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SIXTH UKRAINIAN REPUBLIC CONFERENCE ON ORGANIC CHEMISTRY

- USSR -

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[Following is a translation of an unsigned article in the Russian-language periodical Ukrainskiy khimicheskiy zhurnal (Ukrainian Chemical Journal), Kiev, Vol. XXVI, No. 2, 1960, pages 273-277.]

The conference, which was convened by the Department of Chemical and Geological Sciences and the Institute of Organic Chemistry of the Academy of Sciences Ukrainian SSR, together with the Ministry of Higher and Special Secondary Education Ukrainian SSR, took place in Kiev on 10-14 November 1959. About 300 Chemists participated in the conference, including workers of scientific institutes, higher educational institutions, and chemical plants of Kiev, Kharkov, Lvov, Dnepropetrovsk, Odessa, Chernovitsy, Shostka, Moscow, and Leningrad.

At the first plenary session G. V. Uvarov, the vice-chairman of the State Committee for Chemistry of the Council of Ministers USSR, came forward with the report "Concerning the Present State and Prospects of the Development of the Organic Chemical Industry."

It was reported that in 1965, 12-13 million tons of organic raw material will be needed for chemical production. Petroleum (3-3.5 million tons) and by-product gases (4 million tons) will be the primary suppliers of this material. Natural gas will provide 2.8 million tons and the by-product coke industry about 1 million tons. From the waste products of agricultural production and the wood industry about 1-1.5 million tons will be utilized, mostly in the production of hydrolysis spirit and furfural. The primary trend in the chemical processing of natural gases is pyrolysis into acetylene and hydrogen, in which the hydrogen is used mainly for ammonia synthesis, and acetylene for the production of acetaldehyde, acetic acid, acrylonitrile, and vinyl chloride.

Urea production will increase considerably. The high concentration of bound nitrogen in this compound is of great importance due to the great distances entailed in the transportation of our fertilizers. Urea will also be added to cattle feed and will be processed into plastics. Of the poisonous chemicals of agriculture, the production of organophosphorus compounds will be greatly increased. Considerable development will also be given to the production of herbicides, seed-treating agents, and defoliants (for the removal of the leaves of the cotton plant in cotton harvesting).

Original reports were given in two parallel sections of the conference.

The sessions of Section I were devoted to questions of the reactivity of organic compounds and the mechanism of organic reactions, organophosphorus compounds, the chemistry of monomers and polymers. I. V. Smirnov-Zamkov and G. A. Piskovitina (Kiev) reported that the steric orientation of the addition of hydrogen bromide to unsaturated compounds depends on the nature of the solvent and the temperature. More acid solvents and low temperatures favor cis-orientation. Addition according to the cis-scheme is possible in two ways: through the open or through the ring complex. F. M. Vaynshteyn and Ye. A. Shilov (Kiev) studied the kinetics of iodination and determined the kinetic isotope effect for a series of primary, secondary, and tertiary aromatic amines and their derivatives. These reactions proceed as trimolecular reactions with the participation of the one or the other base as the proton acceptor. The iodide cation acts as the iodizing agent, and molecular iodine in the case of tertiary amines. In the report of R. V. Vizgert and Ya. P. Berkman (Lvov) the dependence of the reactivity of aryl sulfonates on the structure of reagents in nucleophilic substitution reactions was examined. A. F. Rekasheva and I. P. Semchenko investigated the hydration of acetylene in the presence of mercury salts in heavy water and indicated that the hydrogen atom on the carbon atom of the aldehyde group does not lose its bond with the carbon, whereas the formation of the methyl group of the acetaldehyde is accompanied by the partial substitution of another hydrogen atom of the acetylene molecule with deuterium. I. P. Gragerov and L. F. Levit (Kiev), reacting Caro acid on aniline, o-anisidine and p-nitroaniline in H_2O^{18}, established that the nitroso and azoxy compounds formed do not contain excess H_2O^{18}. This means that the oxidation takes place with the help of a heterolytic mechanism. Heavy water H_2O^{18} was also used by L. V. Sulima (Kiev) in order to determine the hydroxylation mechanism of allyl alcohol with hydrogen peroxide in the presence of tungstic, molybdic, or selenic acid. From the derived data it follows that the reaction proceeds through the oxide form. B. G. Yasnitskiy and A. P. Zaytsev (Kharkov) showed that the oxidation of chloroacetaldehyde with nitric acid into monochloroacetic acid proceeds through a complex in which oxides of nitrogen, nitric acid, and water take part. A technique for the production of monochloroacetic acid by this method has been worked out. S. N. Solodushenkov (Rubezhnoye) showed that the rate of hydrolysis of tricyanogen chloride to cyanuric acid is proportional to the hydrogen ion concentration in the first two stages. Forms were established for the kinetic equations and the energy parameters of the reaction. In the report of M. S. Malinovskiy and A. G. Yudasina (Dnepropetrovsk) data were presented on the chemistry of unsymmetrical α-oxides, based on a study of the reactions of

