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New method of chlorination of β-naphthol and its derivatives. I. S. Ioffe. *Anilinokrasochnaya Prom.*, 5, 226-7(1935).—Twenty-five per cent aq. $FeCl_3$ is added to boiling 0.1% aq. 2,3-$HOC_{10}H_6CO_2H$, and the soln. is filtered after 30 min. from the ppt. of 2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarboxylic acid. The filtrate is decolorized with HCl, when a ppt. of 2,1,3-$HOC_{10}H_5ClCO_2H$ is obtained. Similarly, 2,6-$HOC_{10}H_6SO_3Na$ affords 2,1,6-$HOC_{10}H_5ClSO_3H$, 2,3,6-$HOC_{10}H_5(SO_3Na)_2$ gives *1-chloro-β-naphthol-3,6-disulfonic acid* (*Na*, *Ba* and *Pb salts*), and β-$C_{10}H_7OH$ yields 2,2'-dihydroxy-1,1'-binaphthyl and 1,2-$ClC_{10}H_6OH$.

B. C. A.

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Biaryls and their derivatives. IV. Oxidation of 2-naphthol-6-sulfonic acid and 2,6-dihydroxynaphthalene. I. S. Ioffe and S. G. Kuznetsov. *J. Gen. Chem.* (U. S. S. R.) 6, 877-85(1936); cf. *C. A.* 30, 2709^4.—The oxidation of 2,6-$HOC_{10}H_6SO_3H$ (I) by $FeCl_3$ in H_2O at elevated temps. gave 2,6-$HOC_{10}H_5(SO_3H)Cl$ and no 2,2'-dihydroxy-1,1'-binaphthyl-6,6'-disulfonic acid (II) as was expected (cf. *C. A.* 28, 1691^9). At 20-5° the reaction proceeded normally, giving 90% II after 20 days of interaction. II, heated with 25% H_2SO_4 at 170-80° for 12 hrs., gave 2,2'-dihydroxy-1,1'-binaphthyl, m. 216°. II, fused with KOH at 300° for 15 min., produced 47.7% of 2,6,2',6'-tetrahydroxy-1,1'-binaphthyl (III), m. 318-20° (uncor.) (decompn.). 2,6-$C_{10}H_6(OH)_2$ (IV) gave with 1 mol. of $FeCl_3$ III and with 1.5 mols. of $FeCl_3$ the tetramer consisting of 4 IV groups with mol. wt. 650 (cf. Saks, *Ber.* 39, 3006(1906); Willstätter and Parnas, *Ber.* 40, 1406 (1907)). II is highly sol. and cannot be sepd. with NaCl. The sepn. was effected by making the reaction mixt. slightly alk. with $Ba(OH)_2$, neutralizing the filtrate with AcOH, evapg. the soln. to a small vol. and filtering from $BaCl_2$. The filtrate was treated with $Ba(OAc)_2$ and the I in the soln. was removed by coupling it with the theoretical amt. of *p*-$O_2NC_6H_4N_2Cl$. The filtrate was treated with the exact amt. of H_2SO_4 and the filtrate from $BaSO_4$ was repeatedly evapd. to dryness, giving II.$7H_2O$ (dil. alc.). **V. Optical activity of 2,2'-dihydroxy-1,1'-binaphthyldisulfonic acids.** I. S. Ioffe and I. V. Grachev. *Ibid.* 950-5.—The dibrucine salts of the 6,6'- and 7,7'-disulfonic acids of 2,2'-dihydroxy-1,1'-binaphthyl were sepd. by fractional crystn. into the diastereomeric dibrucine salts of *l*- and *d*-acids. The latter by the action of alkali sepd. the optical antipodes, *l*- and *d*-acid. These show optical rotation only in the form of the Na salts in alk. soln., and none in a free state or in acid soln. The antipodes of the 7,7'-disulfonic acid are more stable than the 6,6'-acid. The racemization of the 2 acids proceeds more rapidly in an alk. soln. than in an acid one.

VI. Oxidation of 2-naphthol-3-carboxylic acid. I. S. Ioffe and L. Z. Smolyanitskaya. *Ibid.* 1295-9.—The oxidation of 2,3-$HOC_{10}H_6CO_2H$ (I) with 3 mols. of $FeCl_3$ proceeded with the formation of 2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarboxylic acid (II), m. 331°, and 1,2,3-$Cl(HO)C_{10}H_5CO_2H$ (III), m. 231°, at a ratio depending on the conditions of the reaction. In aq. medium the Na salt of I gave 60% II and 0% III, while free I under these conditions produced 60% II and 25% III. Similar results were obtained by working in dil. alc. and AcOH. With a large excess of HCl no II and 60% III were formed. I (5 g.), heated with 2.5 g. of dry CuO in 10 cc. $PhNO_2$ at 210-20° for 6 hrs., gave 2.5 g. II. II is not affected by boiling with $FeCl_3$ or by CuO in $PhNO_2$ at 200-40°. At 300° the latter procedure results in the cleavage of CO_2 and formation of dihydroxybinaphthyl, m. 220°. Cyclization of II with the formation of a perylene ring was effected by heating a mixt. of 10 g. of Pb salt of II with 40 g. of anhyd. $AlCl_3$ at 150° for 1 hr. The product, m. above 350°, is a dye for animal fibers, giving in acid bath an orange dyeing changing to a beautiful brown-chocolate after mordanting with $K_2Cr_2O_7$. The presence of a perylene ring was demonstrated by the formation of perylene on distn. with Zn dust. The product is, probably, 1,12-dihydroxyperylene-2-carboxylic acid or 1,12-perylenequinone-2-carboxylic acid. **VII. Oxidation of 2-hydroxyanthracene.** I. S. Ioffe. *Ibid.* 1210-12.—The oxidation of 2-hydroxyanthracene with $FeCl_3$ in alc. or AcOH resulted in the formation of 2-hydroxy-1,1',0,2'-dianthrylene oxide (I) and a brown compd. of unknown structure. I is unstable, changing at 200° to the brown compd., m. above 300°. I gives with HCl the oxonium salt and with Ac_2O in dry pyridine the Ac deriv., m. 247-50° (uncor.).

Chas. Blanc

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Biaryls and their derivatives. VIII. Influence of the medium acidity on the interaction of β-naphthol with ferric chloride. I. S. Ioffe, S. G. Kuznetsov and S. Litovchik. *J. Gen. Chem.* (U. S. S. R.) 8, 1688-4(1938); cf. *C. A.* 32, 1048.—The effect of the medium acidity on the formation of 2,2'-dihydroxy-1,1'-binaphthyl (I) by the interaction of β-$C_{10}H_7OH$ (II) with $FeCl_3$ in H_2O (Dianin, *J. Russ. Phys.-Chem. Soc.* 6, 183(1874)) was studied by refluxing 5.8 g. II in 1100 cc. of dil. HCl of various concns. with 20 cc. of 1 *N* $FeCl_3$ for 3-38 hrs. At a ratio of 28 mols. of HCl to 1 mol. of II the formation of 1,2-$ClC_{10}H_6OH$ (III) begins with 3.4% and gradually rises with the increasing concn. of HCl to 32.4% III at a ratio of 180 mols. of HCl to 1 mol. of II. The formation of I decreases correspondingly from 72.4 to 27.5%. III, m. 70°, was sepd. from I, m. 216° (C_6H_6) by steam distn. Chas. Blanc

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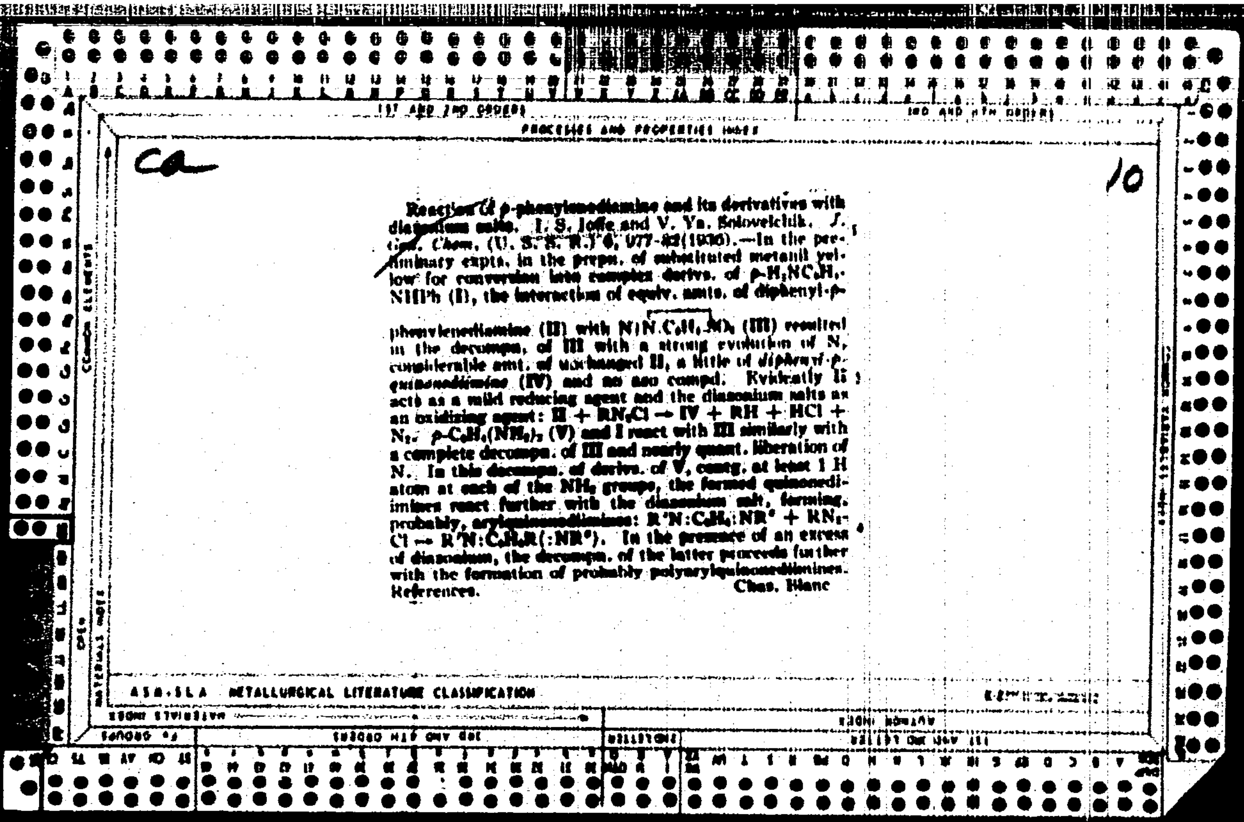

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Reaction of p-phenylenediamine and its derivatives with diazonium salts. I. S. Ioffe and V. Ya. Solovelchik. *J. Gen. Chem.* (U. S. S. R.) 6, 977-82(1936).—In the preliminary expts. in the prepn. of substituted metanil yellow for conversion into complex derivs. of p-$H_2NC_6H_4NHPh$ (I), the interaction of equiv. amts. of diphenyl-p-phenylenediamine (II) with $N:N.C_6H_4.SO_3$ (III) resulted in the decompn. of III with a strong evolution of N, considerable amt. of unchanged II, a little of *diphenyl-p-quinonediimine* (IV) and no azo compd. Evidently II acts as a mild reducing agent and the diazonium salts as an oxidizing agent: II + $RN_2Cl \rightarrow$ IV + RH + HCl + N_2. p-$C_6H_4(NH_2)_2$ (V) and I react with III similarly with a complete decompn. of III and nearly quant. liberation of N. In this decompn. of derivs. of V, contg. at least 1 H atom at each of the NH_2 groups, the formed quinonediimines react further with the diazonium salt, forming, probably, arylquinonediimines: $R'N:C_6H_4:NR'' + RN_2Cl \rightarrow R'N:C_6H_3R(:NR'')$. In the presence of an excess of diazonium, the decompn. of the latter proceeds further with the formation of probably polyarylquinonediimines. References. Chas. Blanc

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IOFFE, I.S.

