PORADOVSKY, K.

EXCERPTA MEDICA Sec.10 Vol.11/4 Obstetrics-Gynaec.Apr58

597. THE TREATMENT OF TRANSVERSE PRESENTATION - O liečbe priečnej polohy - Poradovský K. and Kraus E. Gyn. pôr. Odd.KÚNZ, Žiline - ČSL. GYNAEK. 1957, 1-2 (73-80) Graphs 2 Tables 5

Of a total of 6,117 deliveries transverse presentation occurred in 105 cases (1.7%). The maternal death rate was zero. Total perinatal mortality was 15.2%; hospital perinatal mortality was 7.6%. The corrected mortality among newborn infants was 3.8% (after deducting monsters and immature foetuses). In the treatment of transverse presentation, external version was carried out in 24.8% and internal version in 39%; caesarean section was done in 31.5% of the cases. Perinatal mortality with external version was 3.8%, with internal version and subsequent extraction 56.4%, with internal version and manual assistance in breech presentation zero and with caesarean section 6.1%.

[illegible] [redacted]

Vaginal hysterectomy as a surgical treatment for complicated uterine prolapse. Cesk. gyn. 22[36] no.[illegible] Sept 57.

1. Gyn. por. odd. KUNZ v Ziline, prednosta Dr. Karol [illegible].
(UTERUS, dis.
prolapse, compl., vaginal hysterectomy (Cz))
(HYSTERECTOMY, in var. dis.
vaginal, in complicated uterine prolapse (Cz))

PORADOVSKY, K.; KHRADECKY, L.; MACH, M.; KLUCKOVA, I.; POKORNY, J.;
PONTUCH, A.; ZAJACOVA, E.

Obstetrical surgery and perinatal mortality. Cesk. gynek. 29 no.6:534-545 Ag '64.

1. Gyn.-por. klin. Lek. fak. University P.J. Safarika v Kosiciach (prednosta doc. dr. K. Poradovsky, CSc,) Gyn.-por. klin. Lek. fak. University Karlovy v Plzni (prednosta prof. dr. V. Mikolas); Gyn.-por. klin. Lek. fak. University J.E. Purkyne v Brne (prednosta prof. dr. L. Havlasek [deceased]) a Gyn.-por. klin. Lek. fak. University Komenskeho v Bratislave (prednosta prof. dr. S. Stefanic).

PORADOVSKY, K.

Importance of the parametrium for labor activity in the 1st stage of labor. Cesk. gynek. 28 no.7:466-469 S '63.

1. Gyn.-por. klin. Lek. fak. UPJS v Kosiciach, prednosta doc. dr. K. Poradovsky, CSc.

(LABOR) (UTERUS) (LABOR PRESENTATION)

PORADOVSKY, K.; ZIDEK, S.

Survey of perinatal mortality in eastern Slovakia in 1962.
Cesk. gynek. 29 no.6:444-447 Ag '64.

1. Gyn-por. klin. Lek. fak University P.J. Safarika v Kosiciach
(prednosta doc. dr. K. Poradovsky, CSc.).

PORADOVSKY, K.doc. dr., CSc.; PACIN,J.; RIMAROVA, J.

Anticoagulants. Cesk. gynek. 30 no.1:26-31 Mr '65.

1. Gyn.-por. klinika Lekarske fakulty University P.J. Safarika v Kosiciach (prednosta: doc. dr. K. Poradovsky, CSc.) a Krajska ved.-inform. kancelaria SPOFA v Kosiciach.

PORADOVSKY,K., doc. dr. CSc.; (Kosice, Fakultna nemocnica); RIMAROVA, J.

Effective pharmacotherapy of obstetric shock. Cesk. gynek. 30 no.1:57-61 Mr'65.

1. Gyn.-por. klinika Lekarske fakulty University P.J. Safarika v Kosiciach (prednosta: doc. dr. V. Poradovsky, CSc.) a Krajska ved.-inform. kancelaria Spofa v Kosiciach.

PORADOVSKY, K.

Medical management of premature labors. Bratisl. lek. listy 42 no.11/12: 655-665 '62.

1. Z Porodnicko-gynekologickej kliniky Univerzity P.J. Safarika v Kosiciach, prednosta prof. MUDr. T. Schwarz.
(INFANT PREMATURE) (INFANT MORTALITY) (CESAREAN SECTION)

PORADOVSKY, K.

On shock in labor. Cesk. gyn. 28 no.1/2:65-70 F '63.

1. Gyn.-por. klin. Lek. fak. UPJS v Kosiciach, prednosta doc. dr. K. Poradovsky, CSc.

(LABOR) (HEMORRHAGE UTERINE) (MATERNAL MORTALITY)

PACIN, J., doc.; PORADOVSKY, K.; KAHANEC, D., CSc.

Arterial and venous differences in umbilical blood coagulation studied with the aid of thromboelastography. Cesk. gynek. 27/41 no.8:593-597 '62.

1. Gyn.-por. klin. Lek. fak. UPJS v Kosiciach, prednosta prof. dr. T. Schwarz.
(THROMBOELASTOGRAPHY) (UMBILICAL CORD)

PORADOVSKY, K. CSSR

no academic degree indicated

Obstetrical-gynaecological clinic, P.J. Safarik University (porodnicko-gynecologicka klinika Univerzity P.J. Safarika), Kosice; director: prof. T.SCHWARZ, MD

Bratislava, Bratislavske lekarske listy, No 11-12, 1962, pp 655-665.

"Obstetrical Conduct of Premature Deliveries"

PORADOVSKY, K., doc.; SEDLIAK, M., CSc.; ZIDEK, S.; KAHANEC, D.

Successful management of afibrinogenemia following amniotic fluid embolism. Cesk. gynek. 27/41 no.8:598-602 '62.

1. Gyn.-por. klin. Lek. fak. UPJS v Kosiciach, prednosta prof. dr. T. Schwarz.

(EMBOLISM AMNIOTIC FLUID) (AFIBRINOGENEMIA)
(SHOCK) (OXYTOCICS)

PORADOVSKY, K.

On the fiftieth anniversary of Dr. Ernest Dlhos. Cesk.gyn. 25[39] no.5;400-404 Je '60.
(BIOGRAPHIES)

PORADOVSKY, Karol, C.Sc

Indications for artificial amniotic rupture during the first stage of labor. Cesk.gyn. 25[39] no.5:391-396 Je '60.

1. Gynek. porod. odd. KUNZ v Ziline, prednosta dr. Karol Poradovsky, C.Sc.

(DELIVERY)
(AMNION)

PORADOVSKY, Karol

Surgical therapy of tubal occlusion. Cesk. gyn. 24[38] no.9: 700-703 Nov. 1959.

1. Gyn.-por. odd. KUNZ v Ziline, prednosta dr. Karol Poradovsky.
(STERILITY, FEMALE, surg.) (FALLOPIAN TUBES, dis.)

PORADOVSKY, Karol, C.Sc.

Lacerations of the cervix and perforations of the uterus in artificial interruption of pregnancy. Cesk.gyn.25[39] no.9: 682-688 N '60.

1. Gyn.por.odd. KUNZ v Ziline, prednosta dr. Karol Poradovsky.
(ABORTION THERAPEUTIC compl)

h

COUNTRY : POLAND
CATEGORY : Chemical Technology. Chemical Products and Their Applications. Cellulose and Its *
ABS. JOUR. : RZKhim., No. 23 1959, No. 84350

AUTHOR : Jaroszewski, J.; Poradowska, H.
INST. : -
TITLE : Experimental Production of the Electro-Insulating Asbestos Paper

ORIG. PUB. : Przegl. papiern., 1959, 15, No 5, 150-154

ABSTRACT : On the basis of laboratory and commercial casting a conclusion was made pertaining to the possibility of production of such a paper from 100% asbestos. The conducted experiments employed asbestos of the following different grades: Soviet, African and Chinese. The best results were obtained with the Soviet asbestos type L-1-60, purified of the accompanying mineral substances. As a binding agent, it is recommended to employ starch as an additive to a roll in a quantity of 5% basis weight of

*Derivatives. Paper.
CARD: 1/2

PORADOWSKA, Henryka, mgr inz.

Contribution to studies on the smoothness of newsprint.
Przegl papier 18 no.8:246-249 Ag '62.

1. Instytut Celulozowo-Papierniczy, Lodz.

PORADOWSKA, Henryka, mgr inz.

Paper in the service of the motorization industry. Przegl papier 20 no.6:186-189 Je '64.

1. Pulp and Paper Institute, Lodz.

PORADOWSKA, Wanda

[redacted]

Clinical manifestations of mechanical obstruction of the esophagus in children. Polski przegl.chir. 27 no.7:699-710 July 1955.
(ESOPHAGUS, diseases,
obstruct.mechanical,clin.manifest. in child)

PORADOWSKA, Wanda; LODZINSKI, Kazimierz; KUBICZ, Stanislaw

Pulmonary tissue resection in staphylococcal pneumonia in infants. Pediat. Pol. 39 no.6:677-683 Je '64.

1. Z Kliniki Chirurgii Dzieciecej (Kierownik: prof. dr med. W. Poradowska), i z Zakladu Radiologii (Kierownik: doc. dr med. S. Kubicz) Instytutu Matki i Dziecka w Warszawie (Dyrektor: prof. dr med. B. Gornicki).

PORADOWSKA, W.

"O oparzeniach u dzieci" (About burns at children), by W. Poradowska. Reported in New Books (Nowe Ksiązki), No. 11, June 1, 1956.

PORADOWSKA, W.; JAWORSKA, M.; LODZINSKI, K.

On the etiology of myelomeningocoele: Report of three cases.
Acta chir. plast. 5 no.4:285-288 '63.

1. Surgical Department of Institute of Mother and Child,
Warsaw (Poland) Director: Prof. W. Poradowska, M.D.

(MENINGOCELE) (MATERNAL-FETAL EXCHANGE)
(GENETICS, HUMAN)

PORADOWSKA, W.; JAWORSKA, M.

Etiology of bilateral cleft lip and palate. Acta chir. plast. 5 no.3:175-180 '63.

1. Surgical Department of the Institute of Mother and Child, Warsaw (Poland) Chief: Prof. W. Poradowska, M.D. Director of the Institute: Prof. B. Gornicki, M.D.

(CLEFT PALATE) (HARELIP)
(PREGNANCY COMPLICATIONS)
(GENETICS, HUMAN)

JAWORSKA, M.; PORADOWSKA, W.

Cleft lip and cleft palate: A summarized statistical survey. Acta chir. plast. 5 no.3:181-186 '63.

1. Surgical Department of the Institute of Mother and Child, Warsaw (Poland) Chief: Prof. W. Poradowska, M.D. Director of the Institute: Prof. B. Gornicki, M.D.

(CLEFT PALATE) (HARELIP)
(PREGNANCY COMPLICATIONS)
(GENETICS, HUMAN) (STATISTICS)

KUBICZ, Stanislaw; PORADOWSKA, Wanda; JANISZEWSKA, Maria

Cases of congenital defects of pulmonary vessels. Pol. przegl. radiol 27 no.5:403-416 S-O '63.

1. Panstwowe Sanatorium P.-Gruzlicze dla Dzieci im. J. Marchlewskiego w Otwocku[illegible]Zaklad Radiologii Instytutu Matki i Dziecka (Kierownik: doc. S. Kubicz) i Oddz. Chirurgiczny Instytutu Matki i Dziecka (Kierownik: prof. W. Poradowska).

PORADOWSKA, Wanda; LODZINSKI, Kazimierz; KUBICZ, Stanislaw; BOROWICZ, Krystyna

Congenital pulmonary cysts in infants and small children. Pol. przegl. chir. 36 no.3:357-364 Mr '64.

1. Z Oddzialu Klinicznego Chirurgii Dzieciecej (Kierownik: prof. dr W. Poradowska), z Zakladu Radiologii (Kierownik: doc. dr S. Kubicz), z Zakladu Anatomii Patologicznej (Kierownik: dr K. Borowicz, i z Instytutu Matki i Dziecka w Warszawie (Dyrektor: prof. dr B. Gornicki).

KUBICZ, S.; PORADOWSKA, W.; RONDIO, Z.; SWIDERSKI, J.

Surgical treatment of aortic coarctation in a 3-year-old boy. Pediat. pol. 36 no.6:633-643 '61.

1. Z Oddzialu Chirurgii Dzieciecej--kierownik: prof. dr med. W. Poradowska Z Zakladu Fizjopatologii--kierownik: doc. dr med. A.Chroscicki i z Zakladu Rentgenodiagnostyki--kierownik: doc. dr med. S.Kubicz Instytutu Matki i Dziecka w Warszawie Dyrektor: prof. dr med. Fr. Groer.

(AORTIC COARCTATION surg)

PORADOWSKA, Wanda; JAWORSKA, Mieczyslawa

Classification of congenital fissures of the palate. Polski przegl. chir. 35 no.1:65-71 '63.

1. Z Instytutu Matki i Dziecka w Warszawie Dyrektor: prof. dr B. Gornicki z Oddzialu Chirurgicznego Kierownik: prof. dr W. Poradowska.

(CLEFT PALATE) (CLASSIFICATION)

PORADOWSKA, Wanda; LODZINSKI, Kazimierz; KUBICZ, Stanislaw; BOROWICZ,
Krystyna

Pulmonary echinococcosis in a child. Polski przegl. radiol. 26
no.2:123-129 '62.

1. Z Oddzialu Chirurgii Dzieciecej Kierownik: prof. dr med.
W. Poradowska z Zakladu Radiologii Kierownik: doc. dr med. S.Kubicz
z Zakladu Anatomii Patologicznej Kierownik: dr med. K.Borowicz
z Instytutu Matki i Dziecka Dyrektor: profl dr med. B.Gornicki.
(LUNG DISEASES in inf & child)
(ECHINOCOCCOSIS in inf & child)

PORADOWSKI, Szymon

Report from the Third General Meeting of the Section of Zoological Garden, Polish Zoological Society, held in Torun September 5, 1962. Przegl zoolog 7 no. 1:112-115 '63.

PORADNYA, A.I., doktor tekhn. nauk, prof.; SHLYAPNIKOVA, A.G., inzh.; PUCHKOVSKIY, N.V., kand. tekhn. nauk, nauchn. red.; DNEPROVA, N.N., red.izd-va; CHERKASSKAYA, F.T., tekhn.red.

[Organization, planning and economics of construction work] Organizatsiia, planirovanie i ekonomika stroitel'nykh rabot. Leningrad, Gosstroiizdat, 1963. 258 p. (MIRA 17:2)

VOL'SKI, V. [Wolski, W.]; POLITAN'SKA, U. [Politanska, U.];
PORAVSKI, B. [Porawski, E.]; BOKHYNS'KA, A. [Bochynska, A.]

Ferromagnetic phases in the products of nickel ferricyanide thermal decomposition. Zhur.neorg.khim. 10 no.12:2693-2697 D '65. (MIRA 19:1)

1. Universitet imeni L.Mitskevicha, laboratoriya magnitokhimii, Poznan', Pol'sha.

PORAY-KOSHITS, M.A.; IONOV, S.P.; NOVOZHENYUK, Z.M.

Structure of the crystals of certain trivalentiridium compounds with inner-sphere sulfite groups. Zhur. strukt. khim. 6 no.1. 173 '65. (MIRA 18:12)

1. Institut obshchey i neorganicheskoy khimii imeni N.S. Kurnakova AN SSSR. Submitted June 22, 1964.

IONOV, S.P.; PORAY-KOSHITS, M.A.

Molecular orbits of thiosulfate ion. Zhur.neorg.khim. 10 no.8:1771-1776 Ag '65. (MIRA 19:1)

1. Submitted December 14, 1964.

PORAY-KOSHITS, M.A.

Electronic structure of thiocyanate groups. Zhur.neorg. khim. 10 no.12:2835-2836 D '65. (MIRA 19:1)

GOGANOV, D.A.; PORAY-KOSHITS, Ye.A.

Change in the supermolecular structure of sodium-silicate glass due to heating. Dokl. AN SSSR 165 no.5:1037-1040 D '65. (MIRA 19:1)

1. Institut khimii silikatov im. A.V.Grebenshchikova AN SSSR. Submitted April 20, 1965.

GOGANOV, D. A.; PORAY-KOSHITS, Ye. A.

"Some new results of applying the method of X-ray scattering at small angles to silicate glasses."

report submitted for 4th All-Union Conf on Structure of Glass, Leningrad, 16-21 Mar 64.

AVERYANOV, V. I.; PORAY-KOSHITS. Ye. A.

"Investigation of exfoliation of glasses of lithium silicate system by methods of electron microscopy."

report submitted for 4th All-Union Conf on Structure of Glass, Leningrad, 16-21 Mar 64.

PORAI-KOSHITS, AL. Ye.

DECEASED 1949

Chemistry

See ILC

FOLAK, Feliks; PORASIEWICZ-KACZMARSKA, Jadwiga

Narrow- and wide-pore silicagels as drying agents. Przem chem 40 no.12:702-705 D '61.

1. Katedra Technologii Chemicznej, Uniwersytet Jagiellonski, Krakow.

PORADOWSKI, S.

New name of the zoological garden of the city of Zamosc. Przegl zoolog 6 no.4:315-316 '62.

PORADOWSKI, Szymon

From the activities of the Commission for Systematic Identification and Nomenclature of Animals in Zoological Gardens. Przegl zoolog 6 no.4:316 '62.

PORAWSKI, WIESLAW

SURNAME, Given Names

[illegible] ③

Country: Poland

Academic Degrees: /not given/

Affiliation: /not given/

Source: Warsaw, Medycyna Weterynaryina, Vol XVII, No 8, August 1961, pp 467-468.

Data: "Control of Cattle Tuberculosis on the Terrain of Zakopane."

Authors:
GAILHOFER, Jan
NAWROCKI, Jan
PORAWSKI, Wieslaw.

GPO 901643

PORAWSKI, WIESLAW

SURNAME, Given Names

Country: Poland

②

Academic Degrees: [not given]

Affiliation: [not given]

Source: Warsaw, Medycyna Weterynaryina, Vol XVII, No 8, August 1961, pp 467-468.

Data: "Control of Cattle Tuberculosis on the Terrain of Zakopane."

Authors:
GAILHOFER, Jan
NAWROCKI, Jan
PORAWSKI, Wieslaw.

147

GPO 981643

RAVDEL', A A.; PORAY-KOSHITS, A.B.; SHARIKOV, Yu.V.; CHERNOVA, G.A.

