New methods of preparation of crystalline lithium-organic compounds of aliphatic, alkaryl, and aromatic series. T. V. Talalaeva and K. A. Kocheshkov. *Doklady Akad. Nauk S.S.S.R.* 77, 621–4(1951).—New techniques for the prepn. of RLi are described. Direct action of Li and RX is suitable in cases in which LiX is insol. in the desired solvent. For the prepn. of cryst. EtLi, pentene is much better than C_6H_{12}, the reaction of Li with EtBr is exothermic and gives a LiBr ppt. as a gray-violet solid. The mixt. is treated with C_6H_6 to take up the EtLi and the ext. is concd. and chilled; addn. of pentene ppts. pure *EtLi*, which after drying, m. 95°, is spontaneously flammable in air. A single crystn. from hexane gives an analytically pure product in 35% yield; the yield in original C_6H_6 soln. reaches 65%. Only EtLi is recrystallizable among the aliphatic members. Isolation of PhLi in the PhBr reaction with Li is complicated in Et_2O solns. by complexes of PhLi, LiBr, and Et_2O. Exchange methods of prepn. from other organometallic compds. may employ derivs. of Sb, Bi, Br, iodine, Pb, and Sn. Reaction with compds. based on N, O, S, F, Cl, P, or As is less satisfactory but there is evidence that the last 2 elements may be used. Exchange of BtLi and BuLi was studied with aromatic derivs. of Sb, Bi, Br, and iodine; Pb derivs. are toxic and Sn derivs. are sluggish. The Wurtz reaction is a common side reaction. Pure C_6H_6 is the most widely applicable general reaction solvent. The best yields were obtained with aromatic Sb derivs. Cryst. *EtLi* in C_6H_6 is treated with 0.33 *M* Ar_3Sb at room temp. or with slight heating, and the pptd. *ArLi* filtered off, washed with pentane, and dried. In this manner the following were obtained in analytically pure state (% yield given): *PhLi* 50, *p-MeC$_6$H$_4$Li* 82, *o-isomer* 62, *m-isomer* 48, *p-ClC$_6$H$_4$Li* 48, *p-Br analog* 98, *1-C$_{10}$H$_7$Li* 56. All can be stored in N-filled tubes; all are oxidized and decompd. by air. $(PhCH_2)_3Sb$ gave 56% $PhCH_2Li$; the product is sensitive to heat and cannot be stored for over 1–2 days

TALALAYEVA, T.V.

Crystalline organolithium compounds. Compounds of aromatic series. T. V. Talalaeva and K. A. Kocheshkov. *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.* 1953, 113-20 (Engl. translation).—See *C.A.* 48, 3285h. H. L. H.

TALALAYEVA, T.V.

3

Chemical Abst.
Vol. 48 No. 6
Mar. 25, 1954
Organic Chemistry

Crystalline organolithium compounds. Compounds of aromatic series. T. V. Talalaeva and K. A. Kocheshkov. *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1953, 126–34.—All expts. were performed in closed app. in an atm. of pure N. Diagrams of several pieces of app. are shown. To 0.61 g. EtLi in 82 ml. C_6H_6 was added 3.9 g. $(p\text{-}MeC_6H_4)_3Sb$ in 10 ml. hot C_6H_6, and the mixt. stirred 6 hrs. at room temp. and 54 hrs. at 30–5°, and filtered under N pressure, yielding 73–82% *p-MeC₆H₄Li*, infusible crystals; sparingly sol. in C_6H_6, reacting most violently with EtOH or H_2O but not inflaming in air. A 66% yield is obtained similarly in C_6H_6 from EtLi and $(p\text{-}MeC_6H_4)_3Bi$ and also obtained from EtLi and *p*-MeC_6H_4Br in C_6H_6 after 24 hrs. Similarly 0.69 g. EtLi and 1.97 g. $(o\text{-}MeC_6H_4)_3Sb$ in C_6H_6 in 2 weeks gave 62% *o-MeC₆H₄Li*, fine solid; a 53.6% yield results in a few hrs. with *o-MeC₆H₄I* and EtLi. EtLi and $(m\text{-}MeC_6H_4)_3Sb$ in 2 weeks gave 48% *m-MeC₆H₄Li*, cryst. solid; a 30% yield results in 2 days from *m*-MeC_6H_4I. Heating 0.75 g. EtLi and 2.25 g. Ph_3Sb in C_6H_6 5 hrs. gave 50% *PhLi*, infusible needles, fuming in air but not inflaming, reacting violently with H_2O, sol. in abs. Et_2O but only sparingly in C_6H_6 or petr. ether. Similarly EtLi and PhI in C_6H_6 immediately gave 52.1% PhLi, mixed with some LiI; PhBr gave 78% after 24 hrs. but if the mixt. is allowed to stand 1 month, the PhLi ppt. is replaced by that of LiBr. To 1.57 g. PhLi in 40 ml. dry Et_2O was added 2 g. $SnBr_4$ in C_6H_6 with cooling; after 2 hrs. the usual treatment gave 79% Ph_4Sn, m. 224–5°. PhLi in Et_2O with Ph_2CO gave 70% Ph_3COH. EtLi (0.79 g.) and 2.9 g. $(p\text{-}BrC_6H_4)_3Sb$ in warm C_6H_6 gave in 12 hrs. 100% *p-BrC₆H₄Li*, crystals inflaming in air; BtLi with $p\text{-}C_6H_4Br_2$ in 6 hrs. gave 76.1% of the same product. $(p\text{-}ClC_6H_4)_3Sb$ gave 45.8% *p-ClC₆H₄Li*, which does not inflame in air; EtLi and $p\text{-}C_6H_4BrCl$ gave 88.8% same product in 24 hrs. EtLi and $(1\text{-}C_{10}H_7)_3Sb$ gave 56.4% *1-C₁₀H₇Li*, while *p*-PhC_6H_4Br gave 44.4% *p-PhC₆H₄Li*.