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New diphenylamine derivatives. J. S. Joffe, S. D. [illegible], and [illegible] (J. Gen. Chem. Russ., 1936, 6, [illegible]).—[illegible] acid, NH$_2$Ph, and K$_2$CO$_3$ in 60% EtOH (16 hr., [illegible]) yield the K salt of [illegible] acid, from which the internal salt of the corresponding [illegible] [illegible] with boiling H$_2$O, and [illegible] acid by the Sandmeyer reaction. R. T.

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Biaryls and their derivatives. IX. Sulfonation of 2,2'-dihydroxy-1,1'-binaphthyl. I. S. Ioffe, S. G. Kuznetsov and A. A. Panov. *J. Gen. Chem.* (U.S.S.R.) 6, 990-1002 (1936); cf. *C. A.* 30, 3420^{9}.—Digesting 2,2'-dihydroxy-1,1'-binaphthyl (I) with 4 parts of 96% H_2SO_4 on a boiling water bath for 60 hrs. gave 83% *2,2'-dihydroxy-1,1'-binaphthyl-6,6'-disulfonic acid* (II), and 13% *2,2'-dihydroxy-1,1'-binaphthyl-6-sulfonic acid* (III). II is identical with the acid obtained by oxidation of 2,6-$HOC_{10}H_6SO_3H$ with $FeCl_3$ in H_2O (*C. A.* 30, 1047^{9}), and gives by fusion with KOH 2,6,2',6'-tetrahydroxy-1,1'-binaphthyl (IV), m. 318-20°. The sepn. of II and III depends on the different solubilities of their Ba salts. III fused with KOH at 325° for 15 min. gave 60% *2,2',6-trihydroxy-1,1'-binaphthyl*, m. 305-7° (sealed capillary). X. **Nitration of 2,2'-dihydroxy-1,1'-binaphthyl.** I. S. Ioffe. *Ibid.* 1003-5.—Ten g. I in 200 cc. of 100% AcOH was treated at 5° with 4.2 g. of 95% HNO_3 in 80 cc. of 100% AcOH, and the mixt. digested on a boiling water bath for 1 hr. The filtered ppt. was washed with AcOH and water, then dissolved in 1 *N* NaOH and repptd. with dil. HCl, giving 70% *6,6'-dinitro-2,2'-dihydroxy-1,1'-binaphthyl* (V), m. above 300° (decompn.). V (9.5 g.) in 800 cc. of 1 *N* NaOH reduced with 150 cc. of 1 *N*

(1930).—The catalytic reduction of adrenalone (I) to adrenaline (II) was studied by the action of H on I.HCl in H_2O at room temp. (15-17°) in the presence of Pt, Pd and Ni, with and without carriers. Optimum results of 95% II were obtained at atm. pressure in 24 hrs. with 3% Pd-animal C and in 4 hrs. with 10% Pd-animal C (Mannich, *Arch. Pharm.* 253, 181(1915)), and in 4 hrs. with Pt black prepd. by the method of Loew (*Ber.* 23, 290(1890)) and Willstätter (*C. A.* 6, 2113), and in 2.5 hrs. with Pt black prepd. by the method of Adams (*Org. Syntheses* 8, 92(1928)). The reaction with $NiCl_2$ ignited at 310° was accelerated by the addn. of 1-2 drops of HCl to dissolve some of the pptd. free I, and was completed in 24 hrs. with 70% II. The reduction with 24% Ni-silica gel (heated at 420-60°) at 2 atm. gave 60% II in AcOH and 64% II in alc. in 24 hrs. The ratio of catalysts to I was 1:3 and 1:5. No improvement of the catalytic action was observed at higher temps., nor in case of Pt and Pd at elevated pressures. Greater activity resulted by increasing the concn. of catalysts in the carriers. Thirty references.

Chas. Blanc

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Binaphthyls and their derivatives. XII. Selective absorption of azo dyes derived from dihydroxynaphthalenes and polyhydroxybinaphthyls by vegetable fibers. I. S. Ioffe and M. A. Chigrev. J. Gen. Chem. (U. S. S. R.) 6, 1014-21(1936); cf. C. A. 31, 675^1.—Expts. in the prepn. and dyeing of azo dyes derived from 2,7,2',7'-tetrahydroxy-1,1'-binaphthyl, 2,6,2',6'-tetrahydroxy-1,1'-binaphthyl, 2,6,2'-trihydroxybinaphthyl, and 2,7- and 2,6-dihydroxynaphthalene, are described in detail. The monoazo dyes were obtained by coupling with p-$HO_3SC_6H_4N_2Cl$ (I), and the disazo dyes with I and p-$O_2NC_6H_4N_2Cl$. All 8 dyes gave on wool red dyeings of various shades. Cotton is poorly dyed orange-brown to faint rose unstable to water and soap. Chas. Blanc

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Interaction of 1-bromo-2-naphthol with p-nitrobenzenediazonium salts. I. S. Ioffe. *J. Gen. Chem.* (U. S. S. R.) 6, 1074-8(1936).—In the interaction of 1,2-$BrC_{10}H_6ONa$ (I) with salts of p-$O_2NC_6H_4N_2OH$ (II) with displacement of the Br in I by the diazo component (I + II → $O_2NC_6H_4N_2C_{10}H_6OH$ (III) + NaBrO (cf. Hewitt and Mitchell, *J. Chem. Soc.* 89, 1167(1906)), no traces of NaBrO could be detected in the filtrate. It is completely decompd. in the process of formation, oxidizing and brominating I, II and III. The resulting para red, m. 160-80°, contains 28.2% Br and is of brown shade. In the presence of Na_2SO_3 the destructive action of NaBrO is overcome, giving 90% of bright red III, m. 250-1°. Chas. Blanc

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Bromination of 2,7-dihydroxynaphthalene. I. S. Ioffe and N. M. Fedorova. *J. Gen. Chem.* (U. S. S. R.) 6, 1079-84(1936); cf. *C. A.* 28, 1001⁹, and preceding abstr.—In the direct bromination of 2,7-$C_{10}H_6(OH)_2$ (I), the identification of the position of the Br atoms in the mono- and poly-Br derivs. is based on the reaction of aromatic diazonium salts (p-$O_2NC_6H_4N_2Cl$) in aq. NaOH with 1,2-$BrC_{10}H_6OH$ with the formation of azo compds. by displacement of the Br atom in position 1, and with isomeric Br derivs. of β-$C_{10}H_7OH$ with the formation, by coupling, of the usual azo compds. contg. Br (cf. Veselý and Štursa, *C. A.* 27, 5320). I is substituted by Br first in positions 3 and 6, and then considerably more slowly in positions 1 and 8. Contrary to Scholl (*Chem. Zentr.* 3, 720(1932)) I with Br gives 3,6-dibromo-2,7-dihydroxynaphthalene and not the 1,8-di-Br isomer. I, m. 183-4° (32 g.) in 160 cc. of 100% AcOH at 5-7° was treated with liquid Br in definite ratios, and the Br products were purified in the usual manner. 3,2,7-$BrC_{10}H_5(OH)_2$, m. 135°. 3,6,2,7-$Br_2C_{10}H_4(OH)_2$, m. 144-6° (C_6H_6), 155-9° (100% AcOH). 1,3,6,2,7-$Br_3C_{10}H_3(OH)_2$, m. 205°. Tetra-Br deriv. of I, m. 203-4°, resulted only with the aid of an $AlCl_3$ catalyst; its structure was not detd. C. B.

2-Methyl-1,9-aceanthrene. Alfredo Dansi and Antonio Sempronj. *Gazz. chim. ital.* 60, 183-6(1930).—A preliminary note. The mechanism of the reaction between β-methylanthracene (I) and $(COCl)_2$ in the presence of $AlCl_3$ was studied. I (10 g.), $(COCl)_2$ (30 g.) and $AlCl_3$ (7.5 g.) in CS_2 (200 cc.) agitated at 0° for 3 hrs., heated at 100° for 4 hrs., decompd. with ice and HCl, steam-distd., extd. with dil. Na_2CO_3 (to remove β-methylanthraceneearboxylic acid formed as secondary product), the residue extd. with hot dil. aq. $NaHSO_3$, and the new residue purified, yield 4 g. of *methylaceanthrenequinone* (II), scarlet, m. 258° (decompn.). Oxidized with CrO_3 in AcOH, it yields the acid, m. 298°, described by Meyer, Fleckenstein and Günther (*C. A.* 2[illegible], 4294). *Monosemicarbazone*, ocher-color, m. 278-80° (decompn.). The $NaHSO_3$ soln. from the prepn. of II decompd. with HCl yields 1.5 g. of an *isomer* (III) of II, red, m. 208-8°. Oxidized with CrO_3 in AcOH, III yields the acid, m. 294-5°, described by Butescu (*C. A.* 7, 1498). II and Zn dust (20 parts) distd. in a current of H, and the solidified product purified with C_6H_6 and sublimation, yield a *hydrocarbon* $C_{17}H_{14}$ (IV), golden yellow, m. 122°, sol. in concd. H_2SO_4. Under the same conditions, III yields a *hydrocarbon* $C_{17}H_{14}$ (V), silky light yellow, m. 99°; its solns. in concd. H_2SO_4 are fluorescent green-yellow. The C_6H_6 solns. of IV and V show intense blue fluorescence. The yields of IV and V were 0.025-0.05 g. from 5 g. of II and III, resp. Reduction of II and III by the Kishner-Wolff method ($H_2NNH_2.H_2O$) gave no definite products. IV is probably 2-methyl-1,9-aceanthrene, while the constitution of V is less certain. The results obtained in the reaction of I, $(COCl)_2$ and $AlCl_3$ should be compared with those of Butescu (*loc. cit.*) and Meyer, Fleckenstein and Günther (*loc. cit.*). *Ibid* 264.—A correction.