isomerization, hydration and formation of oxamines. L. M. Litvinenko, N. F. Levchenko, and R. S. Cheshko investigated the kinetics of the acylation of aromatic amines with p-nitrobenzoyl chloride and picryl chloride in order to establish how the influence of the para-substitutent is transmitted through the benzene rings bound by groups $-CH_2-CH_2-$, -CH=CH-, -C≡C- or the hetero-atoms (O, S, Se, NH). It appeared that unsaturated groups, in spite of the conservation of the conjugated chain, decrease the effect of the substitutent just as much as the saturated group $-CH_2-CH_2-$. The connective hetero-atoms even increase the effect of the substitutent, although in an optical sense they are insulators. F. F. Krivonos (Sumy) investigated the reaction for the formation of hexachlorane by the chlorination of benzene in the presence of alkali. A. V. Dombrovskiy (Chernovitsy) reported on the method of producing 1,4-arylbutadienes and triarylethylenes by the reaction of aryl diazonium salts on divinyl and 1,1-diphenylethylene. S. I. Burmistrov and Ye. A. Titov (Dnepropetrovsk) have synthesized a group of arensulfonylquinonimines and esters of quinonoximes with arensulfo acids and with carboxylic acids and have investigated their reactions, especially the formation of indophenols. A. Ye. Kretov, A. Ye. Syrovatko, and A. P. Moiseyenko (Dnepropetrovsk) studied the chlorination of isomeric xylols in the side groups to the dichloro and hexachloro substituted derivatives and produced esters of dicarboxylic acids from the products of chlorination. S. S. Gitis (Dnepropetrovsk) presented new data on the transalkylation reactions of alkyl, aryl, and arylalkyl esters of different dinitrophenols.

One session of Section I was devoted to organophosphorus compounds. M. S. Malinovskiy and V. V. Alekseyev (Dnepropetrovsk) reported on the reactions of alkyl phosphites with thiocarbamyl chlorides and isothiocyanates. In the first case an Arbuzov regrouping takes place, in the second case thioamides of the formula $(RO)_2POCSNHR'$ are produced. In the work of M. S. Malinovskiy with Z. F. Solomko 35 new mixed anhydrides which form phosphoric and zanthogenic acids were synthesized and the structure of their molecules was determined. I. N. Zhmurova (Kiev) studied the reaction of aromatic amines with phosphorus pentachloride and found that weakly basic amines (2,4-dinitroaniline, trichloroaniline) form trichlorophosphazoaryls, and the more basic amines produce dimers of the composition $(ArNPCL_2)_2$, differing sharply in their properties from the monomers. G. I. Derkach (Kiev), reacting phosphorus pentachloride on diesters of acylamido phosphoric acids, produced C-chloro-P,P-di-aroxyisophosphazoacyls and investigated their reactions. The reactions with hydrogen sulfide leading to diesters of thioacylamido phosphoric acids, concerning which V. A. Shokol (Kiev gave a report, are relevant here. Zh. M. Ivanova (Kiev) showed that phenyl-tetrafluoro phosphorus and its homologs and analogs can be used for the production of a series of compounds with the grouping C-P-F.

Phenyl-α-fluoromethyl phosphinic acid, difluoroanhydrides of p-tolyl and p-chlorophenyl thiophosphinic acids and other compounds were synthesized.