G. M. Kosolapoff

TALALAYEVA, T.V.

Crystalline organolithium compounds. Benzyllithium. T.V. Talalaeva and K.A. Kocheshkov. Bull. Acad. Sci. U.S.S.R. Div. Chem. Sci. 1953, 263-6 (Engl. translation) See C.A. 48, 6389i. H.L.H.

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

Crystalline organic lithium compounds. Benzyllithium. Izv. AN SSSR. Otd. khim.nauk. no.2:290-293 Mr-Ap '53. (MLRA 6:5)

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

Benzyllithium as the simplest aryl-alkyl Li compd differs from both aromatic and aliphatic Li compds by its greater reactivity, which is utilized mostly for analytical purposes. Crystalline benzyllithium was obtained by reacting tribenzylantimony with ethyllithium in a pentane-benzene soln. Its properties were investigated. 256T29

TALALAYEVA, T.V.

4

✓Crystalline organolithium compounds. Fluorenyllithium and lithium phenylacetylide. T. V. Talalaeva and K. A. Kocheshkov. *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.* 1953, 357–8(Engl. translation).—See *C.A.* 48, 6390*b*.
H. L. H.

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

Crystalline organic lithium compounds. Fluorenyllithium. Lithium phenylacetylide. Izv. AN SSSR. Otd.khim.nauk. no.2:392-393 Mr-Ap '53. (MLRA 6:5)

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

Using the exchange reaction H metal (Shorygin's reaction), crystalline fluorenyllithium was prepd by interacting fluorene with ethyllithium. Crystithium phenylacetylenide was synthesized on the basis of the same reaction.
256T31

TALALAYEVA, T. V.

CZECH

Synthesis and roentgenographic study of crystals of organoantimony compounds of types Ar_3Sb and Ar_3SbX_2.

V. P. Ghishkova, T. V. Talalaeva, Z. P. Razumanova, G. S. Zhdanov, and K. A. Kocheshkov. *Sbornik Statei Obshchei Khim.* 2, 992-6(1953).—The RLi from 19.6 g. o-MeC_6H_4I and 4.1 g. Li in Et_2O treated with ice cooling with 6.5 g. $SbCl_3$, stirred 1 hr., strained into ice (to remove residual Li) and extd. with Et_2O gave 84% (o-$MeC_6H_4)_3Sb$ (I), m. 102°. Similarly was obtained 71.8% *m-isomer* (II), m. 72°, along with (m-$MeC_6H_4)_2SbCl_3$, m. 137° (from the mother liquor). p-ClC_6H_4MgBr and $SbCl_3$ gave 77.5% (p-$ClC_6H_4)_3Sb$ (III), m. 110.5-11°, which with dry Cl_2 gave the *dichloride* (IV), m. 189.6°. Similarly p-BrC_6H_4MgBr gave 30% (p-$BrC_6H_4)_3Sb$ (V), m. 136-6.5°, *dichloride* (VI), prepd. as usual, m. 185°. 1-$C_{10}H_7MgBr$ gave 92.6% (1-$C_{10}H_7)_3Sb$ (VII), m. 223-3.5°. Treatment of the Ar_3SbCl_2 with hot aq.-alc. KF soln. gave 75-90% Ar_3SbF_2. In this way were obtained the following (Ar_3Sb and m.p. given): *Ph*, 115°; o-MeC_6H_4, 195.5°; Ar_3SbF_2 (Ar and m.p. given): *Ph*, 115°; o-MeC_6H_4, 195.5°; m-MeC_6H_4 (VIII), 109.5-9°; p-MeC_6H_4 (IX), 118-18.5°; p-ClC_6H_4, m. 115.5-16°; p-BrC_6H_4, 149-9.5°; 1-$C_{10}H_7$, 279-80°. (p-$MeC_6H_4)_2SbBr_2$ with H_2S in EtOH sattd. with