C. C. Davis

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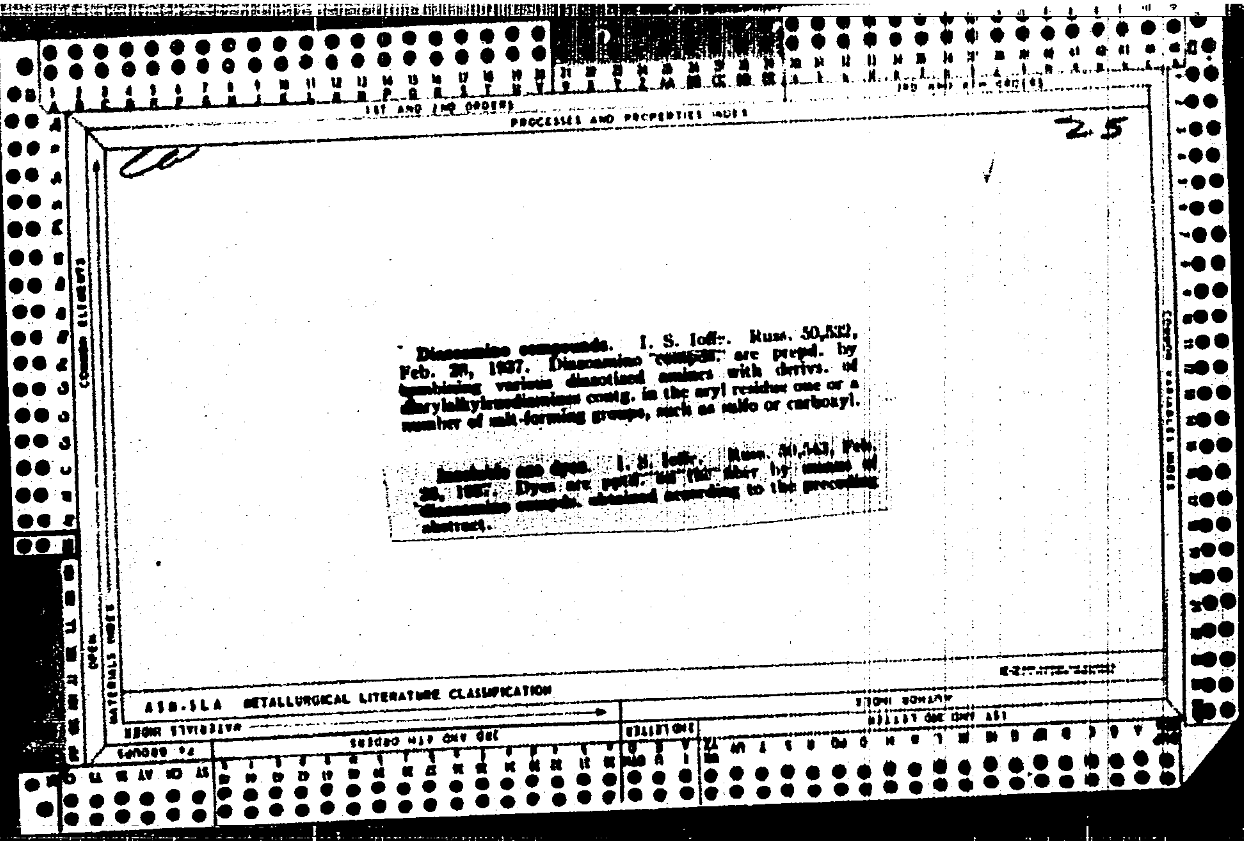
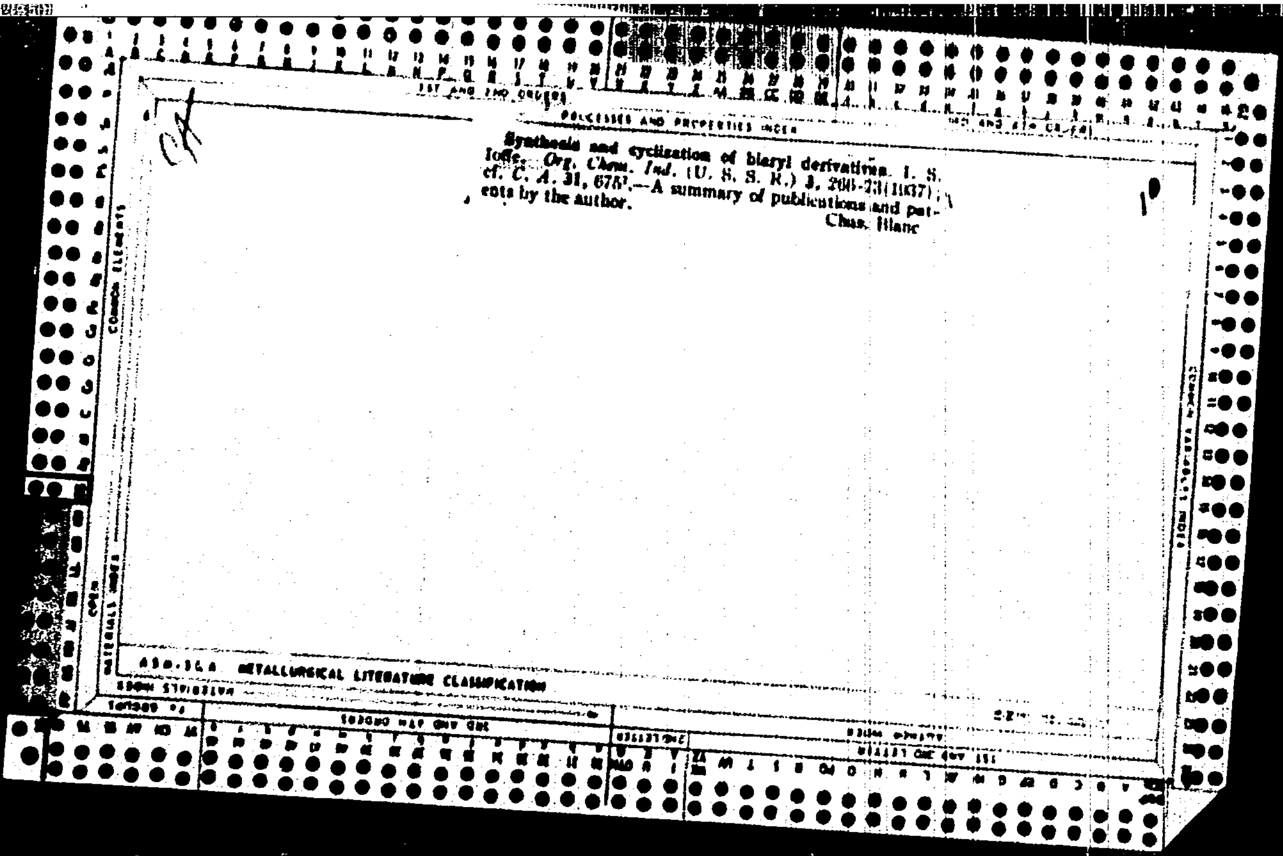


Diazoamino compounds. I. S. Ioffe. Russ. 50,532, Feb. 28, 1937. Diazoamino compds. are prepd. by combining various diazotized amines with derivs. of diarylalkylenediamines contg. in the aryl residue one or a number of salt-forming groups, such as sulfo or carboxyl.

Insoluble azo dyes. I. S. Ioffe. Russ. 50,543, Feb. 28, 1937. Dyes are pptd. on the fiber by means of diazoamino compds. obtained according to the preceding abstract.



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Synthesis and cyclization of biaryl derivatives. I. S. Ioffe. *Org. Chem. Ind.* (U. S. S. R.) 3, 200-73(1937); cf. *C. A.* 31, 678^{7}.—A summary of publications and patents by the author.

Chas. Blanc

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N-Nitrosamines and their use in the production of ice dyes. I. S. Ioffe and M. I. Rozova. *Org. Chem. Ind.* (U. S. S. R.) 4, 170-2(1937).—A discussion of patent literature, with 18 references. Chas. Blanc

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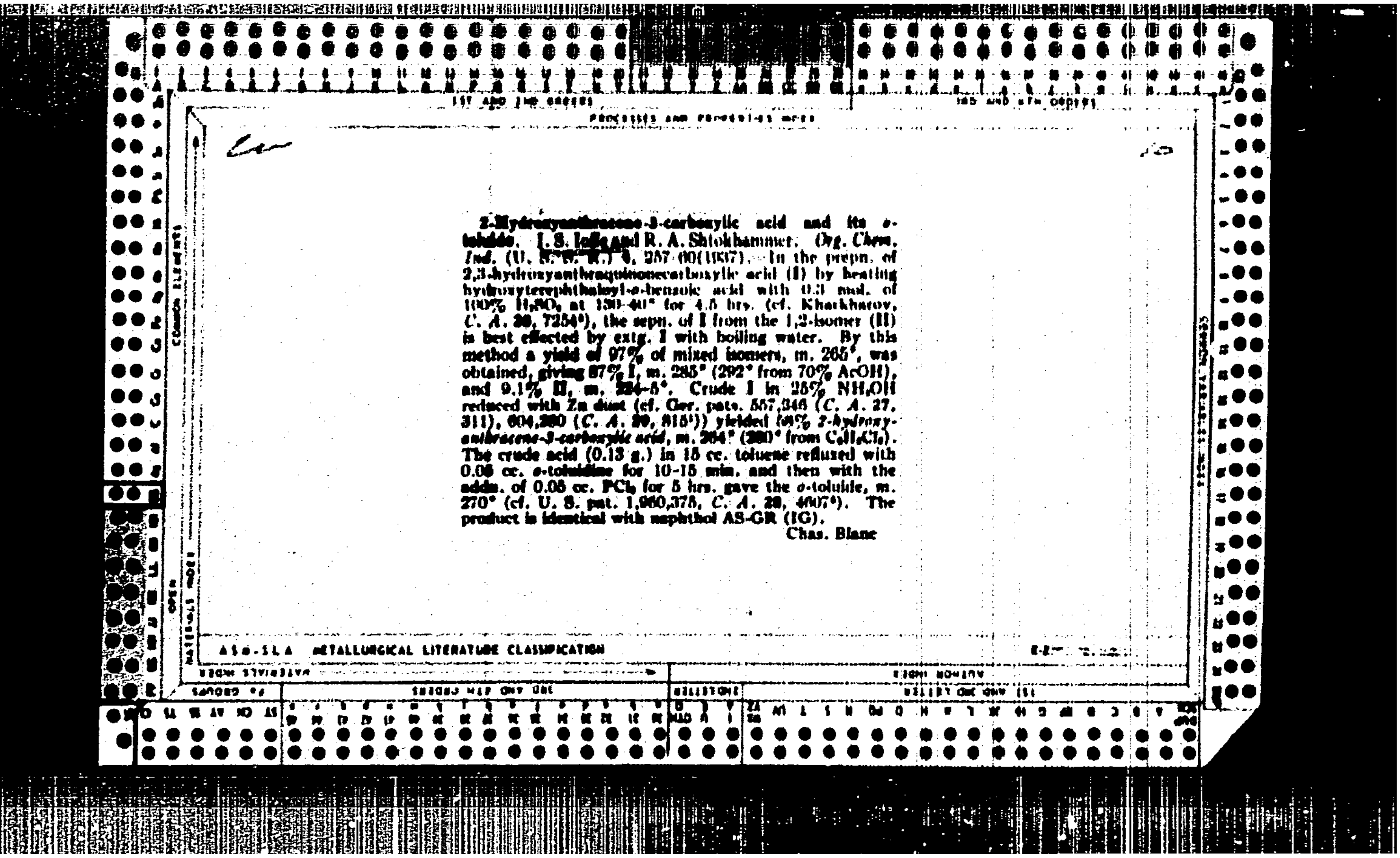