The program of one of the meetings of Section I comprised questions of the chemistry of monomers and polymers. The report of N. K. Moshchinskaya, N. N. Budinskaya, Z. G. Kislitsyn, Z. E. Krukovskaya, and M. S. Ogiy (Dnepropetrovsk) contained new data on the condensation of formaldehyde with aromatic hydrocarbons. S. Ye. Gornostayeva and K. A. Kornev (Kiev) worked out a method for the aminomethylation of aromatic hydrocarbons and esters by the reaction of N-chloromethylphthalamide in nitromethane in the presence of $ZnCl_2$. By reduction of the condensation products the aliphatic-aromatic diamines are produced. The reactions of dicyandiamide with aromatic aldehydes and cyanamide with oxides of propylene and styrene were examined in the reports of A. Ye. Kretov and A. Ye. Kretov and I. S. Matveyev (Dnepropetrovsk). Dicyandiamide produces acyl, alkyl, nitro derivatives and methyl picrate derivatives. Oxazolidines are produced from cyanamide with oxides. The polymerization conditions for ethylene oxide and the properties of the polymers formed were the subject of the report of M. Kh. Gluzman, B. I. Dashevskaya, and V. M. Boden' (kharkov). In the closing session of Section I, V. A. Bogolyubskiy, G. P. Gumelyuk, and L. V. Grechko (Shostka) reported on the synthesis of certain derivatives of hydroquinone.

The sessions of Section II were devoted to the chemistry of dyes and intermediate products, adsorption spectra of organic compounds, and the chemistry of heterocyclic compounds.

I. A. Troyanov (Rubezhnoye) reported on a very simple method of synthesizing thioindigoid dyes by means of sulfuring arylmethyl ketones. As a result of the selection of appropriate conditions, excellent yields were successfully produced for thioindigoids in a series of derivatives of benzene, naphthalene, anthracene, acenaphthene, and heterocyclic nitrogen compounds. I. S. Dokunikhin and Yu. Ye. Gerasimenko (Rubezhnoye) synthesized a group of symmetrical and unsymmetrical derivatives of thioindigo, containing substituents in the benzene nucleus. It was shown that substituents, increasing the polarity of the molecule of thioindigo, deepen the color of the dye; and substitutents which lower the polarity, on the contrary, heighten it. A group of new dyes was produced by I. S. Dokunikhin and Ya. B. Shteynberg (Rubezhnoye) by the condensation of quaternary salts of N-methylbenz-(c,d)-indolin-2-thione with 3-oxythionaphthene, indoxyl, acenaphthene and with the quaternary salts of heterocyclic nitrogen compounds containing active methylene groups. V. M. Krasovitskiy, N. S. Dokunikhin, and R. M. Matskevich (Kharkov) obtained new direct diazo dyes from 1,3-diaminodiphenyl derivatives of thiodiazole and oxadiazole. Isomers of these dyes with meta-locations of the azo groups are less deeply and substantively colored. N. N. Vorozhtsov and S. M. Sheyn (Rubezhnoye) found that α-napthol in

conditions of alkali fusion is cleaved, forming benzene, naphthalene, toluene, acetic acid, o-toluic and -o-tolylpropionic acids. V. L. Plakidin and V. V. Reznichenko (Rubezhnoye) nitrated naphthalide, 3-oxynaphthalide, and 3-acetoxynaphthalide and produced mononitro derivatives which form dihydronitrohaphtholene benzimidazole on condensation with o-phenylene diamene. G. T. Pilyugin and Ye. N. Opanasenko (Chernovitsy) condensed p-methoxydiphenylamine with paraldehyde and with vinylbutyl ether. Perchlorates of 1-phenyl-6-methoxyquinaldine and p-methoxyphenylquinaldine were separated. From these cyanine dyes are produced. I. K. Ushenko (Kiev) reported on the radical displacement of hydrogen atoms after Meerwein in the benzene rings of 2-methylbenzthiazole, quinaldine, 2-methylbenzoxazole, and 2-methylbenzimidazole to unsaturated functions. Amino derivatives of these heterocyclic compounds were diazotized and the diazo compounds were processed with cinnamic, p-methylcinnamic p-methoxycinnamic, -thienylacrylic, piperonylacrylic, sorbic and other unsaturated acids and their esters, also with coumarin and acrylonitrile. As a result more than 40 bases with unsaturated residues on the benzene rings were produced, and from the quaternary salts of these bases -- cyanine dyes. It was shown that the introduction of unsaturated substitutents strongly displaces the adsorption zone into the long wave portion of the spectrum. M. A. Al'perovich, Yu. A. Naumov, and I. K. Ushenko (Shostka) reported on the separation by means of chromatography on aluminum oxide of the cis-and transisomers of 2-methyl-5-styrylbenzthiazole synthesized by them. The adsorption maxima for symmetrical carbocyanonines derived from these compounds were determined. Z. I. Miroshnichenko and M. A. Al'perovich (Shostka) synthesized 2-methyl- -thionaphthenthiazole (cyclization of 3-thioacetaminothionaphthene after Jacobsen) and 2-methyl- -thionaphthenthiazole (from 3-amino-2-oxythiazole and P_2S_5). From the quaternary salts of these heterocyclic compounds cyanine dyes were obtained. L. M. Yagupol'skiy and V. I. Troitskaya (Kiev) reported on the synthesis of intermediate products and dyes containing trifluoromethyl and trifluoromethylsulfonyl groups in the benzene nucleus. Imidocarbocyanines containing trifluoromethylsulfonyl became effective sensitizers. Dyes were also produced from 2-methyl-5,6-(difluoromethylendioxy)-benzthiazole.