4

788

V.P. Glushkova

Me$_3$ gave 83% (p-MeC$_6$H$_4$)$_3$SbS, m. 111.5–12°. The following phys. constants were obtained on x-ray analysis (crystal habit, a, b, c, β, γ, space group, σ_a, σ_b, m.p., resp.): I, hexagonal, 14.4, —, 5.5, —, 2, —, 1.32, 1.35, 102°; II, rhombic, 21, 16.7, 10.2, —, 8, D_{2h}^{15}, 1.37, 1.41, 68°; (p-MeC$_6$H$_4$)$_3$Sb, rhombohedral, 12.7, —, 20.2, —, 6, C_{3i}, C_{3}^{2}, 1.38, 1.35, 127°; III, rhombic, 15.8, 14.8, 15.1, —, 8, D_{2h}^{15}, 1.71, 1.68, 111°; IX, monoclinic, 26.8, 10.4, 22.1, 113, 12, C_{2h}^{5}-C2/c, 1.47, 1.48, 113°; (p-MeC$_6$H$_4$)$_3$SbCl$_2$, cubic, 12.718, —, —, —, 4, O^{6}-P4$_3$, 3, 1.45, 1.44, 157°; (p-MeC$_6$H$_4$)$_3$SbBr$_2$, cubic, 12.817, —, —, —, 4, O^{6}-P4$_3$, 3, 1.70, 1.69, 234°; (p-MeC$_6$H$_4$)$_3$SbI$_2$, triclinic, —, —, —, —, —, —, —, —, 181°; VIII, monoclinic, —, 0.8, —, —, —, —, —, —, 109°; (m-MeC$_6$H$_4$)$_3$SbCl$_2$, monoclinic, 11.2, 12.6, 15.6, 112.5, 4, C_{2h}^{5}-P2$_1$/c, 1.54, 1.52, 137°. G. M. Kosolapoff

Smw

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

Structure of some crystalline organolithium compounds. Dokl.AN SSSR 104 no.2:260-263 S '55. (MLRA 9:2)

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

TALALAYEVA, T.V.; NAD', M.N.; KOCHESHKOV, K.A.

Etherates and dioxanates of lithiumorganic compounds. Dokl. AN SSSR 109 no.1:101-104 Jl-Ag '56. (MLRA 9:10)

1. Chlen-korrespondent Akademii nauk SSSR (for Kocheshkov).
2. Fiziko-khimicheskiy institut imeni L.Ya. Karpova.
(Lithium organic compounds)

[illegible], [illegible], KH[illegible], [illegible], [illegible], [illegible]

"Hi[illegible] P[illegible] Obtained Using Organometallic Complexes Containing Lithium and Titanium" paper No. N[illegible], submitted at the International High-P[illegible] Conference, Nottingham, 21-24 July 19[illegible].

A[illegible] Nauk SSSR, Leninskiy Prospekt 14, Moscow, USSR

AUTHORS: Rodionov, A., Shigorin, D., Talalayeva, T., Kocheshkov, K. 62-1-28/29

TITLE: Letters to the Editor (Pis'ma redaktoru)

PERIODICAL: Izvestiya AN SSSR Otdeleniye Khimicheskikh Nauk, 1958, Nr 1, pp 120-120 (USSR)

ABSTRACT: On the strength of the research of the infrared spectra of the compounds R - Li and R - O - Li the authors of this letter discovered the formation of an intermolecular lithium binding $\overset{-\delta}{C}\overset{+\delta}{}\!\!-\!\!Li\ldots\ldots\overset{-\delta}{C}\overset{+\delta}{}\!\!-\!\!Li\ldots\ldots$ and $\overset{-\delta}{O}\!\!-\!\!Li\ldots\ldots\overset{-\delta}{O}\overset{+\delta}{}\!\!-\!\!Li\ldots$ A comparison of the spectra of the vapors, solvents, and powders in vaseline oil as well as an analysis of the kind of oscillation of the molecules made possible the precise determination of the frequency of the valent oscillations of the groups C--Li (of the free and those taking part in the formation of the lithium binding; see table). The intermolecular lithiumbinding $\overset{-\delta}{C}\overset{+\delta}{}\!\!-\!\!Li-$ is constant. With the binding $-Li\ldots\overset{-\delta}{O}\overset{+\delta}{}-$ the latter is, however, still more stable. The formation of especially resistent intermolecular lithium bindings has to be traced back to the peculiarity of the atom of the lithium: Small

Card 1/2

radius, comparatively small ionization potential, better possibility of utilizing the -orbit. All this makes possible a immediate more and more active taking part of its electron in the intermolecular interaction than is the case with the hydrogen atom. There is 1 table.