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2-Hydroxyanthracene-3-carboxylic acid and its o-toluidide. I. S. Ioffe and R. A. Shtokhammer. *Org. Chem. Ind.* (U. S. S. R.) 4, 257-60(1937).—In the prepn. of 2,3-hydroxyanthraquinonecarboxylic acid (I) by heating hydroxyterephthaloyl-o-benzoic acid with 0.3 mol. of 100% H_2SO_4 at 130-40° for 4.5 hrs. (cf. Kharkharov, *C. A.* 30, 7254⁹), the sepn. of I from the 1,2-isomer (II) is best effected by extg. I with boiling water. By this method a yield of 97% of mixed isomers, m. 265°, was obtained, giving 87% I, m. 285° (292° from 70% AcOH), and 9.1% II, m. 234-5°. Crude I in 25% NH_4OH reduced with Zn dust (cf. Ger. pats. 557,246 (*C. A.* 27, 311), 604,280 (*C. A.* 29, 815⁵)) yielded 68% *2-hydroxyanthracene-3-carboxylic acid*, m. 264° (280° from $C_6H_4Cl_2$). The crude acid (0.13 g.) in 15 cc. toluene refluxed with 0.06 cc. o-toluidine for 10-15 min. and then with the addn. of 0.08 cc. PCl_3 for 5 hrs. gave the o-toluidide, m. 270° (cf. U. S. pat. 1,960,375, *C. A.* 28, 4607⁶). The product is identical with naphthol AS-GR (IG).

Chas. Blanc

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Diaryls and their derivatives. XIII. Azo dyes from 6,6'-diamino-2,2'-dihydroxy-1,1'-binaphthyls. I. S. Ioffe. J. Gen. Chem. (U. S. S. R.) 7, 1082-5 (1937); cf. C. A. 31, 3281³.—When this compd. is diazotised, only 1 diazo group couples. The other is converted to an OH group, even when an excess of the coupling reagent is present. Violet-colored compds. are obtained by coupling the amine with 2-naphthol, 2-naphthol-3-carboxylic acid and 2-naphthyl-3,6-disulfonic acid.

H. M. Leicester

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Biaryls and their derivatives. XIV. Ring closure in 6,6'-dinitro-2,2'-dihydroxy-1,1'-binaphthyl. I. S. Ioffe and I. S. Gorelik. *J. Gen. Chem.* (U. S. S. R.) 7, 1102-5(1937); cf. *C. A.* 31, 6834°.—This binaphthyl does not form a perylene deriv. under any condition, probably because of the decrease in reactivity due to the NO_2 groups. If it is treated with strong H_2SO_4 at 40° for 30 min., it gives 6,6'-dinitro-1,1'-binaphthyl 2,2'-oxide, sol. only in H_2SO_4 and pyridine. This compd. can be reduced to an amine which can be diazotized. H. M. L.

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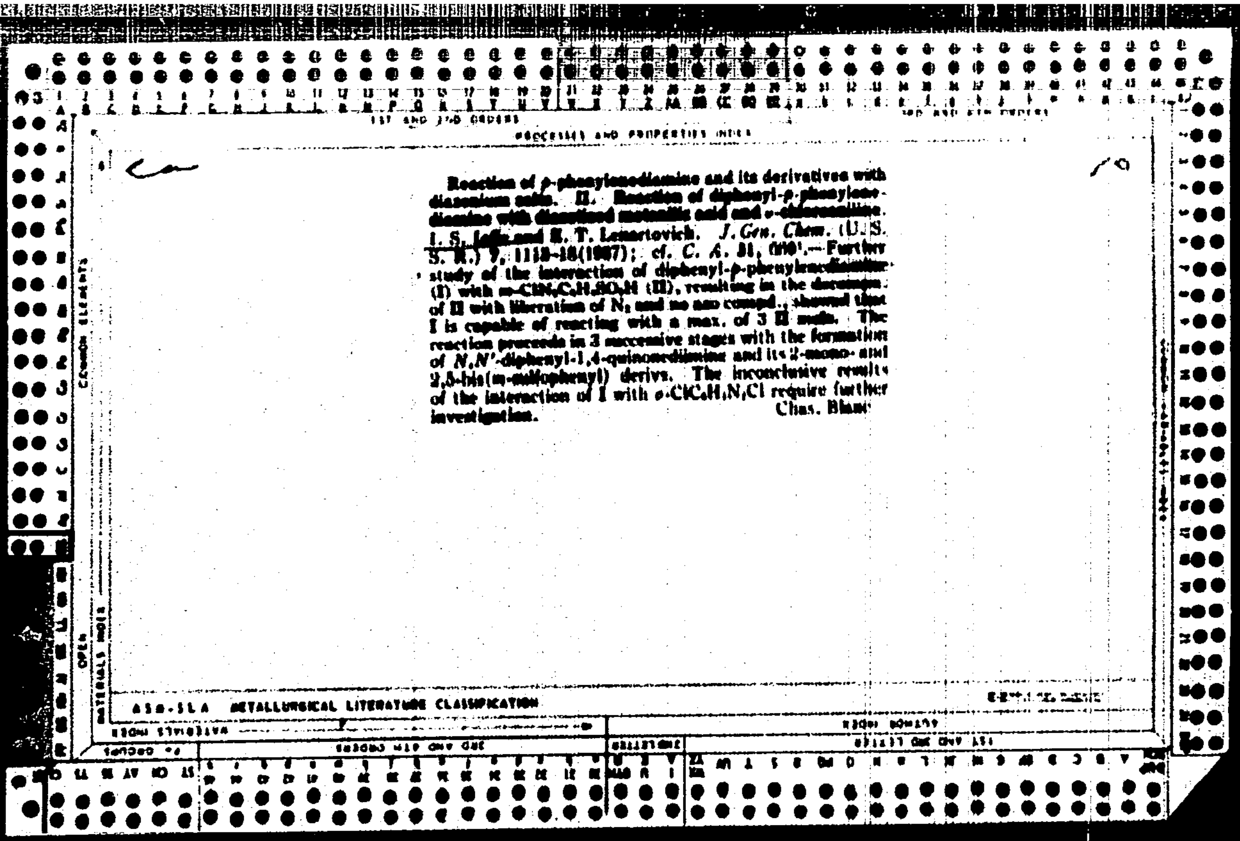

Reaction of *p*-phenylenediamine and its derivatives with diazonium salts. II. Reaction of diphenyl-*p*-phenylenediamine with diazotized metanilic acid and *o*-chloroaniline. I. S. Ioffe and E. T. Lenartovich. *J. Gen. Chem.* (U.S.S.R.) 7, 1113-18(1937); cf. *C. A.* 31, [illegible].—Further study of the interaction of diphenyl-*p*-phenylenediamine (I) with $m\text{-}ClN_2C_6H_4SO_3H$ (II), resulting in the decompn. of II with liberation of N_2 and no azo compd., showed that I is capable of reacting with a max. of 3 II mols. The reaction proceeds in 3 successive stages with the formation of *N,N'*-diphenyl-1,4-quinonediimine and its 2-mono- and 2,5-bis(*m*-sulfophenyl) derivs. The inconclusive results of the interaction of I with $o\text{-}ClC_6H_4N_2Cl$ require further investigation. Chas. Blanc

Biaryls and their derivatives. XV. The reaction of 2-naphthol-3,6-disulfonic acid with salts of trivalent iron. I. S. Ioffe and R. Chernysheva. *J. Gen. Chem.* (U. S. S. R.) 7, 2398-2401(1937); cf. C. A. 31, 7410⁹.—When the Na salt of this acid is heated for 18 hrs. with $FeCl_3$, it gives the Na salts of 1-chloro-2-naphthol-3,6-disulfonic acid (I) and 2,2'-dihydroxy-1,1'-binaphthyl-3,6,3',6'-tetrasulfonic acid (II). If the reaction is carried out in the presence of a large excess of HCl, I is almost the only product, and if $Na(OAc)_2$ is present to remove all the HCl formed, II is the chief product. If the oxidation is carried out with $Fe_2(SO_4)_3$, only II is formed. The Cl in I is easily split off by $AgNO_3$ or diazonium salts. **XVI. The reaction of salts of trivalent iron with 2-naphthol-5-sulfonic acid and 2-naphthol-5,7-disulfonic acid.** I. S. Ioffe and V. I. Kobyakova. *Ibid.* 2152-60.—When 2-naphthol-5-sulfonic acid is oxidized by $FeCl_3$, even in the presence of excess HCl, or by $Fe_2(SO_4)_3$, the only product is 2,2'-dihydroxy-1,1'-binaphthyl-5,5'-disulfonic acid. With $FeCl_3$, 2-naphthol-5,7-disulfonic acid gives chiefly 2,2'-dihydroxy-1,1'-binaphthyl-5,7,5',7'-tetrasulfonic acid, but when excess HCl is added, 1-chloro-2-naphthol-5,7-disulfonic acid is also formed. $Fe_2(SO_4)_3$ gives only the binaphthyl compd. **XVII. The reaction of salts of trivalent iron with 2-naphthol-4-sulfonic acid and its derivatives.** I. S. Ioffe and M. A. Benediktova-Fleisher. *Ibid.* 2678-80.—With $Fe_2(SO_4)_3$ or $FeCl_3$, even in the presence of excess HCl, 2-naphthol-4-sulfonic acid gives only 2,2'-dihydroxy-1,1'-binaphthyl-4,4'-disulfonic acid. 6-Nitro-2-naphthol-4-sulfonic acid does not react at all with $Fe_2(SO_4)_3$, and with $FeCl_3$ gives only 6-nitro-1-chloro-2-naphthol-4-sulfonic acid. H. M. Leicester

ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION

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The reaction of 1-chloro-2-naphthol with *p*-nitrobenzenediazonium salts. I. S. Ioffe. *J. Gen. Chem.* (U.S.S.R.) 7, 2067-8(1937).—While 1-bromo-2-naphthol and (p-$NO_2C_6H_4N_2)_2SO_4$ give entirely para red, 1-chloro-2-naphthol also forms about 40% of a light yellow compd. m. 125° (decompn.). This is either $ClC_{10}H_6ON:NC_6H_4NO_2$ or its quinoid isomer. In the presence of $NaHCO_3$, a better quality of para red is obtained in this reaction.