Adsorption spectra of organic compounds made up the program of one session of Section II. A. I. Kiprianov and V. A. Shrubovich (Kiev), continuing the study of steric hindrance, synthesized simple and quaternary salts of 2- -naphthylbenzthiazole, 2- -naphthylbenzthiazole, and 2-(9'-anthranyl)-benzthiazole. In this series the steric hindrance increases to the extent that the distinctions in the adsorption spectra of sulfate and methyl perchlorate disappear in 9'-anthranyl benzthiazole. Yu. S. Rozum(Kiev) reported on a spectral method developed by him for the quantitative determination of isomeric quaternary salts formed in the reaction of dimethyl

sulfate on substituted phenazines, and also of isomeric N-oxides obtained by oxidizing derivatives of phenazine with hydrogen peroxide. This made it possible for the reporter to establish the orientation of substitutents in a series of phenazines. N. Ye. Grigor'yeva (Kharkov) investigated the effect of solvents on the pyridine dyes of Koenig-Zincke, and noted in this respect the difference between dyes that contain and do not contain a hydrogen atom on nitrogen.

At another session of Section II studies on the chemistry of heterocyclic compounds were reported on. N. M. Turkevich, Ye. V. Vladzimirskaya, and O. F. Lymar (Lvov) reported on new condensations leading to derivatives of thiazolidine. The reaction of ethyl urea with chloroacetic acid in the presence of aromatic aldehydes yields 5-arylidene derivatives of 2,3-ethylenpseudothiohydantoin. Analogous reactions with mercaptobenzimidazole lead to tricyclic compounds. Among the products obtained were compounds with pharmacological activity. S. N. Baranov and N. Ye. Tarnavskaya (Lvov) condensed o-phenylene dimaine with -thiokets acids and produced quinoxalines which were subjected to methylation, nitration, and were oxidized to N-oxides. S. N. Baranov and T. Ye. Gorizdra, by condensing 2-thio-4,5-diamino pyrimidines with aryl pyruvic acids, synthesized a group of thiopteridines which are analogs of thiopurines, possessing anti-tumor properties. F. S. Babichev (Kiev) reported on a convenient method for the synthesis of tri-, tetra- and penta-methylene thiazole salts, consisting in the condensation of thiolactams with -halogen ketones. Fifteen quaternary salts of thiazole were produced, and from these some thiazole cyanines. S. A. Fedorova and S. I. Burmistrov (Dnepropetrovsk), by the reaction of aryl thioammelines (aryl-2,4-diaminohexahydro-1,3,5-triazin-6-thiones). A. D. Grabenko, R. G. Dubenko, P. S. Pel'kis, M. Z. Peretyazhko, and L. S. Pupko (Kiev) reported on the synthesis of new drivatives of thiocarbanilide, 1,4-diphenyl-thiosemicarbazide, 1,5-diphenylthio-semicarbazide, 1,6-diphenylhydrazodithiodicarbonamide and aryl amides of dithiocarboxylic acids. All of these compounds are capable of being alkylated on the sulfur and give colored complexes with metal cations. Some possess anti-bacterial activity. K. A. Kornev and L. D. Protsenko (Kiev) synthesized aryl ethylene triamides and acyl diethylene triamides of phosphoric acid and ethylene phosphor-amides which contain four and six ethylenimine groups. All of these compounds show anti-carcinogenic effects. In the report of O. Kh. Vlasova (Dnepropetrovsk) data were presented on the synthesis and properties of phthalic acid esters and phenylcarbamic esters of aryl oxyethanols, of interest as potential herbicides.