ASSOCIATION: Physicochemical Institute imeni L. Ya. Karpov (Fiziko-Khimicheskiy Institut imeni L. Ya. Karpova)

SUBMITTED: December 20, 1957

AVAILABLE: Library of Congress

1. Lithium-Molecular structure 2. Vaseline oil spectra-Analysis
3. Infrared spectra-Applications

Card 2/2

AUTHORS: Rodionov, A. N., Shigorin, D. N., Talalayeva, T. V., Kocheshkov, K. A. SOV/48-22-9-27/40

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 $-C^{-\delta} - Li^{+\delta} \ldots C^{-\delta} - Li^{+\delta}$ ... and $-O^{-\delta} - Li^{+\delta} \ldots O^{-\delta} - Li^{+\delta}$ ... 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 $-Li^{+\delta} \ldots C^{-\delta}$ - 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

Card 1/4

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

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)

5(2,3)

AUTHORS: Rodionov, A. N., Shigorin, D. N., SOV/20-123-1-30/56
Tolalayeva, 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 a-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

Card 1/4

$^{-\delta}_{C} - ^{+\delta}_{Li}$. 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 3-9). 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

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 then 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.

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

Card 4/4

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

Card 1/3

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.

Fluorinated Styrenes. Communication I.2,4-Difluoro Styrene SOV/62-59-1-15/38

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

SUBMITTED: April 19, 1957

Card 3/3

5(2), 5(4)

AUTHORS: Nad', M. P., Talalayeva, T. V., Kocheshkova, E. V., Kocheshkov, K. A. SOV/62-59-1-11/38

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-difторstirol)

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.

Card 1/3

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.

Card 2/3

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

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

SUBMITTED: April 19, 1957

Card 3/3

SOV/62-59-2-14/40

3(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 difluoro-acetic 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

Card 1/3

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

Card 2/3

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

KOCHESHKOV, K.A.; KARGIN, V.A.; TALAIAYEVA, 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)

AUTHOR: Talalayeva, T. V., Rasennikova, S. V., [illegible]
Kocheshkov, K. A.

TITLE: Fluorinated Styrenes (Ftorirovannyye stiroly). VI. 1,3-Difluoro-styrene and 2,5-Difluoro-β-fluoro-styrene (IV. 2,4-Difluorstirol i 2,5-difter-β-ftorstirol)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol 28, [illegible]
pp 1497-1503 (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 [illegible] of the low temperature [illegible]

Fluorinated [illegible]. IV. 1,4-Difluoro-styrene and [illegible]-5-10/75
2,5-Difluoro-β-fluoro-styrene

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

Card 2/3 reduced by zinc in acetamide to form 2,5-difluoro-β-fluoro-

Fluorinated Styrenes. IV. 2,5-Difluoro-styrene and 2,5-Difluoro-β-fluoro-styrene SOV/79-29-5-39/75

styrene. The experimental [illegible] describes the [illegible] and the physical data of the compounds obtained. [illegible] references, [illegible] of which are Soviet.

ASSOCIATION: Fiziko-khimicheskiy institut imeni L. Ya. [illegible] (Institute of Physical Chemistry imeni L. Ya. [illegible])

SUBMITTED: April 2, 1958

Card 3/3

5(2,4) SOV/20-125-3-27/63

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 dipolnyye momenty)

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 125, Nr 3, pp 562-565 (USSR)

ABSTRACT: In an earlier paper (Ref 1) the authors proved the formation of a bond referred to in the title $-CH_2-Li\cdots CH_2-Li$ (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 hexane and investigated at various concentrations. The aim was to clarify

Card 1/3

Intermolecular Lithium Bond, Its Influence Upon the Vibration Spectra of Molecules and Upon the Dipole Moments

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 hexane showed a linear course of the dependence of the dielectricity constant on the concentration in the case of lower concentrations. This course diverges from the straight line on an increase of concentration (0.4-3.0 mols %). The dipole moment of ethyl lithium in benzene remains constant between 0.08-0.43mols% 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

Intermolecular Lithium Bond, Its Influence Upon the Vibration Spectra of Molecules and Upon the Dipole Moments

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

Card 3/3

5 (2, 3, 4)

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

SOV/20-128-4-26/68

TITLE: The Infrared Spectra and Structure of Aromatic Organolithium Compounds

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 128, Nr 4, pp 726 - 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