H. M. Leicester

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Cu

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Biaryls and their derivatives. XVIII Oxidation of 2-hydroxyanthracene-3-carboxylic acid. I. S. Ioffe and R. A. Shtokhammer. *J. Gen. Chem.* (U. S. S. R.) 7, 2710-11 (1937); cf. *C. A.* 32, 2112⁴.—When 2-hydroxyanthracene-3-carboxylic acid is heated in HOAc with at least a 3-fold excess of ferric NH_4 alum, the corresponding biaryl compd. is probably formed, but it at once reacts further to give 80% of *3,3'-dicarboxyl-1,1'-bianthranyl 2,9',2',9-dioxide*, which decomps. above 330°. **XIX. The reaction of 2-hydroxyanthracene with ferric chloride.** I. S. Ioffe and I. S. Khim. *Ibid.* 2712-14.—The brown product obtained along with 2-hydroxy-1,1'-bianthranyl 9,2'-oxide when 2-hydroxyanthracene is oxidized with $FeCl_3$ (*C. A.* 30, 1048⁴) is actually the Fe salt of 2,2'-dihydroxy-9,9'-bianthra-10,10'-dione. **XX. A general consideration of the mechanism of the reaction of 2-naphthol and its derivatives with salts of trivalent iron.** I. S. Ioffe. *Ibid.* 2715-18.—In these reactions equil. exists between compds. of the type $C_{10}H_7OFeCl_2$, $(C_{10}H_7O)_2FeCl$, $(C_{10}H_7O)_3Fe$ and $(C_{10}H_7O)_3Fe-(C_{10}H_7O)$. In acid solns. the formation of the more complex compds. is prevented, and Cl can enter the ring to form a Cl-substituted naphthol. In less acid solns., the complexes tend to form biaryls.

H. M. Leicester

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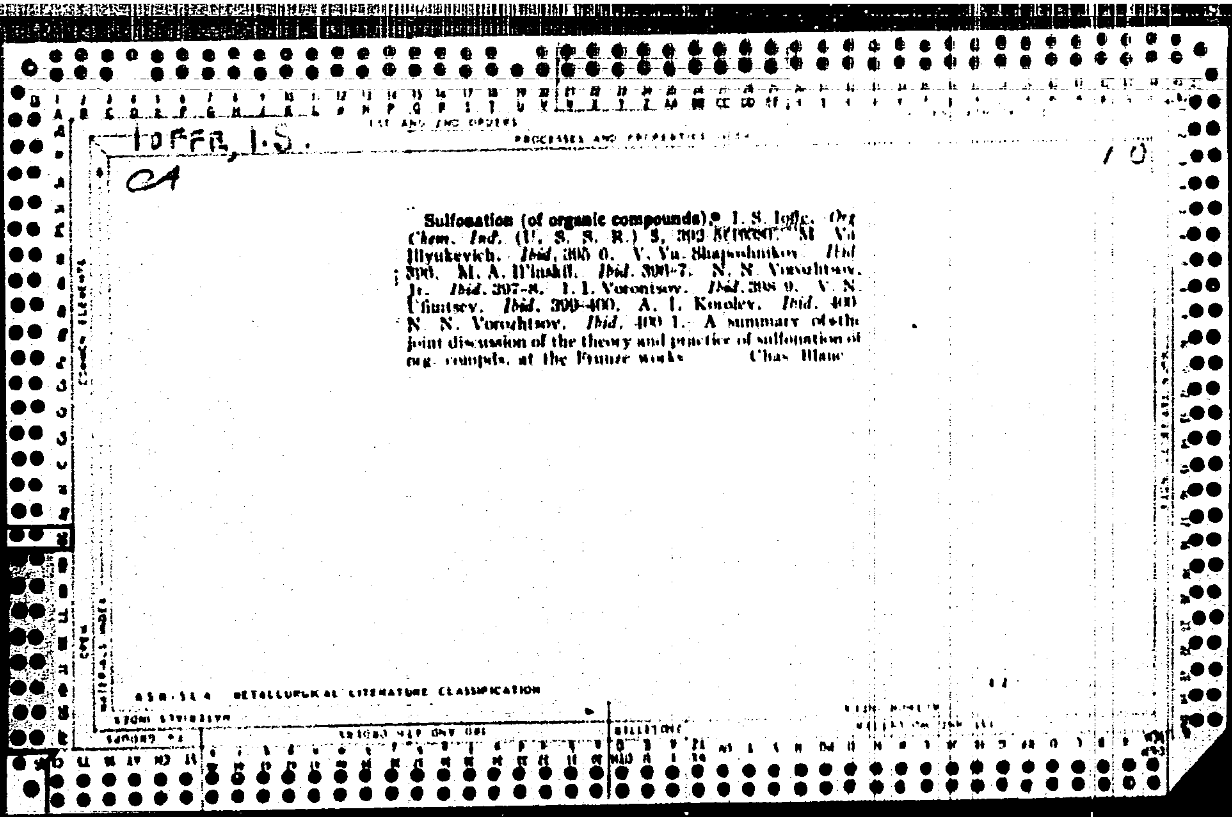

IOFFE, I.S.

CA

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PROCESSES AND PROPERTIES INDEX

Sulfonation (of organic compounds). I. S. Ioffe. *Org. Chem. Ind.* (U. S. S. R.) 5, 393-[illegible] M. Ya. Iliyukevich. *Ibid.* 395-6. V. Ya. Shaposhnikov. *Ibid.* 396. M. A. Il'inskii. *Ibid.* 396-7. N. N. Vorozhtsov, Jr. *Ibid.* 397-8. I. I. Vorontsov. *Ibid.* 398-9. V. N. Ufimtsev. *Ibid.* 399-400. A. I. Korolev. *Ibid.* 400. N. N. Vorozhtsov. *Ibid.* 400-1. A summary of the joint discussion of the theory and practice of sulfonation of org. compds. at the Frunze works. Chas. Blanc

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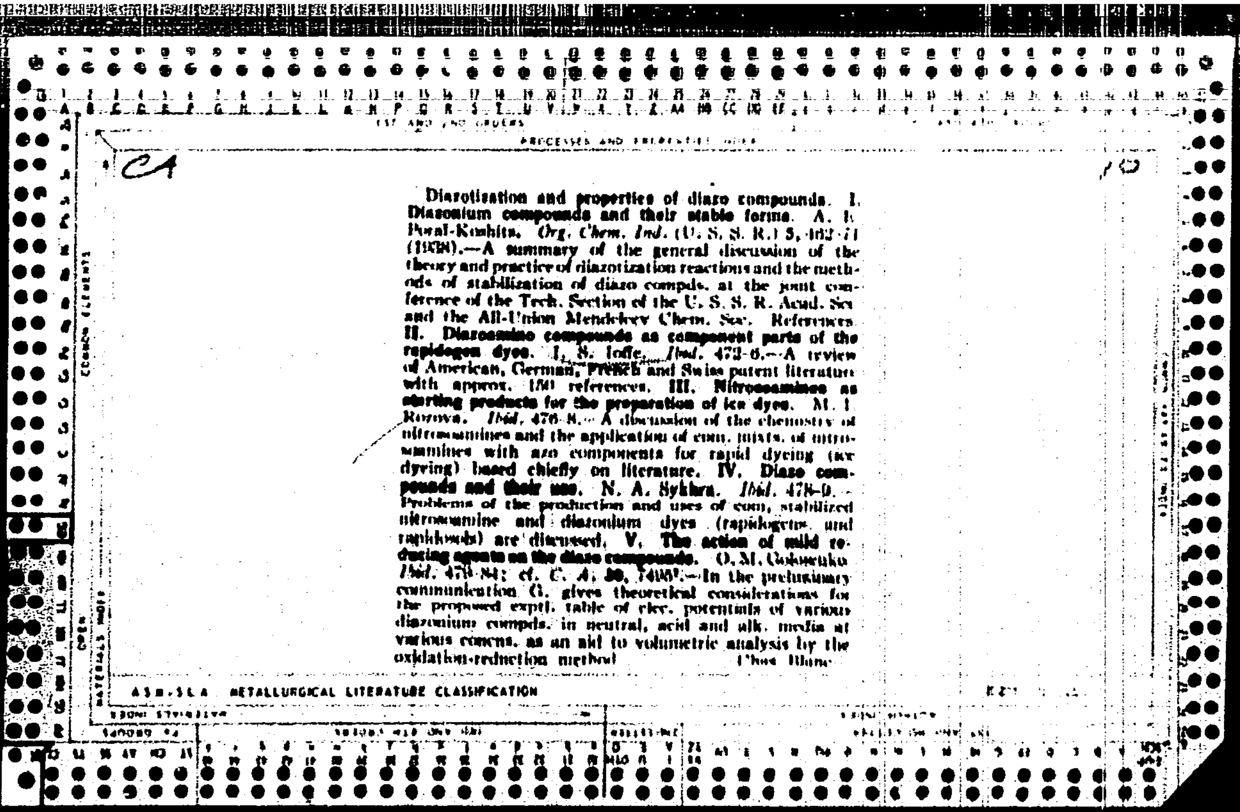

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Diazotization and properties of diazo compounds. I. Diazonium compounds and their stable forms. A. E. Porai-Koshits. *Org. Chem. Ind.* (U. S. S. R.) 5, 462-71 (1938).—A summary of the general discussion of the theory and practice of diazotization reactions and the methods of stabilization of diazo compds. at the joint conference of the Tech. Section of the U. S. S. R. Acad. Sci. and the All-Union Mendeleev Chem. Soc. References. **II. Diazoamino compounds as component parts of the rapidogen dyes.** I. S. Ioffe. *Ibid.* 472-6.—A review of American, German, French and Swiss patent literature with approx. 150 references. **III. Nitrosoamines as starting products for the preparation of ice dyes.** M. I. Rozova. *Ibid.* 476-8.—A discussion of the chemistry of nitrosoamines and the application of com. mixts. of nitrosamines with azo components for rapid dyeing (ice dyeing) based chiefly on literature. **IV. Diazo compounds and their use.** N. A. Sykhra. *Ibid.* 478-9.—Problems of the production and uses of com. stabilized nitrosamine and diazonium dyes (rapidogens and rapidsols) are discussed. **V. The action of mild reducing agents on the diazo compounds.** O. M. Golosenko. *Ibid.* 479-84; cf. *C. A.* **30**, 1400^1.—In the preliminary communication G. gives theoretical considerations for the proposed exptl. table of elec. potentials of various diazonium compds. in neutral, acid and alk. media at various concns. as an aid to volumetric analysis by the oxidation-reduction method. Chas. Blanc