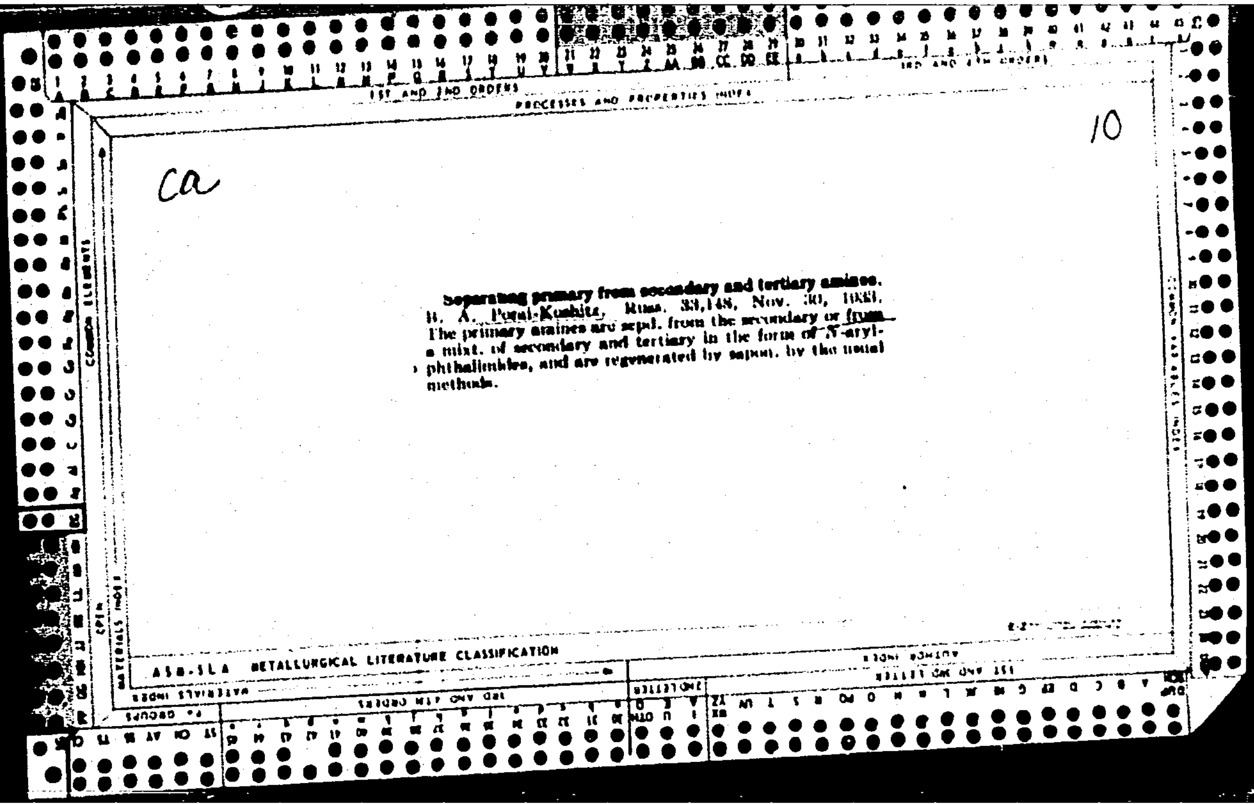
Determination of the coefficient of diffusion of borax and sodium pentaborate in aqueous solutions. Zhur. prikl. khim. 38 no.1:195-197 Ja '65. (MIRA 18:3)

1. Leningradskiy tekhnologicheskiy institut imeni Lensoveta.

RAVDEL', A.A.; PORAY-KOSHITS, A.B.

Determination of the coefficients of diffusion of some organic substances in water and organic solvents. Zhur. prikl. khim. 38 no.1:205-206 Ja '65. (MIRA 18:3)

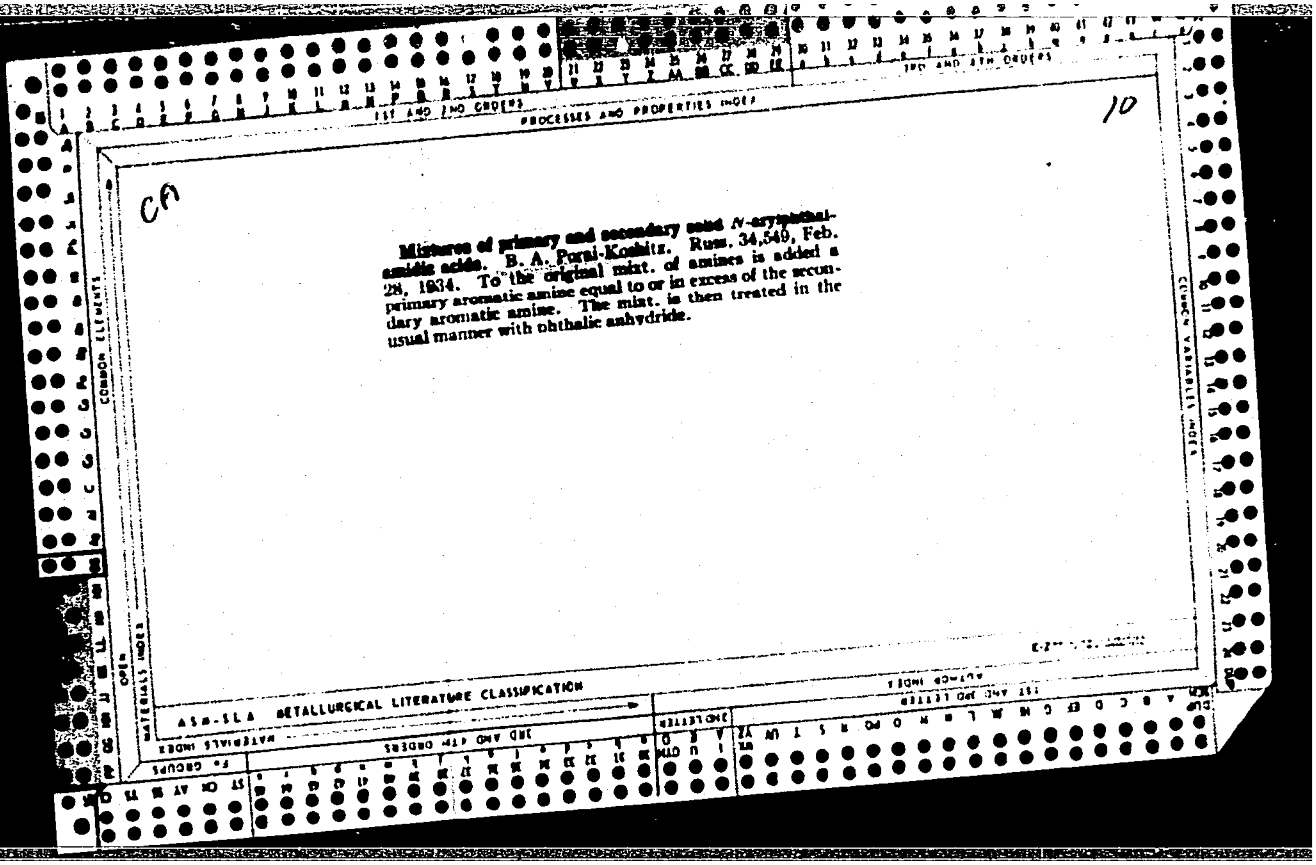
1. Leningradskiy tekhnologicheskiy institut imeni Lensoveta.



ca

10

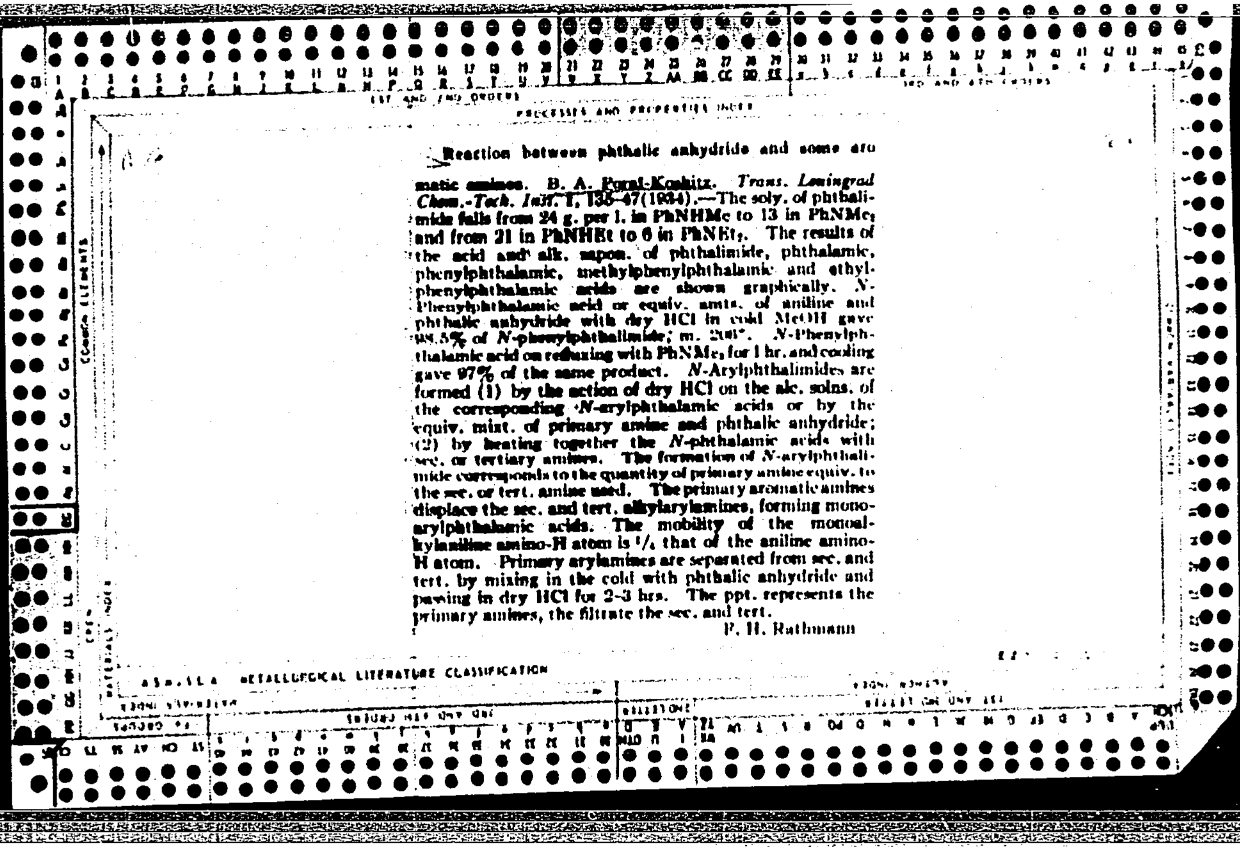
Separating primary from secondary and tertiary amines. B. A. Porai-Koshits, Russ. 33,148, Nov. 30, 1933. The primary amines are sepd. from the secondary or from a mixt. of secondary and tertiary in the form of N-arylphthalimides, and are regenerated by sapon. by the usual methods.



CA

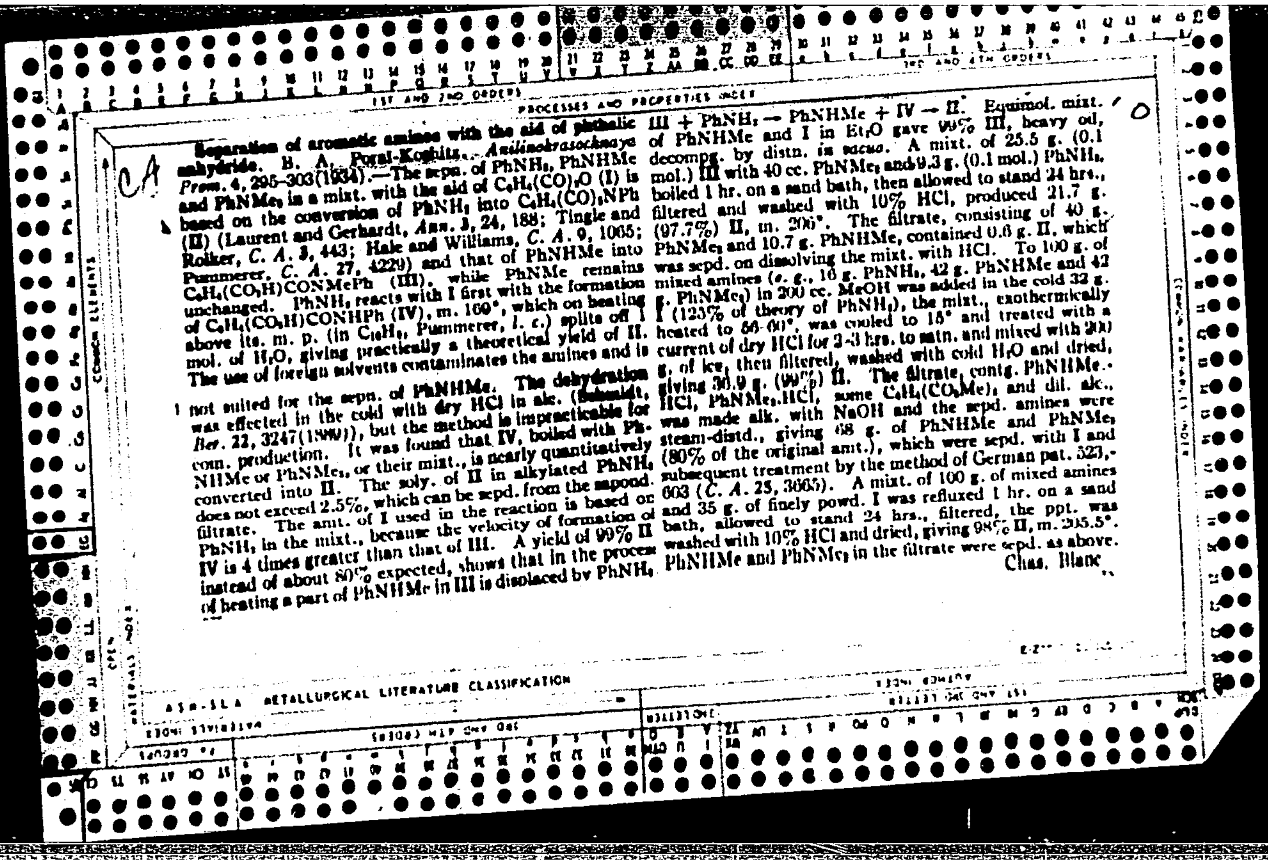
10

Mixtures of primary and secondary solid ***N*****-arylphthalamidic acids.** B. A. Porai-Koshits. Russ. 34,549, Feb. 28, 1934. To the original mixt. of amines is added a primary aromatic amine equal to or in excess of the secondary aromatic amine. The mixt. is then treated in the usual manner with phthalic anhydride.



Reaction between phthalic anhydride and some aromatic amines. B. A. Porai-Koshitz. *Trans. Leningrad Chem.-Tech. Inst.* 1, 135-47(1934).—The soly. of phthalimide falls from 24 g. per l. in PhNHMe to 13 in $PhNMe_2$ and from 21 in PhNHEt to 6 in $PhNEt_2$. The results of the acid and alk. sapon. of phthalimide, phthalamic, phenylphthalamic, methylphenylphthalamic and ethylphenylphthalamic acids are shown graphically. *N*-Phenylphthalamic acid or equiv. amts. of aniline and phthalic anhydride with dry HCl in cold MeOH gave 98.5% of *N*-phenylphthalimide; m. 208°. *N*-Phenylphthalamic acid on refluxing with $PhNMe_2$ for 1 hr. and cooling gave 97% of the same product. *N*-Arylphthalimides are formed (1) by the action of dry HCl on the alc. solns. of the corresponding *N*-arylphthalamic acids or by the equiv. mixt. of primary amine and phthalic anhydride; (2) by heating together the *N*-phthalamic acids with sec. or tertiary amines. The formation of *N*-arylphthalimide corresponds to the quantity of primary amine equiv. to the sec. or tert. amine used. The primary aromatic amines displace the sec. and tert. alkylarylamines, forming monoarylphthalamic acids. The mobility of the monoalkylaniline amino-H atom is 1/4 that of the aniline amino-H atom. Primary arylamines are separated from sec. and tert. by mixing in the cold with phthalic anhydride and passing in dry HCl for 2-3 hrs. The ppt. represents the primary amines, the filtrate the sec. and tert.

P. H. Rathmann



1ST AND 2ND ORDERS

PROCESSES AND PROPERTIES INDEX

3RD AND 4TH ORDERS

CA

Separation of aromatic amines with the aid of phthalic anhydride. B. A. Poral-Koshits. *Anilinokrasochnaya Prom.* 4, 295-303(1934).—The sepn. of $PhNH_2$, PhNHMe and $PhNMe_2$ in a mixt. with the aid of $C_6H_4(CO)_2O$ (I) is based on the conversion of $PhNH_2$ into $C_6H_4(CO)_2NPh$ (II) (Laurent and Gerhardt, *Ann.* 3, 24, 188; Tingle and Rolker, *C. A.* 3, 443; Hale and Williams, *C. A.* 9, 1065; Pummerer, *C. A.* 27, 4229) and that of PhNHMe into $C_6H_4(CO_2H)CONMePh$ (III), while PhNMe remains unchanged. $PhNH_2$ reacts with I first with the formation of $C_6H_4(CO_2H)CONHPh$ (IV), m. 169°, which on heating above its m. p. (in C_6H_6, Pummerer, *l. c.*) splits off 1 mol. of H_2O, giving practically a theoretical yield of II. The use of foreign solvents contaminates the amines and is not suited for the sepn. of PhNHMe. The dehydration was effected in the cold with dry HCl in alc. (Schmidt, *Ber.* 22, 3247(1889)), but the method is impracticable for com. production. It was found that IV, boiled with PhNHMe or $PhNMe_2$, or their mixt., is nearly quantitatively converted into II. The soly. of II in alkylated $PhNH_2$ does not exceed 2.5%, which can be sepd. from the mpood. filtrate. The amt. of I used in the reaction is based on $PhNH_2$ in the mixt., because the velocity of formation of IV is 4 times greater than that of III. A yield of 99% II instead of about 80% expected, shows that in the process of heating a part of PhNHMe in III is displaced by $PhNH_2$ III + $PhNH_2$ → PhNHMe + IV → II. Equimol. mixt. of PhNHMe and I in Et_2O gave 99% III, heavy oil, decompg. by distn. *in vacuo*. A mixt. of 25.5 g. (0.1 mol.) III with 40 cc. $PhNMe_2$ and 9.3 g. (0.1 mol.) $PhNH_2$, boiled 1 hr. on a sand bath, then allowed to stand 24 hrs., filtered and washed with 10% HCl, produced 21.7 g. (97.7%) II, m. 206°. The filtrate, consisting of 40 g. $PhNMe_2$ and 10.7 g. PhNHMe, contained 0.6 g. II, which was sepd. on dissolving the mixt. with HCl. To 100 g. of mixed amines (*e. g.*, 16 g. $PhNH_2$, 42 g. PhNHMe and 42 g. $PhNMe_2$) in 200 cc. MeOH was added in the cold 32 g. I (123% of theory of $PhNH_2$), the mixt., exothermically heated to 56-60°, was cooled to 15° and treated with a current of dry HCl for 2-3 hrs. to satn. and mixed with 200 g. of ice, then filtered, washed with cold H_2O and dried, giving 30.9 g. (99%) II. The filtrate, contg. PhNHMe.HCl, $PhNMe_2$.HCl, some $C_6H_4(CO_2Me)_2$ and dil. alc., was made alk. with NaOH and the sepd. amines were steam-distd., giving 68 g. of PhNHMe and $PhNMe_2$ (80% of the original amt.), which were sepd. with I and subsequent treatment by the method of German pat. 523,603 (*C. A.* 25, 3665). A mixt. of 100 g. of mixed amines and 35 g. of finely powd. I was refluxed 1 hr. on a sand bath, allowed to stand 24 hrs., filtered, the ppt. was washed with 10% HCl and dried, giving 98% II, m. 205.5°. PhNHMe and $PhNMe_2$ in the filtrate were sepd. as above.