Card 1/4

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

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

...ssed. 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

66467

SOV/20-129-1-33/64

~~5(2,3,4)~~ 5.3700 (B)

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

TITLE: The Infra-red Spectra and Structure of Acetylenides of Lithium

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 129, Nr 1, pp 121-124 (USSR)

ABSTRACT: Acetylene and its derivatives can form complexes with each other and with several solvents by means of the hydrogen bond as well as interaction of π-electrons of the group: — C ≡ C — (Ref 2). It could be assumed that the substitution of one hydrogen atom by one lithium atom in acetylene and acetylene derivatives with the aid of electrons of the C-Li bond and the π-electrons of the C≡ C group will increase the complex-forming capacity of these compounds. In order to explain the structure of this group of compounds the authors investigated the spectra of lithium acetylenide, lithium methylacetylenide, lithium ethylacetylenide, lithium tertiary butylacetylenide, and lithium phenylacetylenide. Spectra of acetylenides and phenylacetylenides of potassium and sodium etc. were plotted in comparison. The results are summarized in figures 1 and 2 and table 1. The paper under review proved that

Card 1/2

65487

SOV/20-129-1-33/64

The Infra-red Spectra and Structure of Acetylenides of Lithium

the molecules of lithium acetylenides in crystals form stable complexes (ammonia) with each other as well as with other compounds. The recorded bands about 1060 and 1080 cm^{-1} may be assigned to the valence vibrations of the groups $\equiv C - Li \cdots$ in the complexes. The frequency of the valence vibration of the free groups $\equiv C - Li$ seems to be 1200 cm^{-1}, as was observed in the case of lithium phenylacetylenide. Thus the authors' assumption (Ref 6) that lithium acetylenides show a stronger tendency towards complex formation than acetylene itself has been proved. This may be explained by increased polarity of the $\equiv C - L$ bond (compared with $\equiv C - H$) as well as by a more probable cooperation of one valence electron of the lithium atom using the p-orbit. There are 2 figures, 1 table, and 6 references, 4 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: July 6, 1959

Card 2/2

87118

S/062/60/000/009/004/021
B033/B064

24.2500 2209, 1144 only

AUTHORS: Vasil'yeva, V. N., Talalayeva, T. V., Garlyanova, 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

Card 1/3

87118

3/062/62/000/009/004/021
B033/B064

Dipole Moments of Organolithium Compounds of the Aliphatic Series

moments were measured at 25°C with the help of the pulse 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 $\mu = 0.0127 \cdot 10^{-18} \sqrt{(P_\infty - P_E)T}$ (P_E = electron polarization of the substance). It was 4.1 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

Card 2/3

87118

Dipole Moments of Organolithium Compounds of the Aliphatic Series

S/062/60/000/009/004/021
B023/B064

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,

Card 3/5

An Investigation of the Nature of Secondary Chemical Bonds

S/020/60/133/01/49/070
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 $\rightarrow$ 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

Card 2/4

An Investigation of the Nature of Secondary Chemical Bonds

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<, etc.) the σ,π-conjunction $Li \overset{+\delta}{---} \overset{\sigma}{C}-\overset{-\delta}{C}=\overset{\pi}{C}-$ 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.