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2-Methylamino-5-sulfobenzoic acid as a stabilizing constituent in Rapidogene Ruby Red IL and Red ITR. I. S. Ioffe and N. M. Fedorova. *Org. Chem. Ind.* (U.S.S.R.) 5, 541-3(1938).—Previously it was shown that in Rapidogene Red IL the azo component is Naphthol ASOL and the diazonium component is a diazoamino compd. formed from 2,5-$Cl_2C_6H_3NH_2$ and an unknown amino stabilizing constituent. To det. the nature of the latter the diazoamino compd. was decompd. by boiling the dye with AcOH + HCO_2H, the azo dye, formed by the interaction of the cleaved $Cl_2C_6H_3N_2Cl$ with the Naphthol ASOL, was filtered off, the filtrate contg. the liberated amino stabilizer was evapd. with a little HCl to dryness and the residue was recrystd. Examn. of the latter by the method of analysis and degradation showed that it is *2,5-MeNH(SO₃H)C₆H₃CO₂H* (I). It is identical with the synthetic I, giving the same 2,5-$MeNH(SO_2Cl)C_6H_3COCl$, m. 15[illegible]-7°. The stabilizing constituent in Rapidogene Red ITR is also I. **Alkylaminoacetic acids as stabilizing constituents in Rapidogene Brown IB, Violet B, Blue B, Blue R, Green B and Navy Blue R.** I. S. Ioffe and R. F. Mazel. *Ibid.* 543-4.—The stabilizing constituents in the diazoamino compds. of the Rapidogenes are: $MeNHCH_2CO_2H$ in Brown IB and Violet B, and $BuNHCH_2CO_2H$ in Blue B, Blue R, Green B and Navy Blue R. The alkylaminoacetic acids were identified by coupling with diazotized *p*-chloroanisidine. Chas. Blanc

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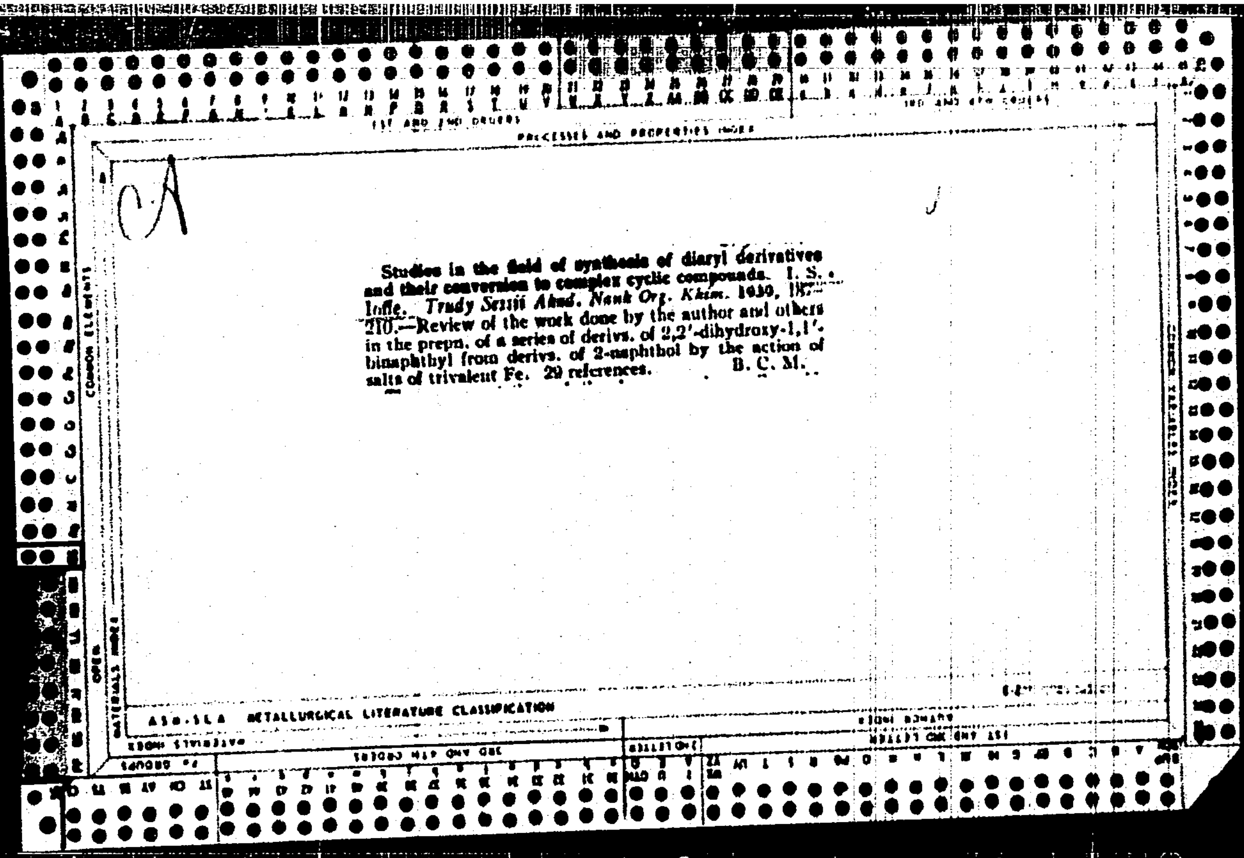

CA

Studies in the field of synthesis of diaryl derivatives and their conversion to complex cyclic compounds. I. S. Ioffe. *Trudy Sessii Akad. Nauk Org. Khim.* 1939, 187-210.—Review of the work done by the author and others in the prepn. of a series of derivs. of 2,2'-dihydroxy-1,1'-binaphthyl from derivs. of 2-naphthol by the action of salts of trivalent Fe. 29 references. B. C. M.

A S M - S L A METALLURGICAL LITERATURE CLASSIFICATION

1ST AND 2ND ORDERS

CA

/3

The relation between diazo compounds and the *p*-phenylenediamine derivatives. I. S. Ioffe. *Izvestiya (Otdel. Tekh. Nauk* 1939, No. 1, 117-21; *Khim. Referat. Zhur.* 1939, No. 7, 104; cf. *C. A.* 33, 6270.—Expts. showed that the *p*-phenylenediamine derivs. contg. at least 1 unsubstituted H atom in each amino group (*p*-$C_6H_4(NHPh)_2$, unsubstituted *p*-$C_6H_4(NH_2)_2$, *p*-$H_2NC_6H_4$-NHPh) are able to decomp. the diazonium salts with evolution of N (when reacting with their salts), being oxidized thereby into the corresponding derivs. of *p*-quinonediimine. The reaction, however, does not stop at this stage and the deriv. of *p*-quinonediimine decomps. the excess diazo compd. with evolution of N and introduction of the aryl residues of the diazo compd. into the quinoid group. An investigation of the reaction of *p*-$C_6H_4(NHPh)_2$ with diazotized metanilic acid and with *o*-chloroaniline (in various mol. ratios) confirmed this supposition. It was found that from the amt. of the evolved N it is possible to det. the whole reaction process of the *p*-phenylenediamine derivs. with the diazo compds. (including the amt. of the aryl residues which were introduced in the quinoid group of the *p*-quinonediimine). In order to obtain a better transformation of the diazo compd. in the 1st part of the process the reactions of the diazotized *p*-nitroaniline with *p*-$C_6H_4(NHPh)_2$ and with *p*-$PhN{:}C_6H_4{:}NPh$ were compared. It was detd. that the reaction takes place in 2 directions (1) $C_6H_4(NHR)_2 + R'N{:}NOH \rightarrow RN{:}C_6H_4{:}NR + R'H + H_2O + N_2$ and (2) $C_6H_4(NHR)_2 + 2R'N{:}NOH \rightarrow RN{:}C_6H_4{:}NR + R'_2 + 2H_2O + 2N_2$. The reduction reaction of the diazo compd. takes place predominantly according to (2). W. R. Henn

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

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C4

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Sulfonation of 1,2-benzanthraquinone and 1,9-benzanthrone. I. S. Ioffe. *Org. Chem. Ind.* (U. S. S. R.) 6, 95-7(1939).—Preliminary expts. indicate that 1,2-benzanthrene-7,12-dione (I) and 1,9-benzanthrone (II) react with 100% H_2SO_4 at 20° and with 95% H_2SO_4 at 140-5° with the substitution in the naphthalene nucleus and formation of isomeric monosulfonic acids. I gave 3 acids with the sulfo group in the positions 3, 4 and 5, which were oxidized to 1,2-anthraquinonedicarboxylic acid. II also gave 3 acids with the sulfo group in the positions 2, 3 and 4, oxidized to anthraquinone-1-carboxylic acid. The sulfonic acids were sepd. as the Ba salts and identified as quinone salts with uncertain m. ps. The results tend to disprove the formation of 1,9-benzanthrone-8-sulfonic acid from II and H_2SO_4 as claimed by Lauer and Irie (C. A. 30, 5967). Ph 1-naphthyl ketone (1-benzoylnaphthalene) reacts with fuming H_2SO_4 at 20° to give 1-benzoylnaphthalene-5-sulfonic acid, identical with the product obtained from the ketone with $ClSO_3H$ in $PhNO_2$ by Dziewoński and Moszew (C. A. 26, 131). Chas. Blanc

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

1. YERSHOV, A.P., IOFFE, I.S.

2. USSR (600)

"The Reaction with Dizao Compounds of Primary Aromatic Amines Containing Salt-Forming Groups -- I. The Tautomerism of Triazenes", Zhur. Obshch. Khim., 9, No. 24, 1939. Sci. Inst. of Organic Intermediate Products and Dyes imeni Voroshilov. Received 7 July 1939.

9. [redacted] report U-1626, 11 Jan 1952.

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Reaction of *p*-phenylenediamine and its derivatives with diazonium salts. III. Transformation of diazonium salt. I. S. Ioffe and V. Ya. Solovelchik. *J. Gen. Chem.* (U.S.S.R.) 9, 1114-18 (1939); cf. *C. A.* 33, 6210^8.—Further study of the interaction of p-$C_6H_4(NH_2)_2$ (I) and its derivs. with diazonium salts (II) showed again that the reaction proceeds in 2 stages in which II, acting as mild oxidizing agents, are decompd. with a nearly complete sepn. of N_2 and the formation of the corresponding biaryls. In the 2nd stage of the reaction the *p*-quinonediimines, formed by oxidation of I derivs., react further with II to form arylquinonediimines (cf. *loc. cit.*). Thus, the Willstätter imines (cf. *C. A.* 1, 2901) and their leuco compd. ($PhNHC_6H_4NHC_6H_4NHC_6H_4NH_2$) react with p-$O_2NC_6H_4N_2Cl$ to yield considerable 4,4'-dinitrobiphenyl, m. 230°, and a product, m. above 330°, probably an aryl deriv. of the imine, which is being investigated.