Chas. Blanc

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

1ST AND 2ND ORDERS

PROCESSES AND PROPERTIES INDEX

3RD AND 4TH ORDERS

Cr

10

Purifying quinoline and its derivatives. B. A. Porai-Koshits. Russ. 47,297, June 30, 1936. Quinoline and its derivs. prepd. by the Skraup method are freed from primary amines by treatment with phthalic anhydride and sepn. of the arylphthalamic acids thus formed as alkali salts.

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

PROCESSES AND PROPERTIES INDEX

Cb

25

Preparation and tinctorial properties of the condensation products in the fluorene series of the type of Naphthol AS. B. A. Poral-Koshits and V. V. Perekalin. *Org. Chem. Ind.* (U. S. S. R.) 4, 165-70(1937).—A modified method of Ger. pats. 264,527 and 293,897 was used in the prepn. of 5 new condensation products in the fluorene series of the general type RHN.C_6H_3.CH_2.C_6H_3.NHR (R = 2,3-naphthioic acid (I), salicylic acid (II) and $AcCH_2CO_2Et$ (III)). To this end, 0.01 mol. of 2,7-diaminofluorene (IV), 2,7-diaminofluorenone (V) and 2,7-diaminofluorenol (VI) were refluxed with 0.02 mol. of the acid and 50% excess PCl_3 in 25 g. p-$C_6H_4Cl_2$ as solvent. For the condensation of IV with III 65 cc. xylene as solvent was used. Of these compds. IV and I, m. approx. 280° (75-80% yield), IV and II, m. 267° (80%), IV and III, m. 167° (44-6%), V and I, m. approx. 330° (40-50%), and VI and I, m. approx. 310° (20-5%). Cotton sateen impregnated with these compds. and then treated with the usual diazotized amines (up to 17 azo components were tested) gave various shades of colors ranging from yellow through red to dark blue. These compds. excel in substantivity and their dyeings in the intensity, fastness to light and other desirable properties Naphthol AS and its derivs. The tinctorial properties of these compds. decline from the IV to VI with the V derivs. occupying the intermediate position. Approx. 15 references. Chas. Blanc

A.S.M.-S.L.A. METALLURGICAL LITERATURE CLASSIFICATION

PROCESSES AND PROPERTIES INDEX

CO-

10

The action of hydrogen chloride on substituted phthalamic acids in alcohol. B. A. Porai-Koshits. *J. Gen. Chem.* (U. S. S. R.) 7, 604-10(1937). *N*-Arylphthalamic acids (I) with dry HCl in cold alc. or MeOH gave 75-90% of *N*-arylphthalimides (cf. *C. A.* **29,** 6580). I are formed when a cold equimol. mixt. of phthalic anhydride (II) and a primary amine in $PhNMe_2$ or $PhNEt_2$ is treated with dil. NaOH and then pptd. with HCl. *N-Phenylphthalimide*, m. 206°. *N-o-Tolylphthalimide*, m. 178-81°. *N-p-Tolylphthalimide*, m. 200°. *N-α-Naphthylphthalimide*, m. 180-1°. *N-β-Naphthylphthalimide*, m. 215-16°. *N-p*-Hydroxyphenylphthalamic acid, obtained from $p\text{-}H_2NC_6H_4OH$ and II in Me_2CO (cf. Piutti and Abati, *Ber.* **36,** 998(1903)), gave *N-p-hydroxyphenylphthalimide*, m. 291°. *N-p-Dimethylaminophenylphthalimide*, m. 258-60° (the HCl salt, m. 218°), from *N-p*-dimethylaminophenylphthalamic acid, m. 157°, obtained from $p\text{-}H_2NC_6H_4NEt_2$ and II in C_6H_6. Boiling naphthalic anhydride in excess of $PhNH_2$ for 30-40 min. resulted in *N-phenylnaphthalimide*, m. 199-200°. This boiled with 10°Bé. NaOH for 12 hrs., then filtered and the filtrate acidified with HCl, gave *N*-phenylnaphthalamic acid, m. 286°. On standing in the air or more rapidly with HCl in alc., it is converted into the imide. **The interaction of some amines with *N*-alkylarylphthalamic acids.** *Ibid.* 611-20. The preliminary results show that the displacement of sec. alkylarylamines in phthalamic acids by primary amines with the formation of monoarylphthalamic acids is a reversible reaction: $PhNMeCOC_6H_4CO_2H + PhNH_2 \rightarrow PhNHCOC_6H_4CO_2H + PhNHMe$. The reaction equil. depends on the relative soly. of the 2 products in the medium used (Et_2O, $PhNMe_2$). Thus in the interaction of *N*-phenylphthalamic acid with PhNHMe in $PhNMe_2$ 76% *N*-phenylphthalamic acid and considerable $PhNH_2$ were formed. *N*-Diphenylphthalamic acid (3.2 g.) and 1 g. $PhNH_2$ in 40 cc. Et_2O was allowed to evap. slowly (8-10 days), giving 0.4-0.5 g. *N*-phenylphthalamic acid, m. 168-9° (alc.). Ethyl-*o*-tolylphthalamic acid, m. 110° (obtained from $o\text{-}MeC_6H_4NHEt$ and phthalic anhydride in C_6H_6), and $o\text{-}MeC_6H_4NH_2$ gave *o*-tolylphthalamic acid, m. 170°. Ethyl-α-naphthylphthalamic acid, m. 165°, and $\alpha\text{-}C_{10}H_7NH_2$ gave α-naphthylphthalamic acid (the imide m. 181°). The investigation is being continued.

Chas. Blanc

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

1ST AND 2ND ORDERS

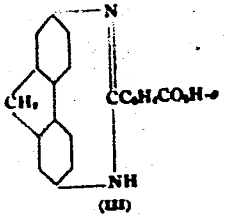
3RD AND 4TH ORDERS

PROCESSES AND PROPERTIES INDEX

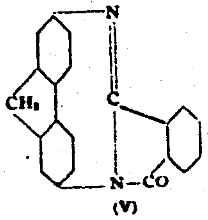
Ca

10

Fluorene. I. Condensation of 2,7-diaminofluorene with phthalic anhydride. B. A. Porai-Koshits and A. M. Efros. *Bull. acad. sci. U. R. S. S., Classe sci. tech.* 1938, No. 3, 43-60; cf. *C. A.* 33, 625^9.—2,7-Diaminofluorene (I) and o-$C_6H_4(CO)_2O$ (II) in H_2O (8 hrs. at the b. p.) yield a *substance* said to be III, m. 280° (decompn.),



(III)



(V)

1 together with *2,7-diphthalimidofluorene* (IV), m. 302°. III is converted into a *substance* (V), m. 340°, by heatin in Ac_2O or C_5H_5N (at the b. p.), or by heating alone a 130°; V is also prepd. from I and II in $PhNMe_2$, at th b. p. 2-Aminofluorene and II in $PhNMe_2$ (2.5 hrs. at th b. p.) yield *2-phthalimidofluorene*, m. 270°, the *7-NC deriv.*, m. 308°, of which is reduced (Zn in EtOH-$CaCl_2$) t *7-amino-2-phthalimidofluorene* (VI), m. 262°, from whic V is obtained by boiling for 5 hrs. with $PhNMe_2$. VI an
2 BzH (25 min. at the b. p.) yield *2-benzylideneamino-7-phthalimidofluorene*, m. 246°, regenerating VI and BzH when hydrolyzed (10% HCl). VI and II in $PhNMe_2$ (5 hrs. at the b. p.) afford IV, while in EtOH (2 hrs. at the b. p.) the product is *2-phthalimido-7-fluorenylphthalamic acid*. V and BzH (35 min. at the b. p.) give the 9-benzylidene deriv. of V, m. 367°. 2-Aminofluorene and BzH (30 min. at the b. p.) yield *2-benzylideneaminofluorene*, m.
3 152°, readily hydrolyzed by acids. B. C. P. A.

ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION

COMMON ELEMENTS

MATERIALS INDEX

COMMON VARIABLES INDEX

AUTHOR INDEX

PORAJ-KOCHITZ, B. A.

"Sur la structure de la Quinophtalone." Poraj-Kochitz, A. E., Poraj-Kochitz, B. A., Louyk, S. A. (p. 123)

SO: Journal of General Chemistry (Zhurnal Obschei Khimii) 1938, Volume 8, No. 2

1ST AND 2ND ORDERS

3RD AND 4TH ORDERS

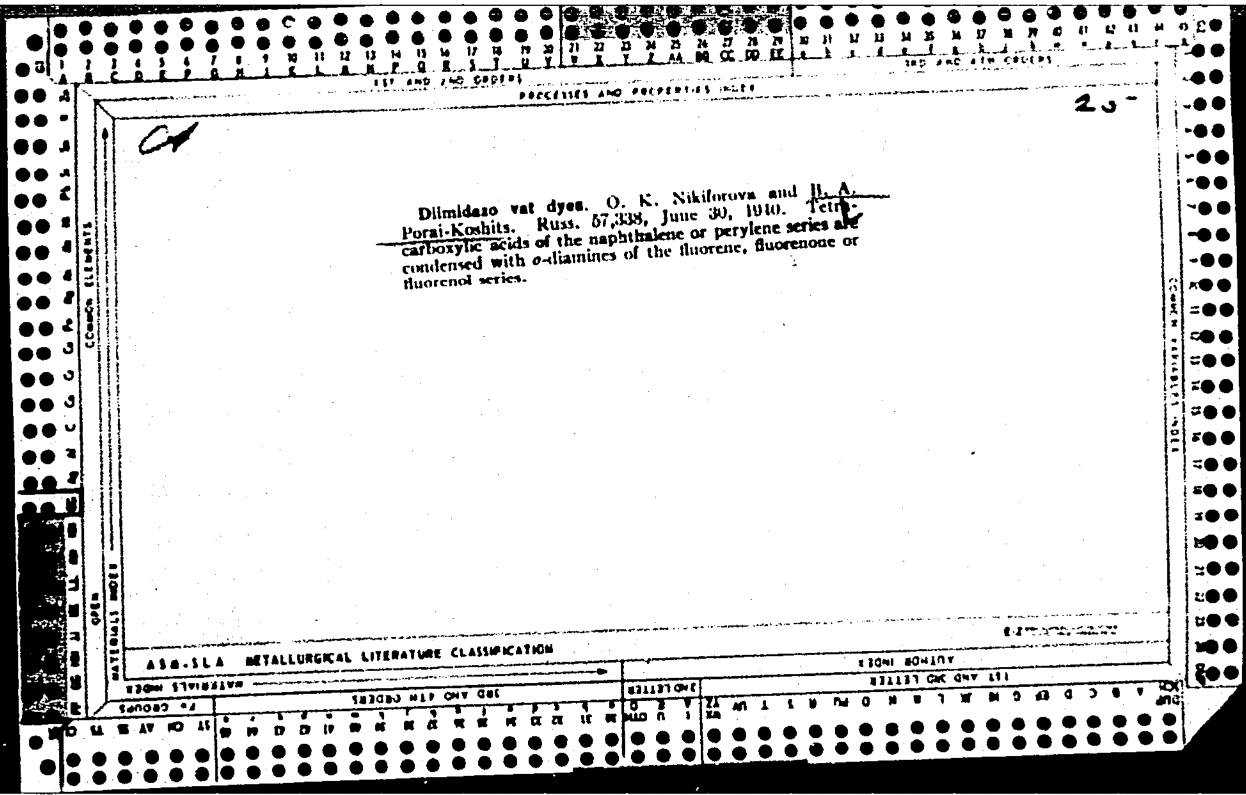
PROCESSES AND PROPERTIES INDEX

ca

10

Fluorene (and its derivatives). B. A. Porai-Koshits. *Org. Chem. Ind.* (U. S. S. R.) 6, 418-64(1939).—A review of literature with 100 references. Chas. Blanc

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION



Ca

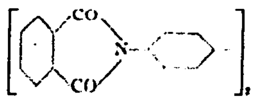
20-

Diimidazo vat dyes. O. K. Nikiforova and B. A. Porai-Koshits. Russ. 67,338, June 30, 1940. Tetracarboxylic acids of the naphthalene or perylene series are condensed with o-diamines of the fluorene, fluorenone or fluorenol series.

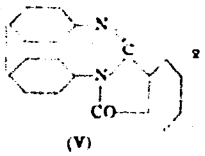
CA

10

Preparation and study of condensation products from phthalic anhydride and benzidine. B. A. Poral-Koshits and P. M. Mostryukov. *J. Gen. Chem.* (U. S. S. R.) **10,** 620-35(1940).—In order to establish clearly the structure of condensation products from phthalic anhydride (I) and benzidine (II), the work previously carried out by Guglialmelli (*C. A.* **26,** 725) on this subject has been repeated. To 14.8 g. I dissolved in 150 ml. hot alc. was added 9.2 g. II in 100 ml. alc. while stirring. The ppt. (23.8 g.) which is easily dissolved in soda and alkalies was boiled with $PhNMe_2$ (III) whereby water was split off and compds. IV and V were obtained, as described by G. IV and V were sepd. by means of cold alc. whereby IV remains at the bottom and V is obtained in the form of a suspension and may be isolated by decantation. Condensation of I and II in III gave a mixt. of IV and V. Pure IV, m. 406°, was synthesized from 100 g. molten I to which 10 g. II was added in small portions. The cooled mass was pulverized, then warmed with 10% soda soln. until the excess I was removed, the undissolved product was filtered off and washed with hot water; yield 14.5 g. Pure V, m. 309°, was synthesized by adding gradually to 100 g. molten II 10 g. I, and cooling, pulverizing and boiling the reaction mass with alc.; yield 15.8 g. When 5 g. IV was added gradually to 50 g. molten II and the mass was then cooled, pulverized and extd. with alc., the residue consisted of V. Similarly, 5 g. V on an analogous reaction with 50 g. molten I, gave IV.



(IV)



(V)

Gertrude Berend

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

1ST AND 2ND ORDERS

PROCESSES AND PROPERTIES INDEX

Ca

10

Reaction between aromatic diamines and dicarboxylic acids. II. Reaction of benzidine with phthalic anhydride. B. A. Porai-Koshits and V. N. Verthina. *J. Gen. Chem.* (U.S.S.R.) 14, 365-81 (1944) (English summary); cf. *C.A.* 38, 1234⁹.—Phthalic anhydride (I) (14.8 g.) in 150 cc. hot EtOH was treated with 9.2 g. benzidine (II) in 100 cc. EtOH to yield 23.8 g. mixed monophthaloylbenzidine, m. 280°, and diphthaloylbenzidine, m. about 307°. When the above reaction was conducted in 200 cc. $PhNMe_2$ and the mixt. was refluxed for 1 hr. there was obtained 23.6 g. of product, m. 370°, which was identical with the above mixt. Molten II (100 g.) was treated gradually with 10 g. I; the melt was cooled, ground, and boiled with EtOH to yield a residue of 10 g. *monophthaloylbenzidine*, m. 302° (m. 300° from $PhNO_2$); the product could not be diazotized, although a free NH_2 group exists as shown by formation of a *benzylidene deriv.*, by refluxing with BzH, m. 321-2°, which rose to 329-30° after repeated crystn. from BzH. Molten I (100 g.) was treated with 10 g. II; the cooled mixt. was extd. with 10% Na_2CO_3 soln. to yield 14.5 g. diphthaloylbenzidine, m. 402° (m. 406° after sublimation). Five g. 4'-nitro-4-aminobiphenyl and 4 g. I were refluxed for 1 hr. in 100 cc. $PhNMe_2$ to yield 98% *4'-nitro-4-phthalimidobiphenyl*, m. 321-2°; reduction with Fe-Zn dust in AcOH gave a non-diazotizable product identical with monophthaloylbenzidine, which apparently is 4'-amino-4-phthalimidobiphenyl having a non-diazotizable amino group. I (26.0 g.) and 36.8 g. II were refluxed in 600 cc. water for 9 hrs. to yield 20 g. *N-(4'-amino-4-biphenyl)-phthalamic acid*, m. 299-300°; *benzylidene deriv.* m. 308-10° (after repeated crystn. from BzH, m. 330°). Molten II (50 g.) was treated with 5 g. diphthaloylbenzidine, cooled, and treated with hot EtOH to yield monophthaloylbenzidine. Similarly, monophthaloylbenzidine and molten I yield the diphthaloylbenzidine, 4,4'-diphthalimidobiphenyl.