Card 3/4

81733

An Investigation of the Nature of Secondary Chemical Bonds

S/020/60/133/01/49/070
B004/B007

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

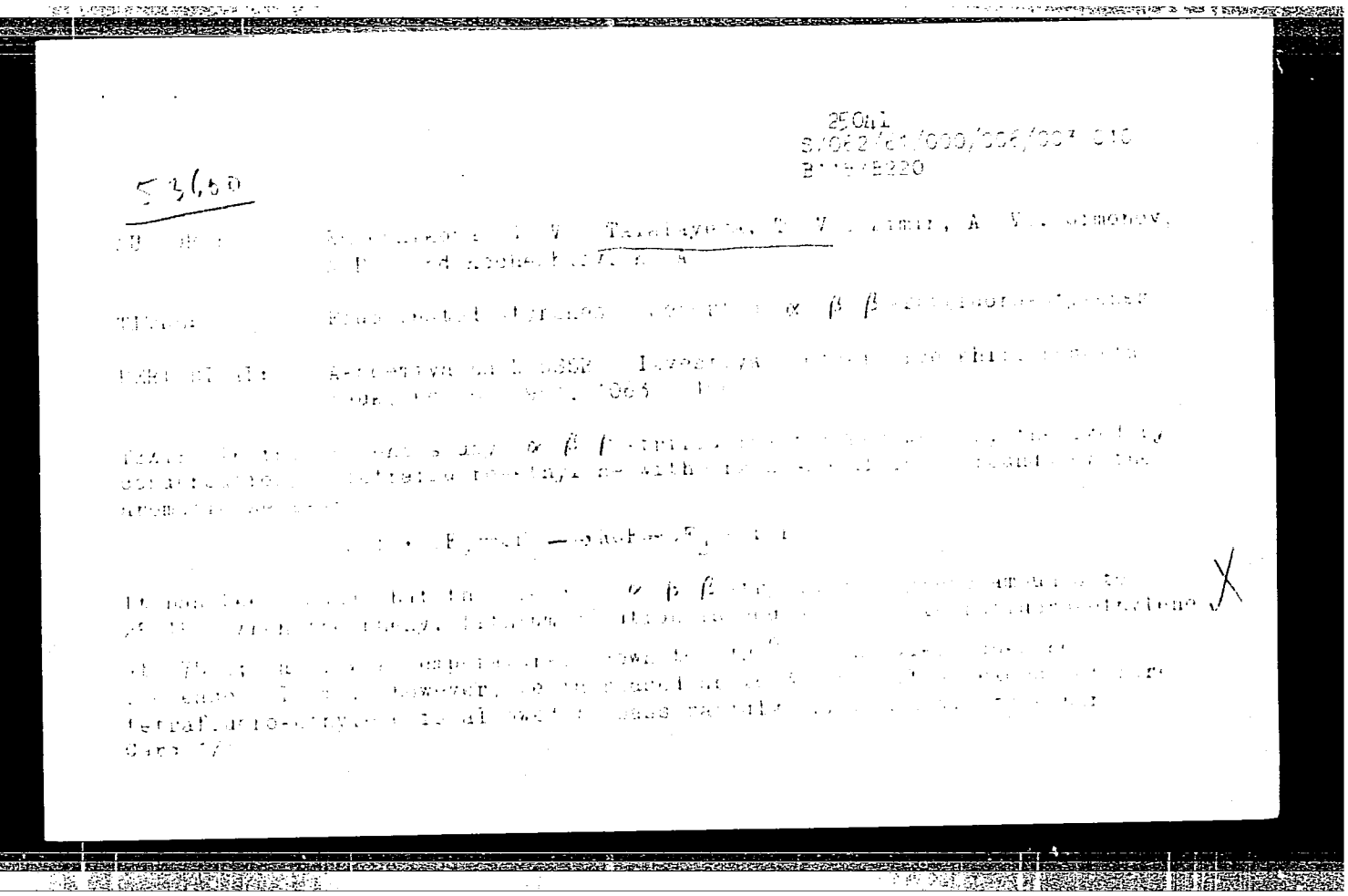
SUBMITTED: March 25, 1960

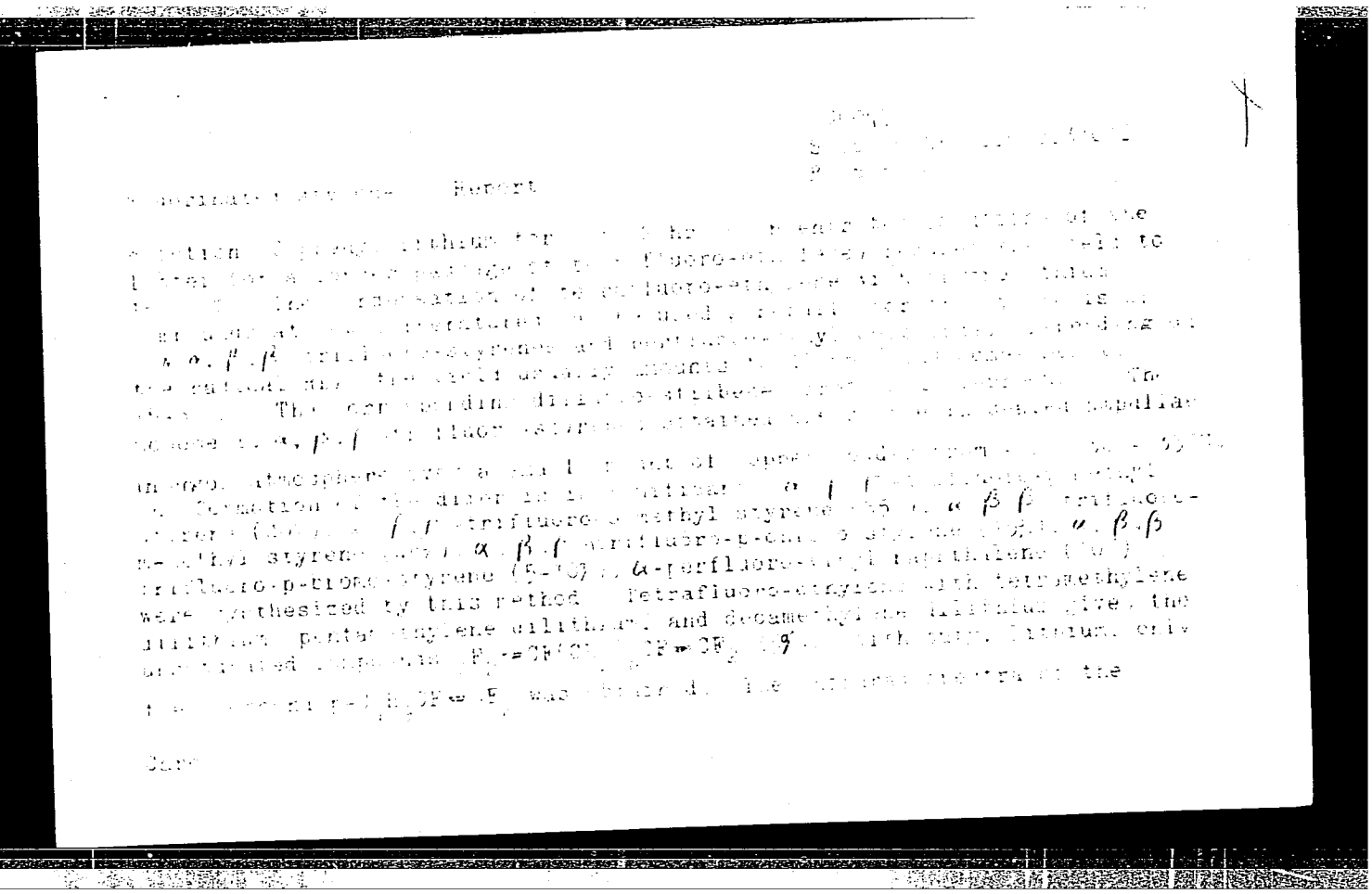
Card 1/4

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)





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, B. A. Warner, J. Amer. Chem. Soc. 76, 1643 (1954); pat. USA 2804484 (1957); 2) S. Dixon, J. Organ. Chem. 21, 400 (1956); 3) D. I. Livingston, P. J. Kamath, R. S. Corley, J. Polymer Sci. 20, 485 (1956); W. G. Bart, 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

S/079/60/030/006/001/XXX
B004/B220

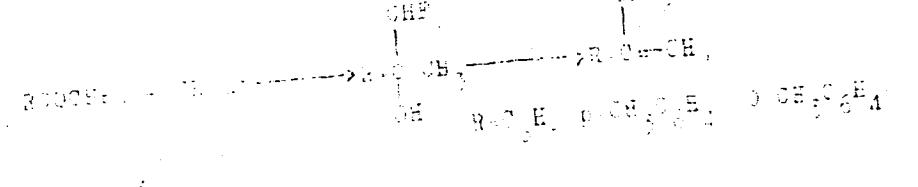
5 3600

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

TITLE: Diarylmethyl styrenes. 3-nitro-4'-α,α,α-trifluoro-methyl styrenes and α-trifluoro-methyl styrenes

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 6, pp. 1044 - 1047

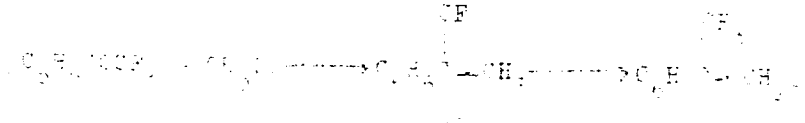
TEXT: The present paper deals with the synthesis of α,α,α-trifluoro-methyl styrene, 4-trifluoro-methyl-4'-methyl styrene, α,α,α-trifluoro-methyl-4'-methyl styrene, α,α,α-trifluoro-methyl styrene, and α,α,α-trifluoro-methyl-4-fluoro-styrene according to the following equation:



Card 1/4

S/062/61/000/006/004/010
B101/B220

Fluorinated styrene Report



Starting from methyl magnesium bromide and fluorine phenyl ketones or bromides, α-trifluoro-methyl styrene and its fluorine-trifluoro-methyl-styrene were obtained in a multi-stage synthesis. The most convenient method proved to be the reaction of methyl lithium and α-di-fluoro-acetophenone or α-trifluoro-methyl phenyl ketone which are readily accessible by synthesis and obtained from the acid 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 - 95%). 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...