Chas. Blanc

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New derivatives of diphenyl-*p*-phenylenediamine. I. S. Ioffe and V. Ya. Solovelchik. *J. Gen. Chem.* (U. S. S. R.) 9, 144 8(1939); cf. preceding abstr.—In studies of the structure of intermediates in the formation of aniline black the following new derivs. of diphenyl-*p*-phenylenediamine were obtained by successive condensation of 1,3,6-$Cl_2(O_2N)C_6H_3SO_3H$ (I) with $PhNHC_6H_4NH_2$ (II) and $PhNH_2$ and subsequent reduction and cleavage of the SO_3H group. I was prepd. by sulfonation and nitration of *m*-$C_6H_4Cl_2$ (cf. Ger. pat. 120,345). *6-Nitro-3-chlorodiphenyl-p-phenylenediamine-4-sulfonic acid* (III) was prepd. in 90.7% yield by refluxing 38 g. of the Na salt of I in 150 ml. H_2O and 26 g. II in 150 ml. alc. with 20 g. Na_2CO_3 for 10 hrs., dilg. with H_2O to 500 ml., filtering and pptg. with 10% HCl. The product dried at 130° forms brown crystals, sparingly sol. in H_2O. The *amine* resulted in 73% yield by stirring 67 g. III in 200 ml. of 5% Na_2CO_3 into the hot suspension of 55 g. Zn dust, 35 g. NaCl and 6 g. $CuSO_4$ in 400 ml. H_2O and boiling the mixt. for 2 hrs. After the addn. of a few drops of $NaHSO_3$, the reaction mixt. is filtered, the filtrate is treated with HCl and the ppt. is dried at a moderate temp. Refluxing 5 g. of the amine with 5 g. $ZnCl_2$ and 140 ml. of 26% HCl (preliminarily boiled with 1 g. Zn dust) for 3 hrs., dilg. with 100 ml. of cold H_2O and adding an excess of NH_4OH yielded 25% of *6-amino-3-chlorodiphenyl-p-phenylenediamine*, m. 148° (benzine). It is a white product, giving colorless soln. in alc., red in C_6H_6 and orange with a green fluorescence in benzine. Autoclaving 30 g. III (Na salt) in 300 ml. of 50% alc. with 8 g. $PhNH_2$ and 20 g. Na_2CO_3 at 160-70° for 20 hrs. and acidifying the filtrate with 10% HCl formed 74.4% *6-nitro-4-phenylaminodiphenyl-p-phenylenediamine-4-sulfonic acid*, greenish powder, insol. in H_2O. The acid when reduced under the conditions analogous to the preceding expt. yielded 70% of the corresponding *amine*. The attempts to obtain from it the isomeric Willstätter leucoimine by cleaving the SO_3H group produced neg. results.

Chas. Blanc

ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION

Sulfonation reaction. IV. Sulfonation of benzanthrone. I. S. Ioffe and N. N. Mel'teva. *J. Gen. Chem.* (U. S. S. R.) 9, 1104-6(1939); cf. *C. A.* 28, 2354.—Benzanthrone (I) with 30% oleum (87.14% SO$_3$) is completely sulfonated in 300 hrs. at 20° and in 6 hrs. at 150°. Weaker acids (contg. up to 5% oleum (82.65% SO$_3$)) are relatively ineffective at temps. below 150°. I with 22% oleum for 24 hrs. at 20° gives, after removal of unreacted I, a mixt. contg. 81% α-benzanthronesulfonic acid (II) and 19% β-isomer (III), sepd. as the yellow Ba salts by fractional pptn. of II from cold water. With I and 95.5% H$_2$SO$_4$ at 160-70° for 8 hrs. the mixt. of sulfonic acids contains 20% II and 80% III. With 100% H$_2$SO$_4$ (IV) under the same conditions appreciable amts. of disulfonic acids are obtained, also isolated as the Ba salts. The Ba salts of both II and III form *quinine salts*, m. 240-2° and 80-2°, resp. Oxidized with Na$_2$Cr$_2$O$_7$ in 30% H$_2$SO$_4$ both II and III give 1-anthraquinonecarboxylic acid, m. 282-4°. **V. Sulfonation of α-naphthyl phenyl ketone.** I. S. Ioffe and G. Z. Naumova. *Ibid.* 1121-3.—α-C$_{10}$H$_7$COPh (V) readily reacts with 95% H$_2$SO$_4$ (VI) at 20°. At 100° with VI or with oleum at low and high temps. V is completely converted into water-sol. products. When heated with VI at 160-70° for 6 hrs. V is hydrolyzed and sulfonated to give BzOH and C$_{10}$H$_6$(SO$_3$H)$_2$, the latter isolated from the sulfonation mixt. as the Ba salt. To prevent hydrolysis V is sulfonated with 10% oleum at 20° for 24 hrs. to give presumably 1-benzoylnaphthalene-5-sulfonic acid (VII), whose aniline salt, m. 235°, is identical with the compd. obtained by Dziewoński and Moszew (*C. A.* 26, 131). With NaOH at 290-320° for 30 min. VII gives α-naphthol, m. 95°. **VI. Sulfonation of 1,2-benzanthraquinone.** I. S. Ioffe and E. N. Kashnitskaya. *Ibid.* 1124-7.—Contrary to Graebe (*Ann.* 340, 249 (1905)) 1,2-benzanthraquinone (VIII) is more readily sulfonated than anthraquinone. VIII with VI at 20° is not sulfonated after 15 days but at 100° the sulfonation is practically complete in 6 hrs. IV, as well as weak oleum, completely sulfonate VIII at 20° in several hrs. VIII sulfonated at elevated temp. gives a monosulfonic acid (IX) whose Ba salt, brown, forms a *quinine salt*, brown, m. 118-25°. At low temps. a monosulfonic acid (X) is obtained whose Ba salt, yellow, gives a yellow *quinine salt*, m. 203-5°. Oxidation of IX or X with KMnO$_4$ in acid soln. gives 1,2-anthraquinonedicarboxylic acid, m. 268°, which indicates that in the sulfonation of VIII the sulfo group enters exclusively in the side benzo nucleus.

John Livak

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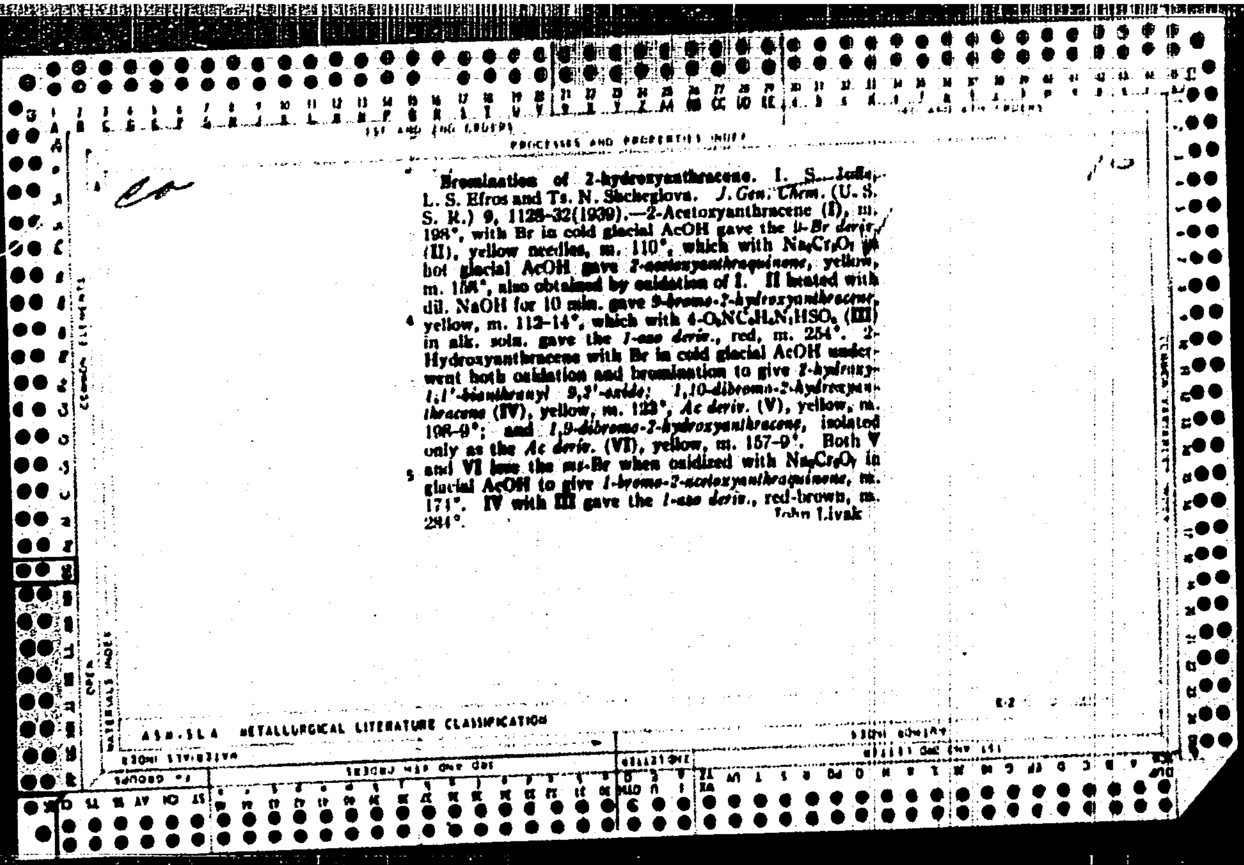

PROCESSES AND PROPERTIES INDEX

Ca

Bromination of 2-hydroxyanthracene. I. S. Ioffe, L. S. Efros and Ts. N. Shcheglova. *J. Gen. Chem.* (U.S.S.R.) 9, 1128-32(1939).—2-Acetoxyanthracene (I), m. 198°, with Br in cold glacial AcOH gave the *9-Br deriv.* (II), yellow needles, m. 110°, which with $Na_2Cr_2O_7$ in hot glacial AcOH gave *2-acetoxyanthraquinone*, yellow, m. 158°, also obtained by oxidation of I. II heated with dil. NaOH for 10 min. gave *9-bromo-2-hydroxyanthracene*,
4 yellow, m. 112-14°, which with $4\text{-}O_2NC_6H_4N_2HSO_4$ (III) in alk. soln. gave the *1-azo deriv.*, red, m. 254°. 2-Hydroxyanthracene with Br in cold glacial AcOH underwent both oxidation and bromination to give *2-hydroxy-1,1'-bianthranyl 9,2'-oxide*; *1,10-dibromo-2-hydroxyanthracene* (IV), yellow, m. 123°, *Ac deriv.* (V), yellow, m. 198-9°; and *1,9-dibromo-2-hydroxyanthracene*, isolated only as the *Ac deriv.* (VI), yellow, m. 157-9°. Both V
5 and VI lose the *ms*-Br when oxidized with $Na_2Cr_2O_7$ in glacial AcOH to give *1-bromo-2-acetoxyanthraquinone*, m. 171°. IV with III gave the *1-azo deriv.*, red-brown, m. 284°.