Discussed and coordinated at special sessions of Sections I and II of the conference were the plans for scientific work for 1960 and the prospective plans up to 1965 with respect to the

following four problems: 1) reactivity, kinetics, and the mechanism of organic reactions; 2) color and structure of organic compounds; 3) chemistry of natural and biologically active compounds; 4) chemistry of insecticides.

From the Resolution of the Sixth Ukrainian Republican Conference on Organic Chemistry

The conference noted the considerable development of scientific work in organic chemistry in the Ukraine, especially in areas related to the solution of tasks assigned in the Seven-Year Plan. The conference approved the creation of new institutes, branches, and test laboratories, and noted with satisfaction the growth of young cadres and the yearning of young chemists to work on the solution of concrete problems in the development of the national economy.

The conference resolved:

1. To consider as necessary the further strengthening of the ties of scientific-research institutions and individual scientists with industry, in particular by a considerable expansion of contract work with industrial and other establishments.

2. To expand work in the field of polymers and synthetic materials.

3. To develop and amplify theoretical investigations and research projects, which guarantee further successes in the solution of practical problems.

4. To expand work on physiologically active substances, and to achieve the fulfillment of resolutions for the organization of the vast testing of these substances.

5. To accelerate the application of the results of research work, it is necessary to build large-scale laboratory testing installations in leading scientific institutions.

6. It is necessary to increase the volume of output of chemical periodicals in the Ukraine. The conference turns to the Presidium of the Academy of Sciences Ukrainian SSR and the Council of Ministers Ukrainian SSR with the request to expand the volume of the Ukrainskiy khimicheskiy zhurnal, beginning in 1960, and to make this journal a monthly. To request the editors of the Ukrainskiy khimicheskiy zhurnal to accelerate the editorial processing of articles. To request the Division of Chemical Sciences of the Academy of Sciences USSR to organize a journal of organic chemistry. To consider necessary an increase in the output of chemical literature by Tekhizdat [Tekhnicheskoye izdatel'stvo -- Technical Publishing House] of the Ukrainian SSR.

7. To request the Ministry of Higher and Secondary Special Education of the Ukrainian SSR to increase the output of specialists in organic chemistry and polymer materials.

8. To improve the staffing of plant laboratories with highly qualified scientific cadres. To liquidate the discontinuity in pay of workers of the higher and lower classifications working in scientific-research institutes and plant laboratories.

9. To request the Gosplan [Gosudarstvennaya planovaya kommissiya -- State Planning Commission] of the Ukrainian SSR to organize in the Ukraine the production of chemical glassware, standard joints, and thermometers.

10. To request the Gosplans of the Ukrainian SSR and the USSR to expand the production of pure-and technical-grade reagents, and to publish catalogs of the pure-and technical-grade chemicals produced in the USSR.

11. In view of the fact that a part of the laboratory equipment, in particular optical devices, has been manufactured according to obsolete patterns, to request the Gosplan USSR to take measures for the organization of the production of more modern laboratory instruments.

12. In view of the fact that in Kiev, and even more in other cities of the Ukrainian SSR, the assortment of wares in the stores of Soyuzreaktivsbyt [Union Reagent Sales] and in laboratory equipment stores is trifling, to request the State Committee for Chemistry of the Council of Ministers USSR and the Gosplans of the USSR and the Ukrainian SSR to take measures to assure a supply of reagents, chemical glassware, and the simplest instruments for commercial organizations.

13. To approve the plans, agreed upon in the coordinating committees of the conference, for scientific-research work in 1960 and the provisional plan for scientific investigations in the current Seven-Year Plan.

14. To convene the Seventh Ukrainian Republican Conference on Organic Chemistry in the second quarter of 1961.

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