G. M. Kosolapoff

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

23

Investigation of the fluorene series. II. Preparation of vat diimidazole dyes of the fluorene series. B. A. Porai-Koshits and O. K. Nikiforova. *J. Applied Chem.* (U. S. S. R.) **13**, 215-21 (in German, 221) (1940); cf. *C. A.* **32**, 9505^8.—The possibility of application of the more complex *o*-diamines to the synthesis of diimidazole dyes was investigated. As an initial substance *2,3-diaminofluorene* (I), m. 198°, was prepd. as follows: Fluorene was nitrated, the 2-nitrofluorene was reduced with Zn dust in alc. soln. in the presence of aq. $CaCl_2$. The 2-aminofluorene (20.3 g.) was boiled with 150 cc. of glacial AcOH under a reflux condenser for 7 hrs. The hot reaction mixt. treated with boiling water yielded 2-acetylaminofluorene (100%), m. 180°, after washing with 50% AcOH and then, with water. The product (25.2 g.) was dissolved in hot glacial AcOH (270 cc.) and, after cooling to 50°, was nitrated with 12.6 cc. of HNO_3 (d. 1.42), yielding 83% of a mixt. (m. 180-90°) of 2-acetylamino-3-nitrofluorene and 2-acetylamino-7-nitrofluorene. The mixt. of isomers (23.3 g.) was suspended in 920 cc. of abs. alc. and boiled in the presence of 40 cc. concd. HCl for 1 hr. under the reflux condenser. After distn. of $^2/_3$ of the alc., the reaction mixt. was allowed to stand for 12 hrs. The ppt. was filtered and boiled with 100 cc. concd. HCl in 2 l. of water for 2 hrs. This operation was repeated 6-7 times, the 2-amino-3-nitrofluorene, m. 187°, formed was filtered out, washed with NH_4Cl soln. and dried. The 2,7-isomer can be pptd. from the filtrate with NH_4OH. The 2,3-isomer (11 g.) was reduced with 50 g. of Zn dust by boiling in 250 cc. of 78% alc. in the presence of $CaCl_2$ (4 g. in 5 cc. of water) for 3 hrs. yielding 78% of I. The condensation of 4 g. of I with 1.76 g. of naphthalenetetracarboxylic acid in 15 cc. of water in a sealed tube at 170-80° for 12 hrs. yielded 3.9 g. of diimidazole vat dye, m. above 300°. The dye was sepd. from unchanged reagents by boiling with 10% soda and then with HCl soln. The fluorene dye was oxidized with $Na_2Cr_2O_7$ to a fluorenone dye ($C_{40}H_{16}N_4O_4$), insol. in alc., Me_2CO, ether, $MeCO_2Et$, C_6H_6, toluene, and xylene, sol. in boiling $PhNO_2$, pyridine and $PhNMe_2$. The fluorenone dye was a mixt. of cis and trans isomers. One colored cotton brownish yellow and other violet. The first had a max. absorption at 4000 A. and the second at 5500 A. The isomers were sepd. by treatment with H_2SO_4 (d. 1.84). The second isomer was less sol. in H_2SO_4 than the first. Treatment of 1 g. of fluorenone dye with a mixt. of 3 cc. of $HOSO_2Cl$ in 15 cc. of pyridine in the presence of 2 g. Fe filings at 60° for 7 hrs. yielded "kubozol," an acid sulfuric acid ester of leuco compds. of the fluorenone dye, which dyed wool bright yellow.

A. A. Podgorny

10

**Reaction between aromatic diamines and dicarboxylic
acids. I. The reaction of *o*-phenylenediamine with
phthalic anhydride.** B. A. Poraĭ-Koshits and M. M. Anto-
shul'skaya. *J. Gen. Chem.* (U.S.S.R.) 13, 339-52(1943)
(English summary).—The authors investigated the reac-
tion between o-$C_6H_4(CO)_2O$ (I) and o-$C_6H_4(NH_2)_2$ (II)
with the following observations. II was prepd. as follows:
400 g. fused Na_2S (60%) in 1200 cc. water was heated,
after filtration, to 80° and treated with 200 g. o-nitroani-
line, added with stirring over 0.5 hr.; the mixt. was re-
fluxed with stirring for 6 hrs. at 100-5°, filtered and let
stand for 24 hrs., when the pptd. II was filtered off and
dried at 60-70°; 93 g. (60%), m. 101.5-2.5°. II (5 g.) and
6.9 g. I were well mixed and heated to 120-30° with stirring
and prevention of return of the evolved water; after 20
min. the mixt. was powdered and extd. with 30 cc. boiling
Ac_2O. The undissolved portion was a mixt. of *diphthaloyl-
o-phenylenediamine* and *phenylenedibenzimidazole*, and was
sepd. by treatment with dil. HCl, crystn. and distn. to
yield products m. 290° and 412°, resp. The Ac_2O soln.
on cooling yields a total of 7.5 g. *benzoylenebenzimidazole*,
m. 209.5-10° (from Ac_2O). The use of benzene for extn.
and crystn. leads to an impure product, which indicates
the presence in the melt of phenylenebenzimidazolecar-
boxylic acid (which by the action of the Ac_2O is converted
to the benzoylenebenzimidazole). I (100 g.) heated to
boiling was treated with 10 g. of II over 20-30 min.; after
boiling for 0.5 hr. the melt was poured into a dish, pow-
dered and extd. with 800 cc. 20% Na_2CO_3 at the b. p.;
the undissolved material was filtered off, washed with
water and dried, to give 17 g. crude diphthaloyl-o-phenyl-
enediamine, m. 285°; washing with hot EtOH gave 1.2
benzoylenebenzimidazole, m. 193-5°, while recrystn.
of the residue from Ac_2O gave pure *diphthaloyl-o-phenyl-
enediamine*, m. 296.5-7°. II (2.5 g.) mixed with 1.76 g.
I was heated to 185-90° for 5-10 min.; on cooling, the
product was powdered and extd. with Na_2CO_3 soln. at the
b. p.; the residue, m. 404-6°, (2.6 g.) was crude *o-
phenylenedibenzimidazole*; this was purified by soln. in
hot 5-7% HCl, filtration and slow crystn., on standing, of
the corresponding HCl salt; the latter was treated in
water with NH_4OH to yield the free base, which was
treated with hot benzene polychlorides (b. 183-7°),
filtered hot, and the ppt. washed with hot benzene, then
sublimed to yield a pure product, m. 414-16°. Fused II
(5 g.) was treated with 2 g. benzoylenebenzimidazole at

195° with stirring; the cooled melt was powdered, extd.
with hot EtOH, purified as above and sublimed to yield
o-phenylenedibenzimidazole, m. 416°. Benzoylenebenz-
imidazole (2 g.) mixed with 10 g. I was heated for 8 hrs.
at 195°, then to 230° to complete the reaction, after which
the powd. melt was extd. with various solvents; under
these conditions the starting products were recovered.
Boiling I (10 g.) was treated with 2 g. benzoylenebenzimi-
dazole and heated for 1 hr. at the b. p.; the cooled
melt was extd. with Na_2CO_3 soln., and the residue extd.
with boiling EtOH and crystd. from AcOH to yield di-
phthaloyl-o-phenylenediamine, m. 296° (yield, 10%).
The above (2.5 g.) mixed with 1.25 g. II was heated at 230-
40° for 20 min.; the cooled melt was extd. with boiling
Ac_2O; the cooled filtrate yielded benzoylenebenzimidazole
m. 208° (50.3%), while the insol. residue was phenylene-
dibenzimidazole, m. 404-6° (30.9%). The latter was
also prepd. by mixing 10 g. II with 2 g. diphthaloyl-o-
phenylenediamine and heating to 240-50° for 2-2.5 hrs.,
followed by extn. with hot EtOH and the usual purifica-

tion, to yield 80% of a product m. 414-17°. Phenylenedibenzimidazole (2 g.) and 10 g. I heated for 7 hrs. at 195-200° failed to react; addn. of the same amt. of the former to 10 g. boiling I also gave neg. results, as did the use of larger excess of I and up to 6 hrs. boiling; use of pyridine or piperidine as catalysts also failed under these conditions.

G. M. Kosolapoff

1ST AND 2ND ORDERS

3RD AND 4TH ORDERS

PROCESSES AND PROPERTIES INDEX

CA

10

Reaction between aromatic diamines and dicarboxylic acids. III. Reaction of benzidine with naphthalic anhydride. B. A. Porai-Koshits and Z. V. Arkhipova. *J. Gen. Chem.* (U. S. S. R.) 14, 842-7(1944)(English summary); cf. *C.A.* 39, 4900^4.—Benzidine (50 g.) was melted at 150° in a porcelain dish and treated gradually with 5 g. naphthalic anhydride (I) with agitation; after 5 min. at 175-80° the mass was cooled, boiled with EtOAc, and filtered to yield 6 g. *4-amino-4'-naphthalimidobiphenyl*, m. 318° (from $PhNO_2$); it is insol. in the usual solvents and cannot be diazotized. The same compd. was obtained by heating equimol. amts. of the reagents in a sealed tube at 190-200°. Heating of equimol. amts. of the reagents in aq. suspension gave a small amt. of alkali-sol. product, m. 325°, which could be diazotized and which on heating to 150-75° lost this property; it is presumed to be *N-(4'-amino-4-biphenylyl)naphthalamic acid*. 4'-Nitro-4-aminobiphenyl (0.55 g.) and 0.51 g. I were refluxed for 1 hr. with 15 cc. $PhNMe_2$ without reaction; the same result was obtained with up to 36 hrs. heating. However, heating in the presence of water in a sealed tube to 180-200° for 8 hrs. gave a good yield of *4'-nitro-4-naphthalimidobiphenyl*, m. over 500°, which does not diazotize nor is its NO_2 group susceptible to reduction by any of the methods tried. I (13.2 g.) was heated to 80° and gradually treated with 1.32 g. benzidine with the final temp. being 250°; after heating to 360° and the usual treatment, there was obtained by sublimation *4,4'-dinaphthaloylbenzidine*, m. about 500°, insol. in the usual solvents. G. M. K.

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

PORAI-KOSHITZ, B. A.

"On the reaction between aromatic amines and dicarboxylic acids. V. Reaction of 2, 7-diaminocarbazole with phtalic anhydride.". Porai-Koshitz, B. A. (p. 1919)
and Salamon, G. S.

SO: Journal of General Chemistry (Zhurnal Obshchei Khimii) 1944, Volume 14, no. 9-10.

1ST AND 2ND ORDERS

PROCESSES AND PROPERTIES INDEX

3RD AND 4TH ORDERS

Ca

10

Reaction between aromatic diamines and dicarboxylic acids. VI. Reaction of tolidine and dianisidine with phthalic anhydride. B. A. Porai-Koshits and D. A. Bodik (Dyestuff Lab. LKhTI (Moscow)). *J. Gen. Chem.* (U.S.S.R.) 15, 248-51(1945)(English summary); cf. *C.A.* 39, $4599^{4,7}$.—It was shown that *o*-tolidine or *o*-dianisidine condense with 1 mol. phthalic anhydride (I) to yield monophthaloyl derivs. without formation of "H"-bonds between N and O atoms. Thus, the Kaufler formula with biplanar structure of these compds. is disproved. Neither monophthaloyl deriv. is capable of dehydration to form a substance analogous to Galiakmelli's "imidazole" (*Gazz. chim. ital.*, 24, 1145(1929)). Both derivs. form diphthaloyl derivs. on further reaction with I. *o*-Tolidine (20 g.) was treated in the molten state at 200° with 4 g. I with stirring, and heated for 1 hr. to 220-50°. The cooled melt was ground and heated with 500 cc. 10% HCl and filtered; the residual *monophthaloyl-o-tolidine-HCl* (II) was suspended in dil. HCl, diazotized with $NaNO_2$, and coupled with alk. soln. of 2-naphthol to yield a bright red deriv. The yield of II was 6 g., m. 280°. Treatment with 10% Na_2CO_3 at 80° gave the free base, m. 210-12° (from EtOH). The base, heated with $PhNMe_2$ at reflux for 3 days, failed to change or to form a cyclic deriv. I (20 g.) was treated in molten state with 2 g. *o*-tolidine over 10-15 min. at 160-80°, heated to 180° for 0.5 hr., cooled, and ground with hot Na_2CO_3 soln. to yield 92% *diphthaloyl-o-tolidine* as a yellowish residue, m. 224° (from AcOH). The compd. could not be diazotized, while heating with an excess of *o*-tolidine at 170-200° for 1 hr. gave good yields of II. II (free base) heated with excess I to 170° gave good yields of the diphthaloyl deriv. *o*-Dianisidine (20 g.) was treated with 4 g. I at 200° and heated there for 1 hr. to yield 47% *monophthaloyl-o-dianisidine*, m. 208-10°, which was readily diazotizable; it failed to cyclize on prolonged heating with $PhNMe_2$, pyridine, $PhNO_2$, or alone. *o*-Dianisidine (2 g.) was added to 20 g. I at 170° and heated for 0.5 hr. to yield 92% *diphthaloyl-o-dianisidine*, m. 328° (from $PhNO_2$).

G. M. Kosolapoff

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

1ST AND 2ND ORDERS

PROCESSES AND PROPERTIES INDEX

3RD AND 4TH ORDERS

CA

25

Azo dyes from 5-amino-1-naphthol and some of its derivatives. I. Monoazo dyes from 5-amino-1-naphthol. A. E. Poral-Koshits, B. A. Poral-Koshits, and V. V. Perekalin (Leningrad Chem. Tech. Inst.). *J. Gen. Chem.* (U.S.S.R.) **15**, 446-60(1945)(English summary).—Monoazo condensation of 5-amino-1-naphthol with equiv. amts. of *p*-nitrophenyldiazonium chloride and phenyldiazonium chloride in a wide range of pH gave only the *o*- and *p*-hydroxy- and *o*-aminoazo dyes; *p*-aminoazo dyes were not obtained at all. *p*-Nitrophenyldiazonium chloride in all pH values gave almost exclusively the hydroxyazo compd., while phenyldiazonium chloride gave, at pH less than 6, the *o*-NH_2 deriv. In all cases in alk. solns. the *p*-OH product predominated, with *o*-OH yield increasing with lowered pH. The *o*-hydroxy dye from PhN_2Cl exists in 2 forms which are readily interconvertible. All of the dyes obtained are weakly acidic, and dye wool to Bordeaux, brown or gray-violet. The products had the following characteristics: *2-(p-nitrophenylazo)-5-amino-1-naphthol* (*o*-hydroxy dye), m. 226-7°, absorption max. 6000 A.; *4-(p-nitrophenylazo)-5-amino-1-naphthol* (*p*-hydroxy dye), m. 245-6°, absorption max. 6100 A.; *6-(p-nitrophenylazo)-5-amino-1-naphthol* (*o*-amino dye), m. 185-6°, absorption max. indefinite; *2-phenylazo-5-amino-1-naphthol* (*o*-hydroxy dye), m. 184-5°, absorption max. 5100 A.; *4-phenylazo-5-amino-1-naphthol* (*p*-hydroxy dye), m. 194-5°, absorption max. 5300 A.; *6-phenylazo-5-amino-1-naphthol* (*o*-amino dye), m. 174-5°, absorption max. 5000 A. The alk. solns. of the *o*-amino dyes become decolorized on standing.

G. M. Kosolapoff

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

1ST AND 2ND ORDERS

PROCESSES AND PROPERTIES INDEX

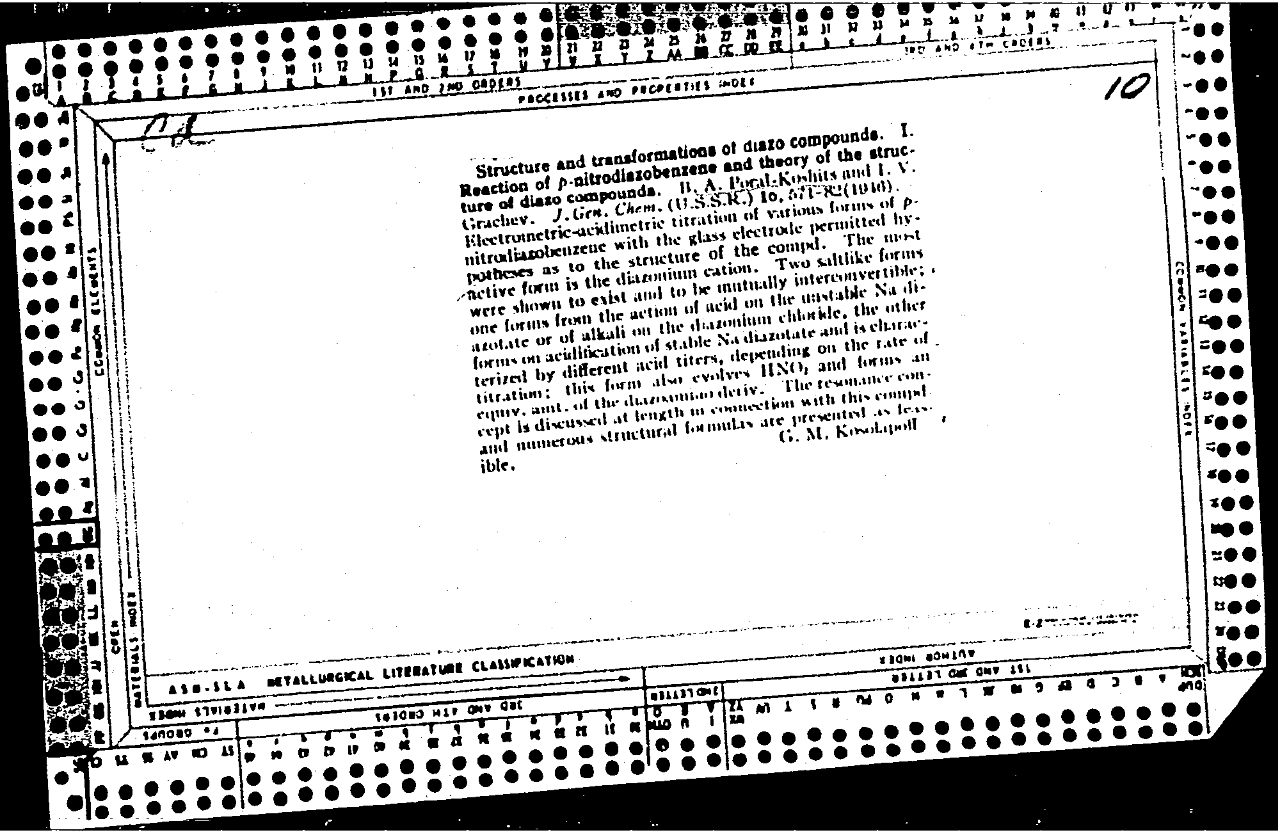
CA

25

Dyes with antipyrine nuclei, and a special case of dehydrogenation. A. E. Poral-Koshits, B. A. Poral-Koshits, and O. F. Ginsburg (Leningrad Chem. and Technol. Inst.). *Compt. rend. acad. sci. U.R.S.S.* **47**, 407-9 (1945); *Doklady Akad. Nauk S.S.S.R.* **47**, 425-7(1945). Benzylidenebisantipyrine, m. 206°, *HCl salt* m. 152°, prepd. in 84.5% yield from PhCHO and antipyrine (I) was oxidized (as the sulfate in HCl) by refluxing with HNO_3 (sp. gr. 1.4) to form a brick-red dye, decompd. about 140°, which crystd. as the *HNO_3 salt*, m. 246°, in 31.2% yield; it has an absorption max. at 4800 A. and satisfactorily dyed animal fibers and cotton. Also, I and p-$Me_2NC_6H_4CHO$ reacting in HCl soln. gave p-dimethylaminobenzylidenebisantipyrine.2HCl (II) (60-75% yield) which swelled and became red at 120-40°, solidified, and m. 178°. II evolved H when heated in a current of CO_2 for 1 hr. at 175-80°, and gave a leuco base, m. 107-8° (decompn.), recryst. from EtOH, when treated with NaOH.