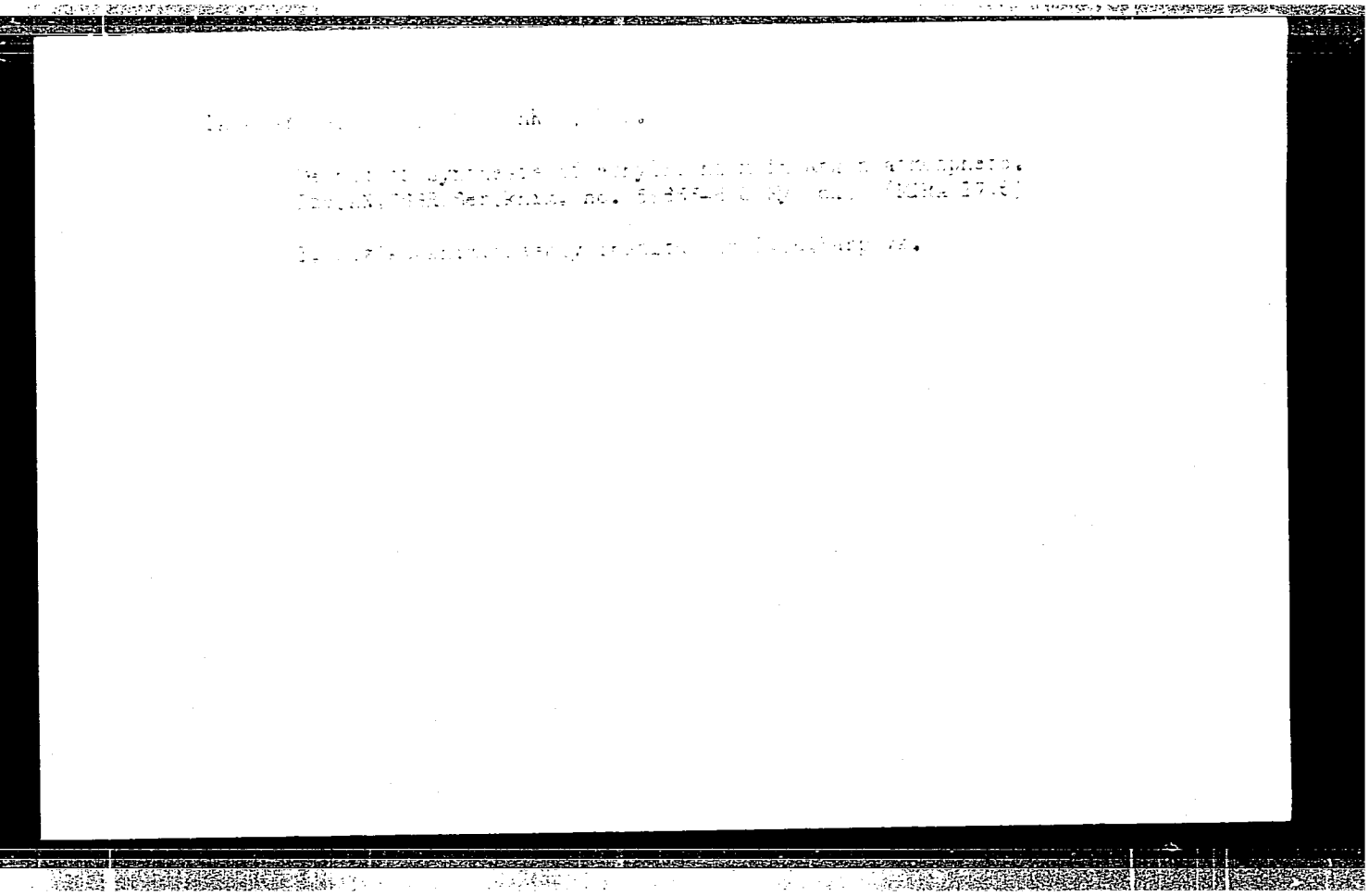
English-language publications read as follows: 1) P. Tarrant, R. E. Taylor, J. Organ. Chem. 24, 238(1958). 2) K. T. Dishard, R.Levine, J. Amer. Chem. Soc. 78, 2268(1956); 77, 3656(1955); I. D. Park, R. E. Noble, I. R. Lacher, J. Organ. Chem. 23, 1396(1956); D. A. Rausch, A. M. Lovelace, L. E. Coleman,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

X

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)

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 H-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

Card 1/3

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

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

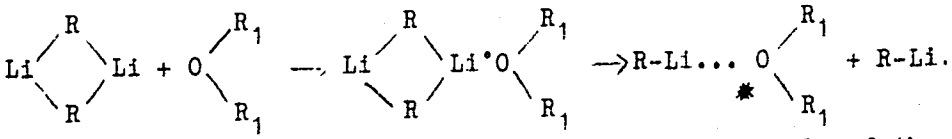
2

(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

Card 2/3

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

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



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 (Physico-chemical 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

Card 1/3

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

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

Card 2/3