Orville J. Sweeting

ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION



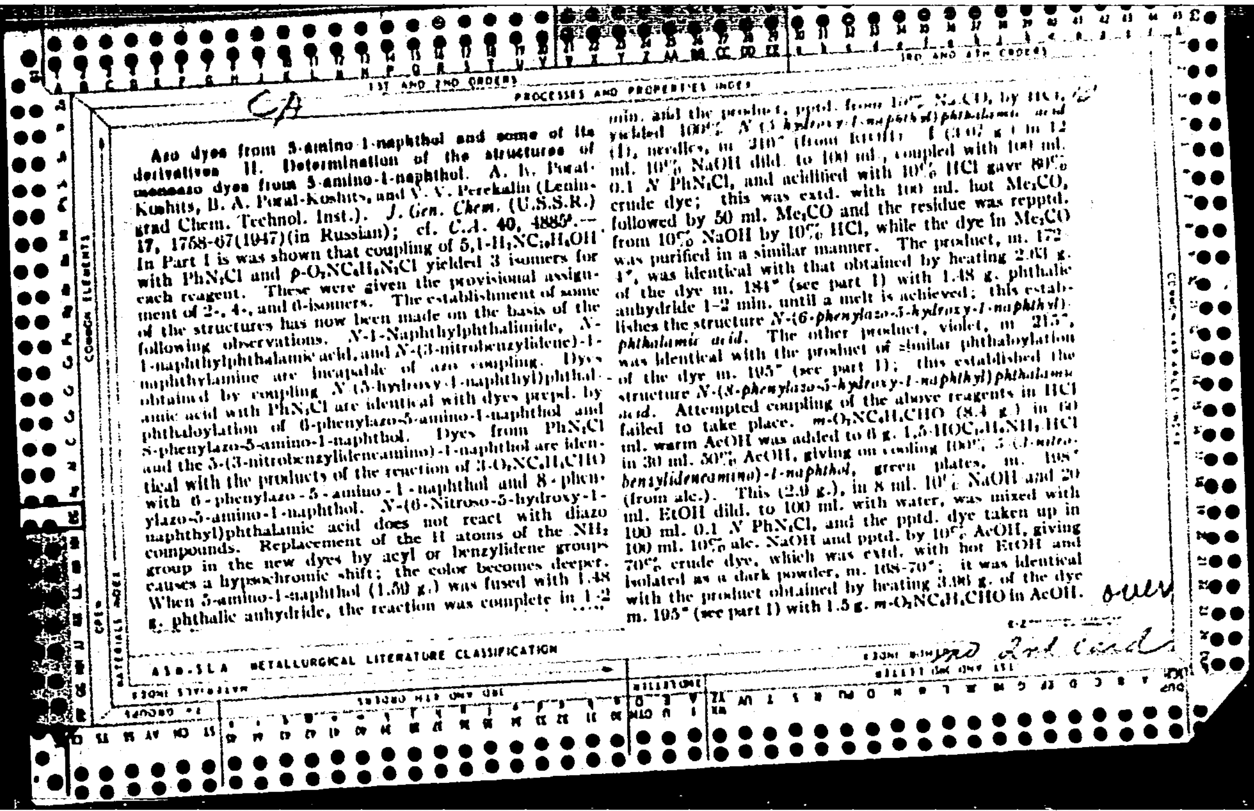
CA

10

Structure and transformations of diazo compounds. I. Reaction of *p*-nitrodiazobenzene and theory of the structure of diazo compounds. B. A. Porai-Koshits and I. V. Grachev. *J. Gen. Chem.* (U.S.S.R.) 10, 671-82(1940). Electrometric-acidimetric titration of various forms of *p*-nitrodiazobenzene with the glass electrode permitted hypotheses as to the structure of the compd. The most active form is the diazonium cation. Two saltlike forms were shown to exist and to be mutually interconvertible; one forms from the action of acid on the unstable Na diazotate or of alkali on the diazonium chloride, the other forms on acidification of stable Na diazotate and is characterized by different acid titers, depending on the rate of titration; this form also evolves HNO_2 and forms an equiv. amt. of the diazoamino deriv. The resonance concept is discussed at length in connection with this compd. and numerous structural formulas are presented as feasible. G. M. Kosolapoff

PORAI-KOSHETS, B.A.

RT-118 (The mechanism of the diazotization reaction). K voprosy of mekhanizme reaktsii diazotirovaniia.
Trudy Vosmogo Soveshchaniia po Anilinokrasochnoi Khimii i Tekhniki, 74-78, 1947.



1ST AND 2ND ORDERS

PROCESSES AND PROPERTIES INDEX

3RD AND 4TH ORDERS

CB

Azo dyes from 5-amino-1-naphthol and some of its derivatives. II. Determination of the structures of monoazo dyes from 5-amino-1-naphthol. A. E. Poraí-Koshits, B. A. Poraí-Koshits, and V. V. Perekalin (Leningrad Chem. Technol. Inst.). *J. Gen. Chem.* (U.S.S.R.) **17**, 1758-67(1947)(in Russian); cf. *C.A.* **40**, 4885⁹.—In Part I is was shown that coupling of 5,1-$H_2NC_{10}H_6OH$ with PhN_2Cl and p-$O_2NC_6H_4N_2Cl$ yielded 3 isomers for each reagent. These were given the provisional assignment of 2-, 4-, and 6-isomers. The establishment of some of the structures has now been made on the basis of the following observations. N-1-Naphthylphthalimide, N-1-naphthylphthalamic acid, and N-(3-nitrobenzylidene)-1-naphthylamine are incapable of azo coupling. Dyes obtained by coupling N-(5-hydroxy-1-naphthyl)phthalamic acid with PhN_2Cl are identical with dyes prepd. by phthaloylation of 6-phenylazo-5-amino-1-naphthol and 8-phenylazo-5-amino-1-naphthol. Dyes from PhN_2Cl and the 5-(3-nitrobenzylideneamino)-1-naphthol are identical with the products of the reaction of 3-$O_2NC_6H_4CHO$ with 6-phenylazo-5-amino-1-naphthol and 8-phenylazo-5-amino-1-naphthol. N-(6-Nitroso-5-hydroxy-1-naphthyl)phthalamic acid does not react with diazo compounds. Replacement of the H atoms of the NH_2 group in the new dyes by acyl or benzylidene groups causes a hypsochromic shift; the color becomes deeper. When 5-amino-1-naphthol (1.59 g.) was fused with 1.48 g. phthalic anhydride, the reaction was complete in 1-2 min. and the product, pptd. from 10% Na_2CO_3 by HCl, yielded 100% *N-(5-hydroxy-1-naphthyl)phthalamic acid* (I), needles, m. 210° (from EtOH). I (3.07 g.) in 12 ml. 10% NaOH dild. to 100 ml., coupled with 100 ml. 0.1 N PhN_2Cl, and acidified with 10% HCl gave 80% crude dye; this was extd. with 100 ml. hot Me_2CO, followed by 50 ml. Me_2CO and the residue was repptd. from 10% NaOH by 10% HCl, while the dye in Me_2CO was purified in a similar manner. The product, m. 172-4°, was identical with that obtained by heating 2.63 g. of the dye m. 184° (see part I) with 1.48 g. phthalic anhydride 1-2 min. until a melt is achieved; this establishes the structure *N-(6-phenylazo-5-hydroxy-1-naphthyl)phthalamic acid*. The other product, violet, m. 215°, was identical with the product of similar phthaloylation of the dye m. 105° (see part I); this established the structure *N-(8-phenylazo-5-hydroxy-1-naphthyl)phthalamic acid*. Attempted coupling of the above reagents in HCl failed to take place. m-$O_2NC_6H_4CHO$ (8.4 g.) in 60 ml. warm AcOH was added to 8 g. 1,5-$HOC_{10}H_6NH_2.HCl$ in 30 ml. 50% AcOH, giving on cooling 100% *5-(3-nitrobenzylideneamino)-1-naphthol*, green plates, m. 198° (from alc.). This (2.9 g.), in 8 ml. 10% NaOH and 20 ml. EtOH dild. to 100 ml. with water, was mixed with 100 ml. 0.1 N PhN_2Cl, and the pptd. dye taken up in 100 ml. 10% alc. NaOH and pptd. by 10% AcOH, giving 70% crude dye, which was extd. with hot EtOH and isolated as a dark powder, m. 168-70°; it was identical with the product obtained by heating 3.96 g. of the dye m. 195° (see part I) with 1.5 g. m-$O_2NC_6H_4CHO$ in AcOH.

ouv

2nd Card

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

1ST AND 2ND ORDERS

PROCESSES AND PROPERTIES INDEX

3RD AND 4TH ORDERS

CA

10

Imidazole derivatives. I. Mechanism of formation of benzimidazole derivatives and the role of hydrochloric acid in this reaction. B. A. Porai-Koshits, O. F. Ginsburg, and L. S. Efros (Leningrad Technol. Inst.). *J. Gen. Chem.* (U.S.S.R.) 17, 1768-73(1947)(in Russian).—Many derivs. of benzimidazole can be prepd. by heating an *o*-diamine with carboxylic acids in the presence of HCl under pressure. The free diamine, resulting from hydrolysis of the HCl salt, is responsible for the reaction, as the HCl salt is incapable of reaction. The catalytic action of HCl is explained by activation of the CO_2H group by addn. of a proton to O, forming a cation of the acid with electron deficiency at the C atom. The intermediate in the reaction is the product of addn. formed as the result of entry of the unshared electron pair of one N of the diamine into the electron-deficient cation of the acid radical. o-$C_6H_4(NH_2)_2$ (0.01 mol.) and 0.01 mol. acid in 10 ml. HCl were heated in sealed tubes at 180-5°; after addn. of NH_4OH the products were filtered off and dried. The following *benzimidazoles* were prepd.: *2-Me*, m. 175° (from H_2O), in 70.5% yield after 40 min. reaction using 5% HCl (*HCl salt*, m. 293°); *2-benzyl*, m. 187° (from benzene) (*HCl salt*, m. 92-4°), in 98% yield from $PhCH_2CO_2H$, using 10% HCl, duration 40 min.; *2-Ph*, m. 290° (from 30% alc.) (*HCl salt*, m. 300°), in 95% yield from BzOH, using 25% HCl, duration 40 min.; *2-(3-pyridyl)*, m. 246-7° (from water) (*HCl salt*, m. 306-8°), from nicotinic acid in 40% yield, using 10% HCl, duration 2 hrs.; *2-naphthyl*, m. 260-2° (from 30% alc.), from 1-$C_{10}H_7CO_2H$, using 15% HCl, duration 40 min.; *2-(p-aminobenzyl)*, m. 211-13° (from alc.), from p-$H_2NC_6H_4CO_2H$ (*HCl salt*, m. 310-12° (from $EtOH$-Et_2O)). *2-benzhydryl*, m. 218-19° (from 60% EtOH), from Ph_2CHCO_2H in 44% yield, using 10% HCl, duration 2 hrs. [*HCl salt*, m. 233-8° (from alc. HCl)]. Heating 0.01 mol. o-$C_6H_4(NH_2)_2$ and 0.01 mol. BzOH 40 min. to 180-5° in a sealed tube gave 65% 2-phenylbenzimidazole; repetition using o-$C_6H_4(NH_2)_2.2HCl$ gave 0% yield; addn. of 0.5 ml. H_2O to the latter mixt. gave 30% 2-phenylbenzimidazole. Heating an equimol. mixt. of the diamine and BzOH in ligroin 40 min. to 180° gave a 48% yield, while replacement of the ligroin by H_2O decreased the yield to 7%. Heating an equimol. (0.01 mol.) mixt. of the diamine and BzOH in 10 ml. HCl of various concns. 40 min. to 180-5° gave the following yields of 2-phenylbenzimidazole: 5% acid, 10.3%; 10% acid, 21.7%; 20% acid, 74.7%; 25% acid, 100%; 35% acid, 48% yield.

G. M. Kosolapoff

COMMON ELEMENTS

MATERIALS INDEX

OPEN

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

CA PORAY-KOSHITS B.A.

Azomethines. I. Hydrolysis reaction of azomethines. B. A. Porai-Koshits, R. M. Poznanskaya, V. S. Shevchenko, and L. A. Pavlova (Leningrad Technol. Inst.). *J. Gen. Chem.* (U.S.S.R.) 17, 1774-87(1947)(in Russian). —The behavior of Schiff bases from aromatic compds. on acid and alk. hydrolysis was investigated. In the majority of cases there is a direct relation between the rate of acid hydrolysis and the basicity of the compd.; the latter most frequently depends on the basicity of the amine used. Theoretical examn. of the mechanism indicates that the major role in acid hydrolysis is played by the protons. An approx. calcn. of the magnitudes of the resonance effect and the alternate charge effect and of the field effect of the substituted groups showed that for the NO_2 group the resonance effect is 4.5 times greater than the field effect, which is 1.5 times greater than the alternate effect. The acid hydrolysis is represented as follows.

$$RCH{:}\dot{N}HR' \to R\dot{C}HNHR' + OH^- \to RCH(OH)NHR' \xrightarrow{H^+} RCH(OH)\underset{\overset{\downarrow}{H}}{\dot{N}}HR' \longleftrightarrow R\dot{C}HOH + H_2\dot{N}R' \xrightarrow{OH^-} R\underset{\diagdown OH}{CHOH} \to RCHO.$$

The substantiation of the mechanism is seen in the dependence of the rate of hydrolysis on the basicity of the base used. In alk. soln. the primary reaction is addn. of OH^-, followed by:

$$RCH(OH)\bar{N}HR' \to R\dot{C}HOH + \bar{N}HR' \to R\bar{N}H_2 + R\underset{\diagdown OH}{CHOH} \to RCHO,$$

where the addn. of OH is simultaneous with polarization of the CN bond; support for this is seen in more difficult hydrolysis in alk. soln. than in acid soln. if such groups are introduced which are not acidic enough to counteract the basic properties of the azomethine. Hydrolyses in 0.1 *N* HCl were followed at room temp. and 50° by analysis of free amine and aldehyde. The following values were obtained (the figures are in the order: hydrolysis rate consts. at room temp. and 50°, activation energy (cal.), amine dissocn. const.): *N*-benzylideneaniline, 1.3×10^{-4}, 2.0×10^{-4}, 3860, 5.3×10^{-10}; *N*-(*p*-nitrobenzylidene)aniline, 1.7×10^{-4}, 1.0×10^{-3}, 15,610, 5.3×10^{-10}; *N*-(*m*-nitrobenzylidene)aniline, 2.2×10^{-4}, 5.7×10^{-4}, 4148, 5.3×10^{-10}; *N*-benzylidene-*p*-nitroaniline, 7.0×10^{-4}, –, –, 1.24×10^{-11}; *N*-benzylidene-*m*-nitroaniline, 1.2×10^{-4}, 5.07×10^{-4}, 6050, 4×10^{-11}; *N*-(*m*-nitrobenzylidene)-*m*-nitroaniline, 2.7×10^{-4}, –, –, 4×10^{-11}; *N*-(*p*-nitrobenzylidene)-*p*-nitroaniline, 0, –, –, 1.24×10^{-11}; *p*-benzylideneaminobenzoic acid, 1.2×10^{-4}, 8.15×10^{-4}, 10,800, 1.5×10^{-11}; *m*-benzylideneaminobenzoic acid, (over)

The dye m. 105°, thus established as being 8-phenylazo-5-amino-1-naphthol, was, in addn., deaminated by treatment of its diazonium deriv. in H_2SO_4 with abs. EtOH at 100°, yielding a red solid, purified by pptn. from 10% NaOH by HCl, identified as 4-phenylazo-1-naphthol, decomp. 200°; in addn., replacement of the NH_2 by a OH group by the conventional diazonium reaction gave 4-phenylazo-1,5-dihydroxynaphthalene, decomp. 210° (the diazo soln. was heated with 10% H_2SO_4). Similar replacement of the NH_2 group in the dye m. 184° (see part I), i.e. 6-phenylazo-5-amino-1-naphthol, gave 2-phenylazo-1-naphthol, m. 138°. The remaining dye isomer (see part I) was shown to be 7-phenylazo-5-amino-1-naphthol by the following: reduction of the dye with hydrosulfite gave 60% 1,2-diamino-5-naphthol, decomp. 200-7°, which (7.63 g.) was heated to 50° in 80% AcOH with 2.08 g. phenanthrenequinone, giving 5-hydroxy-1,2-naphthophenanthrazine, yellow-brown, m. 332-2.5° (from PhCl). **III. Some anomalous cases of reaction of aminonaphtholsulfonic acids with diazo compounds.** V. V. Perekalin. *Ibid.* 1788-1800(in Russian).—Some aminonaphtholsulfonates, e.g., M acid (5-amino-1-naphthol-3-sulfonic acid) (I), γ-acid (7-amino-1-naphthol-3-sulfonic acid) (II), and 8-amino-1-naphthol-3,6-disulfonic acid (P.P-acid), after coupling with 1 mole of diazo deriv. in acid soln. do not couple with a 2nd mol. in alk. soln. although there are no apparent steric factors to explain such a behavior. It may be explained by resonance phenomena and by formation of a H bond between the sulfo group and a *peri*-H atom. By summation of the resonant structures formed individually by each substituent it was possible to arrive at the following table by comparative activities of C atoms in aminonaphtholsulfonic acids and in their mono-o-aminoazo derivs.: I: C activity in the parent substance, o-OH −1, p-OH 0; in monoazo deriv.: o-OH 0, p-OH +1; no disazo dye formation observed. II: −1, 0, 0, +1; disazo dye formation. 6-Amino-1-naphthol-2-sulfonic acid: −2, −1, −2, −1; disazo dyes form

1-naphthol-3,6-sulfonic acid: −1, 0, −1, 0; disazo dyes form. Prognostic extension of such summation gave the following theoretical results: I, 5-amino-1-naphthol-8-sulfonic acid, and 6-amino-1-naphthol-2-sulfonic acid should not form disazo dyes, while 5-amino-1-naphthol-4-sulfonic acid and 5-amino-1-naphthol-2-sulfonic acid should readily couple twice; similarly, 7-amino-1-naphthol-4-sulfonic acid and -2-sulfonic acid should form disazo dyes, while 8-amino-2-naphthol-5-sulfonic acid and 8-amino-2-naphthol-6-sulfonic acid should not give disazo dyes, and 6-amino-2-naphthol-4-sulfonic acid and -8-sulfonic acid should form disazo dyes. The mechanism of action of the substituents was assumed to be the same, differing only in the algebraic sign and only the normal valence bonds were assumed to be operative. Since in 1,5- and 2,8-naphtholsulfonic acids the distance between the O of SO_3H and the adjacent ring H does not exceed 1.7 A. (*peri*-position), the formation of a H bond is likely. In order to investigate the possibilities named above, the following expts. showed that the cause for failure of 2nd coupling by I does not lie in the specific orientation of the substituents but in the presence of the SO_3H group. (No data on products or exptl. data are given.) 2-Phenylazo-5-amino-1-naphthol with PhN_2Cl in alk. soln. (pH 10.5-11.5) gave 2,6-bis(phenylazo)-5-amino-1-naphthol, while an identical product, 2,4-bis(phenylazo)-5-amino-1-naphthol, was produced by similar treatment of either 2-phenylazo-5-amino-1-naphthol or 4-phenylazo-5-amino-1-naphthol; the last 2 substances did not couple with PhN_2Cl in acid medium. From PhN_2Cl at pH 4.5-5.5 with 5-amino-1-naphthol-3-, -4-, -8-, -2-, and -4-sulfonic acids the corresponding monoazoderivs. were obtained and characterized by spectrum analysis and potentiometric titrations (no data given); the resulting 6-phenylazo-5-amino-1-naphthol-3-sulfonic acid, 8-phenylazo-5-amino-1-naphthol-6-sulfonic acid, and 6-phenylazo-5-amino-1-naphthol-8-sulfonic acid with PhN_2Cl in alk. soln. failed to yield any disazo products; similar failure took place with the isomers in which the monoazo

(cont)

1ST AND 2ND ORDERS

PROCESSES AND PROPERTIES INDEX

3RD AND 4TH ORDERS

COMMON ELEMENTS

10

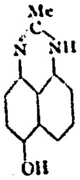
coupling was governed by the OH group. 6-Phenylazo-
5-amino-1-naphthol-2-sulfonic acid and 6-phenylazo-5-
amino-1-naphthol-4-sulfonic acid, however, gave disazo
derivs. which showed a displacement of the absorption
max. toward longer wave lengths in comparison with the
initial materials. Since the pH of the medium does not
affect the location of the absorption max. in o-hydroxy
azo dyes and since the OH group in them can be titrated
with difficulty, the azoid structure (Auwers, *C.A.* 28,
121[a]) appears to be disproved for these compds. The
"quinone-hydrazone" structure is also disproved by the
absence of characteristic —NH— infrared absorption.
Thus, the H of the OH is attached neither to O nor to N,
and the OH group H bonds to —N:N—. This is con-
firmed by the higher pH titration requirement for *o*-OH-
azo dyes than for the corresponding *p*-HO or *o*-amino
derivs. **IV. Nitrosation of 5-acetamido-1-naphthol.**
L. S. Efros, A. E. Poral-Koshits, and B. A. Poral-Koshits
(Leningrad Technol. Inst.). *Ibid.* 1801-6(1947)(in Rus-
sian).—Nitrosation of $5,1\text{-AcNHC}_{10}H_6OH$ gives *2-nitroso-
5-acetamido-1-naphthol* (I), whose structure was confirmed
by formation of *1-acetamido-5,6-naphthophenazine* (II).
To 10 g. $5,1\text{-}H_2NC_{10}H_6OH$ suspended in 100 ml. H_2O
was added 25 ml. Ac_2O and the mixt. was warmed until
soln. occurred; on cooling, 8.5-9 g. *5-acetamido-1-naph-
thol*, m. 174-5° (from water), sepd. This (4 g.) in 50
ml. cold 70% AcOH with 1.4 g. $NaNO_2$ in 6 ml. H_2O,
gave 4 g. I, m. indefinitely with darkening at 200°, sol. in
alkalies, pptd. by acids. I dyes wool in aq. suspension to
a brown shade, with Fe mordant to grass-green shades.
I (1 g.) in 5 ml. EtOH suspension was warmed with 1.5
ml. $PhNHNH_2$; after subsidence of the reaction and
cooling, there was obtained 0.9 g. *2-amino-5-acetamido-1-
naphthol* (III), sandy plates, m. indefinitely, darkening at
142°, decomp. 185-7°, sol. in aq. acids and alkalies, and
capable of being diazotized and coupled. I (2 g.) sus-
pended in 75 ml. AcOH was warmed with 2.5 ml Ph
$NHNH_2$; after subsidence, the mixt. was dild. with
H_2O, giving 1 g. *5,5'-diacetamido-1,1'-dihydroxy-2,2'-
azonaphthalene*, red needles, m. 248-50° (some decompn.;
from alc.), which is almost insol. in aq. alkalies. I
(1.5 g.) and 1.5 g. $o\text{-}(H_2N)_2C_6H_4$ were warmed in 4.5 ml.
AcOH; after subsidence, the product was ground with
EtOH, followed by cold 10% NaOH and washing with
H_2O, giving 1.5 g. II, m. 311-13° (from AcOH); the
same product was obtained by treating a cold suspension
of 0.5 g. III in 10 ml. 70% AcOH with 0.25 g. Cr oxide
in 5 ml. AcOH, dilg. with 100 cc. H_2O, extg. with $CHCl_3$,
evapg. the ext., and warming the residue with 0.2 g. *o*-
$(H_2N)_2C_6H_4$ in 3 ml. AcOH. III (1 g.) and 20 ml. H_2O
heated 15 min. with 10 ml. Ac_2O gave on cooling 0.7 g.
2,5-diacetamido-1-naphthol, m. 245° (from dil. AcOH).
This (5 g.), treated in 100 ml. cold AcOH with 1.5 g.
$NaNO_2$ in 5 ml. H_2O and the ppt. recrystd. from AcOH,
gave 0.8 g. red needles, m. 208°, while diln. of the mother
liquor gave brown-yellow needles, m. 302-4°; both prod-
ucts are insol. in alkali; their structure is unknown.

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

MATERIALS INDEX

OPEN

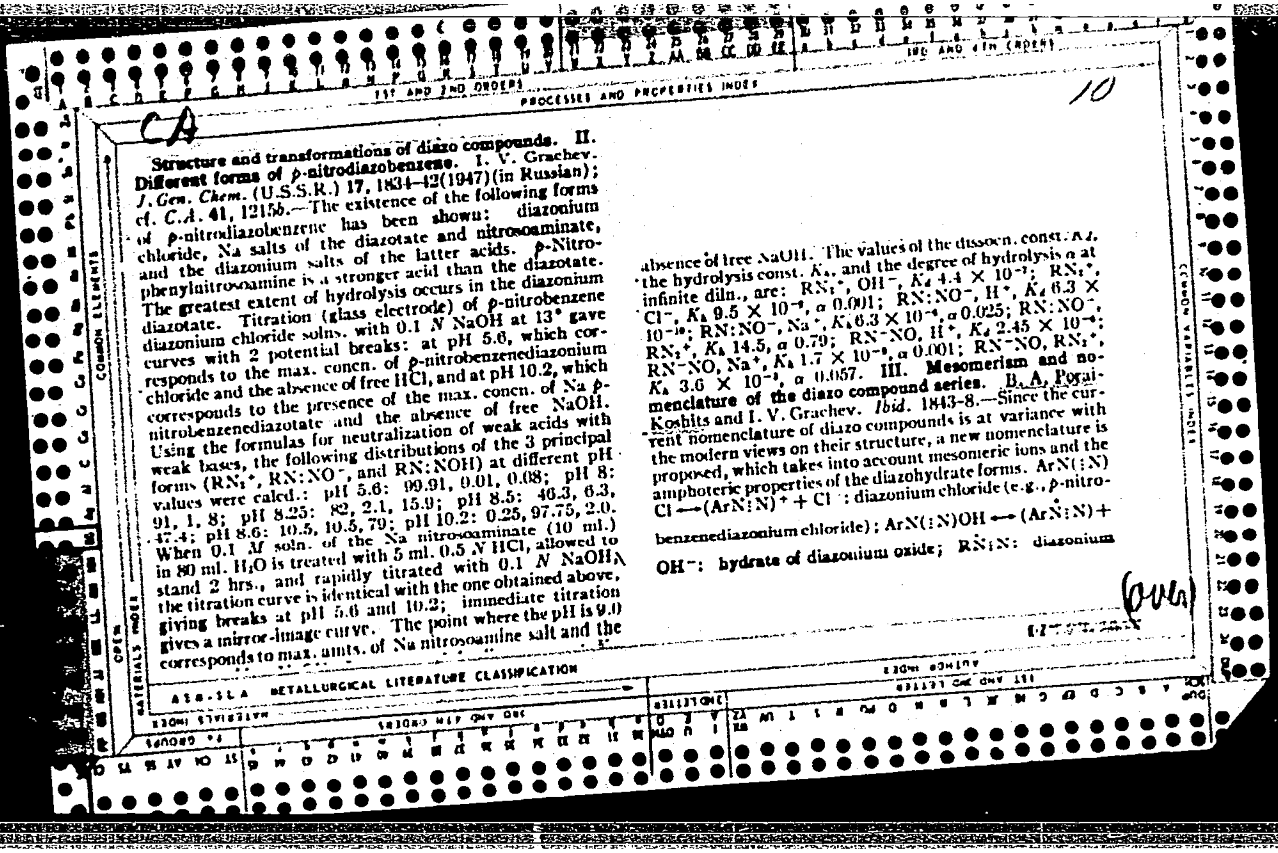
V. Coupling of 5-amino-1-naphthol with diazotized H acid. *Ibid.* 1807-15(in Russian).—Coupling of 5,1-$AcNHC_{10}H_6OH$ (I) and 5,1-$H_2NC_{10}H_6OH$ (II) with diazotized H acid at pH over 4 gives *p*-HO dyes, while at pH below 4 I does not couple. II gives a *p*-aminoazo dye, which hitherto has been considered to be an *o*-amino deriv. (Ger. Pat. 95,190), or an *o*-HO deriv. The structure was established by reduction, followed by oxidation to juglone. I (2 g.) in 10 ml. 10% KOH and 20 ml. H_2O was treated with the diazonium deriv. from 3.2 g. H acid in 30 ml. H_2O, and the blue soln. acidified with AcOH, giving 4.7 g. of a metallic-looking powder, forming a violet soln. in H_2O, blue in dil. alkalies, red in stronger alkalies, absorption max. 520 mμ, dyes wool violet. Titration gave breaks at pH 9 and 4.7, the mol. wt. found being 558; the same product was obtained when coupling was run at pH 4. The product is probably: *8-(8-acetamido-4-hydroxy-1-naphthylazo)-1-naphthol-3,6-disulfonic acid*, since, 5 g. of it in 50 ml. H_2O and a little NaOH, treated with Zn dust, followed by 10 ml. concd. HCl and boiled, gave the *HCl salt of methyl-5-hydroxy-1,8-naphthimidazole* (III), yellow needles without a definite m.p.



(III)

When II was coupled, as above, in alkali and at pH 5, the products obtained were identical: metallic-looking powders, with color behavior similar to that of the Ac deriv. described above; the absorption max. was 510 mμ. The same product was obtained by deacetylation of the Ac compd. by hot 1:4 HCl. Reduction by Zn in HCl gave H acid and 4,5-diamino-1-naphthol-HCl (by addn. of HCl to the filtrate), which on heating with AcOH and 1:3 HCl gave the same imidazole deriv. as described above. If the coupling of II is conducted in AcOH-HCl or at pH 3, again identical products are obtained: a cryst. powder, giving a violet soln. in water, blue in acids, and red in alkalies, with pptn. of some of the dye; heating in alkalies yields NH_3 (detected by odor) and a blue soln., absorption max. 580 mμ (pH 3). Reduction of this product with Zn-HCl gave H acid and a soln. of 5,8-diamino-1-naphthol, which with 10% $FeCl_3$ *in situ* gave juglone, red-orange needles, m. 147° (from $CHCl_3$). This confirms the structure of the dye as: *8-(8-hydroxy-3,6-disulfo-1-naphthylazo)-4-amino-1-naphthol*. The *o*-aminoazo deriv. (1 g.) from PhN_2Cl and II (P.-K. and Perekalin, C.A. **40**, 4885[4]) in 20 ml. H_2O and 10 ml. 10% KOH was reduced by Na hydrosulfite and acidified; after removal of S the filtered soln. was neutralized by NaOAc, treated with 0.8 g. phenanthrenequinone in 200 ml. H_2O with $NaHSO_3$, and boiled 5-10 min. to give 0.75 g. of the corresponding azine, yellow needles, m. 307-10° (from PhBr). Similar treatment of the above dyes failed to give the azine, thus confirming the absence of the *o*-amino structures.

G. M. Kosolapoff



CA

10

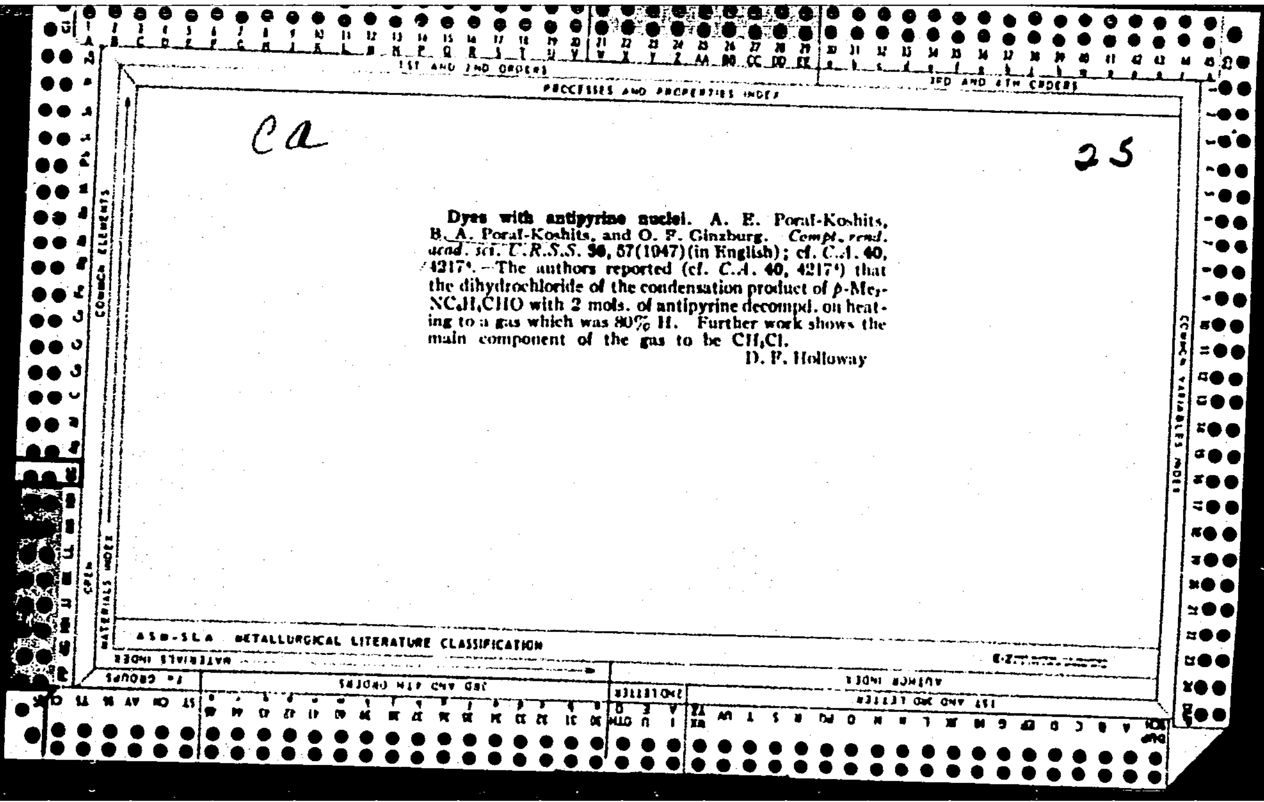
Structure and transformations of diazo compounds. II.
Different forms of *p*-nitrodiazobenzene. I. V. Grachev.
J. Gen. Chem. (U.S.S.R.) 17, 1834-42(1947)(in Russian);
cf. *C.A.* 41, 1215*b*.—The existence of the following forms
of *p*-nitrodiazobenzene has been shown: diazonium
chloride, Na salts of the diazotate and nitrosoaminate,
and the diazonium salts of the latter acids. *p*-Nitro-
phenylnitrosoamine is a stronger acid than the diazotate.
The greatest extent of hydrolysis occurs in the diazonium
diazotate. Titration (glass electrode) of *p*-nitrobenzene
diazonium chloride solns. with 0.1 *N* NaOH at 13° gave
curves with 2 potential breaks: at pH 5.6, which cor-
responds to the max. concn. of *p*-nitrobenzenediazonium
chloride and the absence of free HCl, and at pH 10.2, which
corresponds to the presence of the max. concn. of Na *p*-
nitrobenzenediazotate and the absence of free NaOH.
Using the formulas for neutralization of weak acids with
weak bases, the following distributions of the 3 principal
forms (RN_2^+, $RN:NO^-$, and RN:NOH) at different pH
values were calcd.: pH 5.6: 99.91, 0.01, 0.08; pH 8:
91, 1, 8; pH 8.25: 82, 2.1, 15.9; pH 8.5: 46.3, 6.3,
47.4; pH 8.6: 10.5, 10.5, 79; pH 10.2: 0.25, 97.75, 2.0.
When 0.1 *M* soln. of the Na nitrosoaminate (10 ml.)
in 80 ml. H_2O is treated with 5 ml. 0.5 *N* HCl, allowed to
stand 2 hrs., and rapidly titrated with 0.1 *N* NaOH,
the titration curve is identical with the one obtained above,
giving breaks at pH 5.6 and 10.2; immediate titration
gives a mirror-image curve. The point where the pH is 9.0
corresponds to max. amts. of Na nitrosoamine salt and the

absence of free NaOH. The values of the dissocn. const. K_d,
the hydrolysis const. K_h, and the degree of hydrolysis α at
infinite diln., are: RN_2^+, OH^-, K_d 4.4 × 10^{-7}; RN_2^+,
Cl^-, K_h 9.5 × 10^{-9}, α 0.001; $RN:NO^-$, H^+, K_d 6.3 ×
10^{-10}; $RN:NO^-$, Na^+, K_h 6.3 × 10^{-4}, α 0.025; $RN:NO^-$,
RN_2^+, K_h 14.5, α 0.79; RN^-NO, H^+, K_d 2.45 × 10^{-6};
RN^-NO, Na^+, K_h 1.7 × 10^{-9}, α 0.001; RN^-NO, RN_2^+,
K_h 3.6 × 10^{-3}, α 0.057. **III. Mesomerism and no-**
menclature of the diazo compound series. B. A. Porai-
Koshits and I. V. Grachev. *Ibid.* 1843-8.—Since the cur-
rent nomenclature of diazo compounds is at variance with
the modern views on their structure, a new nomenclature is
proposed, which takes into account mesomeric ions and the
amphoteric properties of the diazohydrate forms. ArN(:N)
Cl ⟶ $(ArN\!:\!N)^+ + Cl^-$: diazonium chloride (e.g., *p*-nitro-
benzenediazonium chloride); ArN(:N)OH ⟶ $(Ar\dot{N}\!:\!N)$ +
OH^-: **hydrate of diazonium oxide;** $R\dot{N}\!:\!N$: diazonium

over

ion; $\mathrm{Ar\bar{N}N{:}O}$: nitrosoaminate ion; $\mathrm{ArNHN{:}O \longleftrightarrow (Ar\bar{N}N{:}O) + H^+}$: nitrosoamine (nitrosoaminic acid); $\mathrm{ArNNaNO \longleftrightarrow (ArN\bar{N}{:}O) + Na^+}$: Na nitrosoaminate; $\mathrm{ArN{:}NN(NO)Ar \longleftrightarrow (ArN{:}\dot{N}) + (O{:}N\bar{N}Ar)}$: diazonitrosoaminate; $\mathrm{ArN({:}N)N(NO)Ar \longleftrightarrow (Ar\dot{N}{:}N) + (O{:}N\bar{N}Ar)}$: diazonium nitrosoaminate; $\mathrm{ArN{:}NCl \longleftrightarrow (ArN{:}\dot{N}) + Cl^-}$: diazochloride; $\mathrm{ArN{:}NOH \longleftrightarrow (ArN{:}\dot{N}) + OH^-}$: hydrate of diazoöxide; $\mathrm{ArN{:}\dot{N}}$: diazo ion; $\mathrm{ArN{:}NOH \longleftrightarrow (ArN{:}NO^-) + H^+}$: diazoicacid; $\mathrm{ArN{:}NO^-}$: diazoate ion; $\mathrm{ArN{:}NONa \longleftrightarrow (ArN{:}NO^-) + Na^+}$: sodium diazoate; $\mathrm{ArN{:}NON{:}NAr \longleftrightarrow (ArN{:}\dot{N}) + (\bar{O}N{:}NAr)}$: diazodiazoate; $\mathrm{ArN({:}N)ON{:}NAr \longleftrightarrow (Ar\dot{N}{:}N) + (\bar{O}N{:}NAr)}$: diazonium diazoate.

G. M. Kosolapoff



Ca

25

Dyes with antipyrine nuclei. A. E. Poral-Koshits, B. A. Poral-Koshits, and O. F. Ginzburg. *Compt. rend. acad. sci. U.R.S.S.* **56**, 57(1947)(in English); cf. *C.A.* **40**, 4217^9.—The authors reported (cf. *C.A.* **40**, 4217^4) that the dihydrochloride of the condensation product of *p*-$Me_2NC_6H_4CHO$ with 2 mols. of antipyrine decompd. on heating to a gas which was 80% H. Further work shows the main component of the gas to be CH_3Cl.

D. P. Holloway

PORAY-KOSHITS, B. A. PA 66T26

USSR/Chemistry - Diazo Compounds Jan/Feb 1948
Chemistry - Titration, Potentiometric

"Composition and Transformation of Diazo Compounds," B. A. Poray-Koshits, I. V. Grachev, Inst of Org Chem, Acad Sci USSR, 14 pp

"Iz Ak Nauk SSSR, Otdel Khim Nauk" No 1

Using potentiometric titration method with glass anode, authors established number of basic laws and constructed new theory on the structure of diazo compounds. Theory has clarified number of previously incomprehensible phenomena.

[redacted] 66T26

PORAY-KOSHITS, B. A.

PA 8/49T66

USSR/Chemistry - Dyes, Azo
Chemistry - Dyes, From 1,5-Naphthalene, Amino Derivatives

May 48

"Information on Azo Dyes Produced From 1, 5-Aminonaphthalene and Some of Its Derivatives, No 6," B. A. Poray-Koshits, L. S. Efros, Lab Tech of Org Dyes, Leningrad Tech Inst, 6¼ pp

"Zhur Obshch Khim" Vol XVIII (LXXX), No 5

Describes potentiometric titration of azo dyes and states some conclusions on their structure. They are resonance systems in which, in the case of the ortho- position of the azo groups to the hydroxyl, there is closed resonance through the

[redacted]

8/49T66

USSR/Chemistry - Dyes, Azo (Contd)

May 48

hydrogen six-member ring. The resultant increase of energy makes the electrical dissociation of an ortho-oxyazo dye with a detached proton impossible. This considerably decreases the acid properties of the compound. The quinone-hydrazone and azide forms of ortho-oxyazo dyes are mesomers, not tautomers. With a para-disposition of the azo-group to the hydroxyl, the energy of dissociation of the dye and detachment of the proton is available, due to the formation of a strongly resonant ion. This considerably increases the acid properties of the compound. Submitted 20 May 1947.

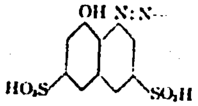
[redacted]

8/49T66

Ca

25

Azo dyes from 5-amino-1-naphthol and its derivatives. VI. Potentiometric titration of azo dyes and some conclusions about their fine structure. B. A. Porai-Koshits and L. S. Efros. *Zhur. Obshchei Khim.* (J. Gen. Chem.) 18, 920-35(1948); cf. C.A. 42, 5800g.—Glass-electrode titrations of 8-X-5-amino-1-naphthol (I), 4-X-5-amino-1-naphthol (II), the N-Ac deriv. (III) of I, and 4-X-2,5-diacetamido-1-naphthol (IV), where X equals the formula shown above, proved that only alk. solns. of I, III, and IV, not II, are titratable with HCl, the 1st 3 giving inflections at, resp., pH 9 and 5.2, 8.8 and 4.2, and 9.2 and 5.1. Consequently, only the OH group in the para position to the N:N group is titratable. The absorption max. of I moves from 510 mμ at pH 3, to 530 mμ at pH 5 (0.07% ionization), 550 mμ at pH 7, and 580 mμ at pH 9 (almost complete ionization). An analogous shift of the max. is found with III. The absorption spectrum of completely ionized I is close to that of II. The oxyazo dyes are resonance systems in which, in the case of OH groups in the ortho position to the N:N group, a closed six-membered resonance ring is formed by H bonds. Owing to the energy gain due to this resonance, electrolytic dissocn. and acid properties are suppressed. The azoid —C(N:NR):COH — and quinonehydrazonic C(:NNHR)C(:O) — forms of the ortho compds. are not tautomeric, but mesomeric structures. With the OH group in the para position to the N:N group, electrolytic dissocn. of H⁺ is energetically favored owing to the formation of a high-resonance anion, hence the strongly acidic properties of these compds. N. Thon



ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

PORAY-KOSHITS, B. A.

PA 149T30

USSR/Chemistry - Synthesis, Dyes Aug 49
Imidazole Derivatives

"Research in the Field of Imidazole Derivatives: II. Synthesis of Several New Phenyl- and Alkye-Phenyl-Derivatives of Benzimidazole," B. A. Poray-Koshits, L. S. Efros, O. F. Ginzberg, Lab of Technol of Org Dyes, Leningrad Tech Inst, 7½ pp

"Zhur Obshch Khim" Vol XIX, No 8

o-Diamines of benzene series, both with greater and lesser basicities than that of o-phenylenediamine, have considerably lower tendency toward condensation with carboxylic acids in an aqueous

149T30

[redacted]

USSR/Chemistry - Synthesis, Dyes (Contd) Aug 49

hydrochloric acid medium of optimum concentration under pressure. Nevertheless, this method can still be used in preparing benzimidazole derivatives except in cases where oxidation of o-diamine prevents its entering into condensation. In these cases derivatives in question may be prepared by melting reagents at 180° C in absence of oxygen. Examples of condensation of 3,4-toluylenediamine and 3,4-diaminochlorobenzene with benzoic acid confirm earlier conclusions on the mechanism of formation of derivatives of benzimidazole in an acidic medium and explain effect of basicity of original amine on course of this reaction. Submitted 27 Mar 48.

149T30

[redacted]

PORAY-KOSHITS, B.A.

[redacted]

Basic character of amines and their reactivity. Voprosy Anilinokrasochnoy Khim., Trudy VIII Soveshchaniya Khim. i Tekh. (Trans 8th Aniline Dye Conf.) '50, 43-55.
(CA 47 no.21:10980 '53) (MLRA 4:4)

CA

Dyes with antipyrine nuclei. II. O. F. Ginzburg and B. A. Porai-Koshits (Leningrad Technol. Inst.). *Zhur. Obshchei Khim.* (J. Gen. Chem.) 22, 715-18(1952); cf. C.A. 42, 8350*d*.—In aq. soln. the ionization of carbinol derivs. formed by the action of alkali on triarylmethane-type dyes is accompanied by cleavage of hydroxyl ion and formation of colored org. cations. The basicity constant of *diantipyrylphenylcarbinol* (I) at 17° is $10^{-5.0}$ as detd. potentiometrically. Two inflection points are found in the titration curve: 1st at pH about 9.5 at the end of titration of free NaOH and the 2nd at pH about 5 at the end of titration of I. G. M. Kosolapoff

PORAY-KOSHITS, B. A.

Chemical Abstracts
Vol. 48 No. 5
Mar. 10, 1954
Dyes and Textiles Chemistry

Dyes with antipyrine nuclei. II. O. F. Ginzburg and B. A. Porai-Koshits (Leningrad Inst. Technol.). *J. Gen. Chem. U.S.S.R.* 22, 770-81(1952)(Engl. translation).— See *C.A.* 46, 7771g. H. L. H.

PORAY-KOSHITS, B.A.

USSR.

Structure of aromatic nitramines. I. Transition of arylnitramines into their sodium salts. G. S. Salyamon, I. V. Grachev, and B. A. Poraĭ-Koshits (State Inst. Applied Chem., Leningrad). *Sbornik Stateĭ Obshcheĭ Khim.* 2, 1315–24(1953).—*N*-nitramines are close in their acid strength to carboxylic acids as shown by their dissocn. constants. The aromatic nitramines and their metallic salts have the same desmotropic form. The observed deepening of color in the *o*- and *p*-nitro derivs. with increase of environment pH is not caused by tautomerism but apparently by quinoidation at the expense of nuclear NO_2 groups. Linear logarithmic relation exists between dissocn. constants of the amines, *N*-nitramines, carboxylic acids, and diazo compounds, which have the same substituents. Titration of nitramines with NaOH gives 2 potential breaks characteristic of salts of weak acids. To 12 g. K in 54 ml. abs. EtOH was added 5 g. K (in small pieces), 60 ml. Et_2O and 40 g. p-$MeOC_6H_4NH_2$; the mixt. was refluxed 6–8 hrs., cooled and treated with 31 ml. EtO-NO_2, yielding 61% K *salt of p-methoxyphenyl-N-nitramine*, which at −2° with 10% HCl (to pH 3) gave colorless *free acid* decomp. 79°, which decomps. in aq. solns. Na salt, colorless powder; K salt very sol. colorless powder. Similarly was obtained *p-tolylnitraminic acid*, m. 52.5–3° (Na salt, sol. in EtOH); *phenylnitraminic acid*, m. 45.5–6°, sol. in H_2O and petr. ether; *p-chlorophenylnitraminic acid*, m. 81.5–2°. p-$MeOC_6H_4N_2Cl$ soln. from 40.24 g. amine in HCl was added slowly at 140–50° to molten 1300 g. KOH and 130 g. H_2O with stirring; diln. with satd. NaCl and similar recrystallization gave crude K *p*-anisylnitrosaminate, which taken up in 1400 ml. 6% KOH was treated in 4 hrs. with 400 g. $K_3Fe(CN)_6$ in 800 ml. H_2O and kept 24 hrs. at 18°, yielding after 8 hrs. at 60°, K *p-anisylnitraminate*, which was then converted to the free acid, as usual. Similarly was prepd. 42% *m-nitrophenylnitraminic acid*, m. 93.5–3°; *p*-

1/4

nitro analog, m. 112-13°; *o-nitro analog*, m. 66.5-6°. The
latter is generally more sol. than *p*- or *m*-analogs. The
method proposed by Orton [*C.A.* 1, 1274; *J. Chem. Soc.*
81, 490, 806(1902)] gave *2,4-dichlorophenylnitraminic acid*,
m. 53.5-4°; *2,3,5,6-tetrachlorophenylnitraminic acid*, m.
133°; *p*-nitrophenylnitraminic acid prepd. by this method
could not be purer than m. 111°. The titration for detn. of
the dissocn. constants were made with glass electrode, with
pK taken as 14.24, with all detns. made at 16°. The follow-
ing values of dissocn. constants were found as pK_a: *p*-
methoxyphenylnitraminic acid 5.00; *p*-tolyl analog 4.88;
phenyl analog 4.74; *p*-chlorophenyl analog 4.60; *m*-nitro-
phenyl analog 4.0; *p*-nitrophenyl analog 3.95; 2,4-dichloro-
phenyl analog 3.33; *o*-nitrophenyl analog 2.88; 2,3,5,6-
tetrachloro analog about 3. Thus the H atom in $ArNHNO_2$
has approximately the same mobility as H in CO_2H. II.
Infrared spectra of absorption and structure of arylnitra-
mines (arylnitraminic acids). G. S. Salyamon and N. G.
Yaroslavskii. *Ibid.* 1325-31.—Infrared absorption spectra
in the region 1.3-1.8 μ were detd. (figures shown) for various
arylnitramines. None show the typical 1.4 μ band which
is characteristic of HO; they do possess a 1.5 μ band which
is that of NH. Hence $ArNHNO_2$ are true nitro derivs. and
not ArN:NOOH. The H atom is capable of hydrogen bond
formation, which may be intra- or intermolecular depending
on structure. The NO_2 group in these substances has less
ability to form hydrogen bonds than the NO_2 group in an
aromatic ring. The interaction between the NH group and
neg. substituents in the ring is shown by lowering of the 1.5
absorption frequency, essentially parallel to the increase of
the acid dissocn. constant of the compds. In the region
studied 2 bands appear (that of NH and that of CH vibra-
tions) which are shown, resp.: *p*-anisyl deriv. 1.502 and

2/4

involved the salt formation studies and examn. of titration
and absorption curves of the substances. When various
arylnitraminic acids were heated in absence of CO_2 with
aq. alkalies 4-6 hrs. to 50-70° and were then titrated with
HCl, the resulting curves were precisely the same as those
obtained from the initial solns. The Na salt of the *p*-anisyl
deriv. kept in 0.1*N* HCl showed the max. yield of *p*-meth-
oxy-*β*,*N*-oxodiazobenzene, 48-52 mole-%, in 1.25 hrs. at 20°
or 3.5 hrs. at 15°; typical titration curves are shown. The
dissocn. constant of the oxodiazo deriv. is 1.3×10^{-4} on the
basis of titration of the 3rd inflection point on the curve.
The residence of the anisyl deriv. in HCl yields as stated
above 1-amino-2-nitro-4-methoxybenzene, m. 122-3°; and
2-nitroanisidine, on acetylation, yields the Ac deriv., m.
116°. The filtered soln. from these substances couples with
2-naphthol yielding (2-nitro-4-methoxyphenylazo)-2-
hydroxynaphthalene, m. 201-4°. In 2 hrs. at 16-18°
there is formed 17-23% nitroaminoanisole and 59-70% di-
azohydrate. Na salt of *p*-anisylnitraminic acid heated
with aq. alc. HCl and 2-naphthol 2.5 hrs. gave 1-*p*-
anisylazo-2-naphthol, red, m. 134-5°, while the filtrate
contained AcH, obtained by oxidation of EtOH by the
formed oxodiazohydrate. If a soln. of K salt of *p*-anisyl-
nitraminic acid after 2 hrs. with *N* HCl is filtered and the
filtrate is treated with phosphotungstic acid soln. there is ob-
tained a ppt. of the complex salt in 20% yield; its composi-
tion is $C_{11}H_{18}O_{41}N_4PW_{11}$; it is sol. in aq. alkalies and is pptd.
on acidification; it decomp. in hot solns. or in H_2SO_4 with
evolution of N_2. In contact with R-salt or 2-naphthol in
basic soln. there is gradually developed a red color probably
caused by transformation of the oxodiazo deriv. into the true
diazonium compound. Mixing diazo solns. with phospho-
tungstic acid gave the phosphotungstates of *p*-methoxydiazo-
benzene, $C_{11}H_{11}O_{41}N_4PW_{11}$, and of 4-methoxy-2-nitrodiazo-
benzene, $C_{11}H_{12}O_{41}N_4PW_{11}$. Both are lightly colored, but
develop pink or violet-brown color on standing. Their prop-
erties are similar to those described above. G. M. K.

4/4

1.665 μ; phenyl analog 1.503 and 1.668; *p*-chlorophenyl analog 1.503 and 1.660; 2,4-dichlorophenyl analog 1.513 and 1.658; 2,3,5,6-tetrachlorophenyl deriv. 1.518 and 1.667; *o*-nitrophenyl analog 1.537 and 1.653; *m*-analog 1.503-1.530 and —; *p*-analog 1.503-1.530 and —; molten PhNHNO$_2$ gives bands at 1.521 and 1.668 μ. III. Raman spectra and structure of sodium salts of arylnitramines. G. S. Salyamon and Ya. S. Bobovich. *Ibid.* 1332-6.—Na salts of arylnitraminic acids in aq. solns. show the characteristic NO$_2$ group frequency in the Raman spectrum. Thus they are truly ArNNa(NO$_2$). Raman spectra for Ar = *p*-anisyl, *p*-tolyl, phenyl, *p*-chlorophenyl, 2,4-dichlorophenyl, and for the compds. PhNMeNO$_2$, PhNHNH$_2$ given. All nitramine salts show a wide band 1300-1405 cm.$^{-1}$ which is split into 2 lines of approximately equal intensity (except for Ph deriv.), which band is caused by symmetric bond vibration of the N-NO$_2$ group. IV. Tautomeric rearrangement of arylnitraminic acids into aryl-*β*,*N*-oxodiazohydrates. G. S. Salyamon, I. V. Grachev, and B. A. Porai-Koshits. *Ibid.* 1337-46.—Arylnitramines (nitraminic acids) do not undergo any tautomeric changes under the action of aq. alk. Mineral acids cause rearrangement of the *p*-anisyl deriv. to 2,4-O$_2$N(MeO)C$_6$H$_3$NH$_2$ and *p*-methoxy-*β*,*N*-oxodiazobenzene, *p*-MeOC$_6$H$_4$N:N(O)OH, the latter being an example of a second tautomeric form of arylnitramines. Contrary to the idea of acid nature of oxodiazohydrates (so-called acinitramines or diazoaryl acids) *p*-methoxyoxodiazobenzene is a base close in strength to NH$_4$OH with dissocn. constant 1.3 × 10^{-5}. This is rather unstable and has properties similar to diazohydrates; it forms salts with acids and does not form diazo coupling products. Tautomeric changes in the nitramine family occur under influence of changed pH; thus lower pH yields the desmotrope with basic properties (oxodiazohydrate) while high pH yields the acidic form (nitraminic acid). The study

3/4

PORAY-KOSHITS, B. A.; REMEIZOV, A. L.

Mutual Displacement of Aromatic Amines from Azomethines and the Influence of the Basicity of the Amines of This Reaction. II. Determination of the Relative Displacing Power of the Amines, page 1577, Sbornik statey po khimii (Collection of Papers on General Chemistry), Vol. II, Moscow-Leningrad, 1953, pages 1680-1686.

Laboratory of the Technology of Dyestuffs imeni A. Ye. Poray-Koshits, Leningrad Technological Inst. imeni Lensovet

PORAY-KOSHITS, B. A.; SOLYAMON, G. S.; and GRACHEV, I. V.

Structure of Aromatic Nitramines. IV. Tautomeric Rearrangement of Arylnitramine Acids to Aryl -B-N- Oxodiazohydrates, page 1337, Sbornik statey po obshchey khimii (Collection of Papers on General Chemistry), Vol II, Moscow-Leningrad, 1953, pages 1680-1686.

State Inst of Applied Chemistry

PORAY-KOSHITS, B. A.; REMEZOV, A. L.

Mutual Displacement of Primary Aromatic Amines from Azomethines and the Influence
of the Basicity of the Amines on This Reaction. III. Mutual Displacements
of Highly Basic Aromatic Amines, page 1590, Sbornik statey po obshchey khimii,
(Collection of Papers on General Chemistry), Vol. II, Moscow-Leningrad, 1953,
pages 1680-1686.

Laboratory of the Technology of Dyestuffs imeni A. Ye. Poray-Koshits, Leningrad
Technological Inst. imeni Lensovet

PORAY- KOSHITS, B.A.

USSR.

Mutual displacement of primary aromatic amines from azomethines and the influence of basicity of the amines on this reaction. I. Reaction of azomethines from *p*-nitroaniline with *p*-anisidine. B. A. Porai-Koshits and A. L. Remizov (Lensovet Technol. Inst., Leningrad). *Sbornik Statei Obshchei Khim.* 2, 1570-6(1953).—Reaction of $PhCH:NC_6H_4NO_2$-*p* or *m*-$O_2NC_6H_4CH:NC_6H_4NO_2$-*p* with *p*-$MeOC_6H_4NH_2$ results in displacement of the *p*-$O_2NC_6H_4NH_2$ in the benzylidene structure by the more basic amine. In completely anhyd. solns., the reaction proceeds much more slowly than under usual conditions. Since the mixts. contain in all cases small amts. of *p*-$MeOC_6H_4NH_2$, it is evident that the reaction proceeds only to a certain degree. The reaction can be run without a solvent in a sealed tube 2-3 hrs. at 120-30°, as well as in MePh, C_6H_6, and CCl_4. In ordinary solvents, the reaction manifests itself within a few minutes. The detn. of *p*-$MeOC_6H_4NH_2$ was performed titrimetrically with 0.1*N* $NaNO_2$ in HCl soln. (after the titration of *p*-$O_2NC_6H_4NH_2$ which gives the 1st end point) with addn. of 1-2 g. KBr. *m*-$O_2NC_6H_4CH:NC_6H_4OMe$-*p*, m. 82-3°. II. Determination of relative displacement ability of amines. *Ibid.* 1677-89.—In displacement of aromatic amines from their benzylidene derivs. by other amines, the reaction takes place reversibly and the equil. constants were detd. for displacement of sulfanilamide from its benzylidene deriv. by *p*-$MeOC_6H_4NH_2$ (K = 800-1460), $PhNH_2$ (240-200), *m*-$O_2NC_6H_4NH_2$ (1.32), and *p*-$O_2NC_6H_4NH_2$ (0.13). The relative ability toward displacement (sulfanilamide = 1) is, resp.: 30-8, 14-16, 1.16, 0.30.

1/2

OVER

PORAĬ-KOSHITS, B.A

The relationship between these factors is given by equation: $a \log K_{OH} + b \log w + c = 0$, where w is the displacement ability of an amine and K_{OH} is its ionization constant. The displacement proceeds by a mechanism analogous to that of salt formation of the amines, with equil. being established among the amines, aldehyde and the benzylidene derivs. of both amines. III. Mutual displacement of highly basic aromatic amines. *Ibid.* 1690-7.—Displacement of $PhNH_2$ and 2,4-dimethylaniline from their *m*-nitrobenzylidene derivs. by each other was examd. This displacement was found to take place among these relatively basic amines regardless of the basic properties of competing amines; the displacement ability depends first of all on amine basicity, then upon structural features. Ionization constant of $PhNH_2$ was detd. to be $10^{-9.44}$, that of 2,4-dimethylaniline $10^{-9.15}$. The displacements were run in sealed tubes at 120-2°. The equil. constants were: for displacement by 2,4-dimethylaniline 10.0, for displacement by $PhNH_2$ 11.2. *N-(m-nitrobenzylidene)-2,4-dimethylaniline*, m. 96.5-6.7° (from EtOH). G. M. Kosolapoff

2/2

PORAY-KOSHITS, B. A.

Imidazole derivatives. V. Amphoteric character of benzimidazole derivatives and their tautomeric transformation. L. S. Efros and B. A. Poral-Koshits (Lensovet Technol. Inst., Leningrad). *Zhur. Obshchei Khim.* 23, 697-705 (1953); cf. *C.A.* 48, 2690*b*, 4634*c*.—Benzimidazole derivs. without *N*-substituents are amphoteric. The tautomers possible in acid solns. form the same cations, and in alk. solns. the same anions, while at the isoelec. point salts are formed from the same cations and anions. $CH_2:CHCN$ with 2-methylbenzimidazole and benzimidazole gave *N*-(cyanoethyl) derivs. which are only bases and have no acidic properties. From potentiometric titrations the acid and base consts. of substituted benzimidazoles were detd. (typical curves are shown). These are as follows (substituent and basicity and acidity consts. resp. shown): *H* (unsubstituted), $10^{-8.6}$, $10^{-12.7}$; *2-Me*, $10^{-7.8}$, $10^{-10.8}$; *2-Ph*, $10^{-9.8}$, $10^{-11.8}$; *2-PhCH₂*, $10^{-8.9}$, $10^{-12.7}$; *2-HO*, $10^{-11.6}$, $10^{-12.7}$; *2-Cl*, $10^{-11.4}$, $10^{-9.9}$; *2-Me₂N*, $10^{-6.6}$, $10^{-11.8}$; *2-HOCH₂*, $10^{-9.4}$, $10^{-10.6}$; *AcOCH₂*, $10^{-9.4}$, $10^{-11.7}$; *2-Et₂NCH₂*, basic consts. $10^{-8.1}$ and $10^{-11.6}$, acidic const. $10^{-12.1}$; *2-(3-pyridyl)* basic consts. 10^{-10} and $10^{-11.6}$, acid const. $10^{-11.3}$; *2-PhCH₂CH₂*, $10^{-7.9}$, $10^{-11.4}$; *2-PhCH:CH₂*, $10^{-9.6}$, $10^{-11.6}$; *6-O₂N*, 10^{-10}, $10^{-11.7}$; *5-H₂N*, basic consts. $10^{-7.4}$ and $10^{-10.7}$, acid const. $10^{-12.3}$; *2,6-di-Me*, 10^{-8}, $10^{-11.3}$; *6-nitro-2-methyl*, $10^{-9.7}$, 10^{-10}; *5,6-dinitro-2-methyl*, $10^{-11.9}$, $10^{-9.7}$; *2-methyl-5,6-diamino*, basic consts. $10^{-6.8}$, $10^{-10.7}$, and $10^{-11.8}$, acid const. $10^{-12.8}$; *6-methyl-3-benzyl*, 10^{-9}, $10^{-11.5}$. Treatment of benzimidazole (5 g.) in EtOH with 0.5 g. Me_3NPhOH and 3.3 g. $CH_2:CH:CN$ at 30-40° and diln. with H_2O gave 83% *1-(cyanoethyl)benzimidazole* (I), m. 108-9° (from H_2O), basic const. $10^{-9.3}$. A similar reaction with 2-methylbenzimidazole requires refluxing 1 hr. and yields 70% *1-cyanoethyl-2-methylbenzimidazole* (II), m. 89-90° (from H_2O, followed by long drying), basicity const. $10^{-8.3}$. Hydrolysis of I in 10% hot NaOH gave benzimidazole with loss of the $CH_2CH_2CO_2H$ group; boiling in 20% HCl also gave benzimidazole. However, hydrolysis with $Ba(OH)_2$ gave 95% *1-benzimidazolepropionic acid*, isolated as the *Ba salt* (from H_2O); similarly was obtained its *2-Me homolog*, crystals (from dil. Me_2CO). However, hydrolysis of II with HCl did not cause cleavage to 2-methylbenzimidazole. Cyanoethylation of 2-phenyl- or 2-benzylbenzimidazoles failed to take place. G. M. K.

PORAY-KOSHITS, B.A.

1/2

Chemical Abst.
Vol. 48 No. 8
Apr. 25, 1954
Organic Chemistry

9 (4)

Imidazole derivatives. VI. Synthesis of some polybenzimidazoles. B. A. Porai-Koshits, L. S. Efros, and E. S. Bochkareva (Lensovet Technol. Inst., Leningrad). *Zhur. Obshchei Khim.* 23, 835-41(1953); cf. *ibid.* 697.—To 1.32 g. 5-methylbenzimidazole in 10 ml. 1:3 H_2SO_4 was added dropwise at 100-3° 2.4 g. chromic acid in 10 ml. H_2SO_4 (1:3) and the mixt. chilled after 15 min., yielding *5-benzimidazolecarboxylic acid sulfate*, which with NaOAc gave the free *acid*, m. 300-25° (from H_2O). This (1.62 g.) and 1.08 g. o-$C_6H_4(NH_2)_2$ in 10 ml. 20% HCl heated in sealed tube 4 hrs. at 180-200°, then neutralized with NH_4OH and filtered, gave *5-(2'-benzimidazolyl)benzimidazole*, isolated as the *di-HCl salt*, m. 362° (from concd. HCl); the free *base* could not be purified owing to the formation of gels. Similar oxidation of 2,5-dimethylbenzimidazole gave 70-5% *2-methyl-5-benzimidazolecarboxylic acid* (I), m. 301-2° (from H_2O). This with o-$C_6H_4(NH_2)_2$ in 20% HCl as above gave after 40 min. at 180-200° *2-methyl-5-(2'-benzimidazolyl)benzimidazole-2HCl*, m. 339-40° (from HCl), which with NH_4OH gave the free *base* (II), m. 340° (from dil. EtOH); this with NH_4OH-$AgNO_3$ in EtOH gave a flocculent *di-Ag salt*; the free base yields a *dipicrate*, m. 282-2.5°. 3,4-$(H_2N)_2C_6H_3$-Me (1.22 g.) and 1.76 g. I in 10 ml. 20% HCl heated in a sealed tube 4 hrs. at 180-200° gave *2,5'-dimethyl-5-(2'-benzimidazolyl)benzimidazole*, m. high and unsharp, which gave a *di-HCl salt*, m. above 300° (from 25% HCl); the free *base* yields a *picrate*, m. 274°. This oxidized with chromic acid as above gave *2-methyl-5-(5'-carboxy-2'-benzimidazolyl)benzimidazole-2HCl* (III), m. about 350° (from 15% HCl); this, decarboxylated by heating with sodalime at 300° gave II (picrate, m. 274°). III with o-$C_6H_4(NH_2)_2$ and 15% HCl 4 hrs. at 180-200° gave 75% *2-methyl-5-[2'-benzimidazolyl-5'-(2''-benzimidazolyl)]benzimidazole-3HCl*, m. above 300° (from dil. HCl). Similarly condensation with 3,4-$(H_2N)_2C_6H_3$Me gave 85-90% *2,5'-dimethyl-5-[2'-benzimidazolyl-5'-(2''-benzimidazolyl)]benzimidazole-3HCl*, m. about 400° (from dil. HCl). 2-Phenyl-5-methylbenzimidazole with chromic acid in aq. H_2SO_4 gave *2-phenyl-5-benzimidazolecarboxylic acid*, isolated as the *HCl salt*, m. 304-5° (from aq. HCl). Electrometric titration of this gives 2 pH breaks; at 8.4 and a weak one whose posi-

(over)

B. A.
Porai-Koshits
2/2

9

(4)

tion is unstated. This heated with o-$C_6H_4(NH_2)_2$ in 15% HCl in sealed tube 6 hrs. at 180-200° gave *2-phenyl-5-(2'-benzimidazolyl)benzimidazole*, m. 308-10° (from dil. EtOH); *HCl salt*, m. 323-6° (from dil. HCl). Similarly 3,4-$(H_2N)_2$-C_6H_3Me gave *2-phenyl-5-(5'-methyl-2'-benzimidazolyl)benzimidazole*, m. 320-31° (from dil. EtOH); *HCl salt*, m. 311-15° (from dil. HCl). This was oxidized as above to *2-phenyl-5-(5'-carboxy-2'-benzimidazolyl)benzimidazole*, isolated as the *HCl salt*, m. 314-19°, which, heated with o-$C_6H_4(NH_2)_2$ and 10% HCl, gave *2-phenyl-5-[2'-benzimidazolyl-5'(2"-benzimidazolyl)]benzimidazole*, isolated as the *di-HCl salt*, does not m. 360° (from aq. HCl). 3,4-$(H_2N)_2$-C_6H_3Me gave *2-phenyl-5-[2'-benzimidazolyl-5'(5"-methyl-2"-benzimidazolyl)]benzimidazole*, isolated as the *di-HCl salt*, does not m. 360°; the free *base* is insol. in org. solvents except AcOH in which it forms the corresponding salt. Heating 2.25 g. 3,4-$(H_2N)_2C_6H_3CO_2H.HCl$ with o-$C_6H_4(NH_2)_2$ and 10 ml. 20% HCl in a sealed tube 40 min. at 180-200° gave 0.1 g. *3,4-diaminophenylbenzimidazole*, m. 325-30° (from 10% HCl); this reacts with HNO_2 without forming a diazonium salt; in AcOH it gives a green ppt. with phenanthrenequinone. Condensation with HCO_2H or AcOH gave the previously described bis-benzimidazole derivs. (cf. *C.A.* 44, 1100*b*). Benzimidazoles have characteristic absorption max. at 2700-800, dibenzimidazoles at 3100-200, and tribenzimidazoles at 3400-500 A.; even the latter absorb but weakly in the visible, being pale yellow. VII. **Preparation of sulfonic acids of benzimidazole by baking method.** L. S. Efros. *Ibid.* 842-3; cf. *C.A.* 48, 2690*b*.—*Benzimidazole* (11.8 g.) ground with 6 ml. concd. H_2SO_4 and washed with Et_2O gave 19 g. cryst. *sulfate*, $C_7H_6N_2.H_2SO_4$ (I). I (5 g.) heated to 220-40° in a wide test tube until H_2O evolution stopped, then to 260-80° until a test with H_2O failed to give a ppt. of benzimidazole on addn. of NH_3, gave 4-4.5 g. *5-benzimidazolesulfonic acid*, m. 365-7° (from H_2O), also formed (0.95 g.) by heating 1.12 g. 3,4-$(H_2N)_2$-$C_6H_3SO_3H$ (II) with 1 ml. HCO_2H and 5 ml. H_2O 40 min. in a sealed tube at 180-90°. *2-Methylbenzimidazole* with H_2SO_4 similarly gave the *sulfate*, which baked as above at 280-90°, yielded 80% *2-methyl-5-benzimidazolesulfonic acid*, needles with very high m.p., also formed by heating II with AcOH to 180-90° as above.

G. M. Kosolapoff

PORAY-KOSHITS, B. A.

11

Imidazole derivatives. VI. Synthesis of some polybenzimidazoles. B. A. Porai-Koshits, L. S. Efros, and B. S. Bolchinova. *J. Gen. Chem. U.S.S.R.* 23, 873-9(1953) (Engl. translation).—See *C.A.* 48, 4523*d*. VII. Preparation of sulfonic acids of benzimidazole by baking method. —L. S. Efros. *Ibid.* 881-2.—See *C.A.* 48, 4524*c*. H. L. H.

ZAKHAROVA, N.A.; PORAY-KOSHITS, B.A.; EFROS. L.S.

Investigation in the field of imidazole derivatives. Part 10. Acylation of 2-oxymethylbenzimidazole and products of its methylation. Zhur.ob. khim. 23 no.7:1125-1230 Jl '53. (MLRA 6:7)

1. Insitut eksperimental'noy meditsiny Akademii meditsinskikh nauk SSSR. (Imidazole derivatives)