John Livak

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

PROCESSES AND PROPERTIES INDEX

Preparation of nitrophenyl α-naphthyl ketones. I. S. Ioffe and S. S. Bravina. *J. Gen. Chem.* (U. S. S. R.) 9, 1133-8(1939).—NO_2 derivs. of α-$C_{10}H_7COPh$ (I) with the NO_2 group in the Ph nucleus cannot be prepd. by the direct nitration of I. Instead these compds. are prepd. either from the corresponding $O_2NC_6H_4CHO$ and α-$C_{10}H_7MgBr$ (*C. A.* 28, [illegible]) or from $O_2NC_6H_4COCl$ (II) and $C_{10}H_8$ (III) by the Friedel and Crafts synthesis. To *m*-II (25 g.) with 17.2 g. III in 75 cc. CS_2 is added 21 g. $AlCl_3$ at 0° over a period of 2 hrs. to give, after standing for 3 days, 70% of crude *m*-nitrophenyl α-naphthyl ketone, light yellow (alc.), m. 124°; phenylhydrazone, bright yellow, m. 194°. In the same manner *p*-II with III gives 65% of the *p*-nitrophenyl deriv., light yellow, m. 89°; phenylhydrazone, not purified. John Livak

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

CA

Biaryls and their derivatives. XXI. Oxidation of α-naphthol. I. S. Ioffe and B. K. Krichevtsov. *J. Gen. Chem.* (U. S. S. R.) 9, 1130-42(1939); cf. *C. A.* 32, 3931¹.—α-Naphthol (25 g.) in 2.5 l. boiling water is oxidized with 500-540 cc. 5% $FeCl_3$ soln., added dropwise and with stirring at 70-80°, to give a mixt. (21 g.) of 4,4'-dihydroxy-1,1'-binaphthyl (I), m. 300°, difficultly sol. in hot benzene, and *1,1'-dihydroxy-2,2'-binaphthyl* (II), m. 220°, sol. in hot benzene. I and II with Ac_2O in pyridine form the *di-Ac derivs.*, m. 217° and 109°, resp. Both I and II form azo dyes. I with diazotized *p*-nitroaniline in alk. soln. gives the *3-azo*, dark red and the *3,3'-diazo deriv.*, dark red, m. above 350°; II gives the *4-azo*, red powder, and the *4,4'-diazo compd.* (III), brick-red, m. above 300°. Of the 4 dyes only III, having 2 OH groups ortho to the azo groups, is insol. in alkali. I (5 g.) with 25 g. $AlCl_3$ heated under anhyd. conditions at 150-160° for 3 hrs. undergoes cyclization with the formation of **3,10-perylenequinone**, dark brown, m. 350°, and **3,10-dihydroxyperylene** (IV), yellow, m. 227°; di-Bz deriv., m. 295°. IV distd. with Zn dust gives **perylene**, orange, m. 260°. II with $AlCl_3$ is recovered unchanged. II (5 g.) with 20 g. $ZnCl_2$ under anhyd. conditions at 220-50° for 4 hrs. gives 2.5 g. 2,2'-binaphthyl 1,1'-oxide, grayish yellow, m. 182°, unchanged when distd. with Zn dust; picrate, m. 173°. I fused with $ZnCl_2$ under the same conditions remains unchanged. **XXII. Biphenanthryl dioxide.** I. S. Ioffe. *Ibid.* 1143-4.—Oxidation of 2-hydroxyphenanthrene with $FeCl_3$ in AcOH or EtOH gives 2,2'-dihydroxy-1,1'-biphenanthryl, which, with an equal wt. of Ag_2O in boiling benzene for 6 hrs., is oxidized to *1,1'-biphenanthryl 2,10',2',10-dioxide* (V), bright yellow, m. 280°. V is extremely stable and remains unaltered after treatment with strong oxidizing agents.

John Livak

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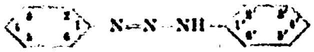
Reaction of diazo compounds with primary aromatic amines containing salt-forming groups. I. Tautomerism of triazenes. A. P. Ershov and I. S. Ioffe. *J. Gen. Chem.* (U. S. S. R.) 9, 2211-18(1939).—The following 18 derivs. of diphenyltriazene,



have been prepd.: *3-Cl,3'-SO$_3$Na; 2,5,2'-Cl$_3$,5'-SO$_3$K; 2,5-Cl$_2$,2'-CO$_2$Na; 2,5-Cl$_2$,3'-CO$_2$Na; 2,5-Cl$_2$,4'-CO$_2$Na; 2,5-Cl$_2$,2'-SO$_3$Na; 2,3-Cl$_2$,3'-SO$_3$Na; 2,5-Cl$_2$,4'-SO$_3$Na; 4-Cl,3'-SO$_3$Na; 2-Cl,3'-SO$_3$Na; 4-Me,3'-SO$_3$Na; 4-Me,4'-SO$_3$Na; 2,5-Cl$_2$,2',5'-(SO$_3$Na)$_2$; 2,5-Cl$_2$,3',5'-(SO$_3$Na)$_2$; 2,5-Cl$_2$,2'-CO$_2$H,4'-SO$_3$Na; 2,5-Cl$_2$,2'-SO$_3$H,4'-SO$_3$Na; 2,5-Cl$_2$,2'-CO$_2$H,5'-SO$_3$Na; 2,5-Cl$_2$,2'-SO$_3$H,5'-CO$_2$Na*. The prepn. of *2,5-dichloro-4'-sulfodiphenyltriazene* is given as example. A soln. of 0.08 mole 2,5-Cl$_2$C$_6$H$_3$N:NNHPh is added slowly while cooling to a soln. of 6.14 g. Na sulfanilate and 10.32 g. NaOAc in 50 ml. H$_2$O. The reaction product is filtered after 1 hr., the residue washed with H$_2$O and dissolved in a 5% NaOH soln. The soln. is filtered and the filtrate is acidified with AcOH. The other compds. listed above are prepd. in a similar way. These triazene derivs. exist in 2 tautomeric forms RN:NNHR' ⇌ RNHN:NR' and the preponderance of one or the other form depends on the character and position of the substituents in the phenyl radicals. **II. General course of reaction.** *Ibid.* 2219-31.—The following new derivs. of diphenyltriazene are prepd.: *4-Me,2'-CO$_2$Na,4'-SO$_3$Na; 4-Me,2'-CO$_2$Na,5'-SO$_3$Na; 4-NO$_2$,4'-SO$_3$Na; 4-NO$_2$,3'-SO$_3$Na; 4-NO$_2$,2'-CO$_2$H,4'-SO$_3$Na*. The mechanism of the reaction between diazo compds. and amines contg. salt-forming groups was investigated under various conditions.

Gertrude Berend

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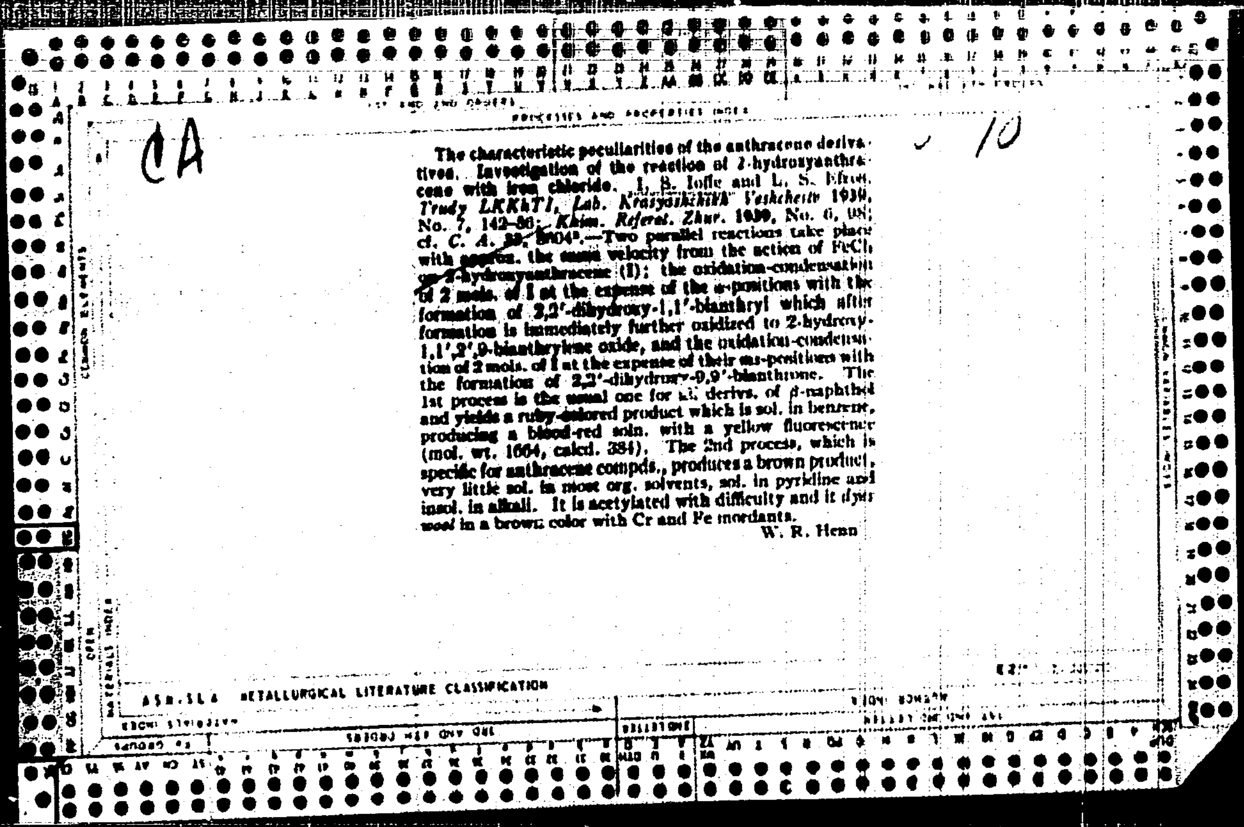

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The characteristic peculiarities of the anthracene derivatives. Investigation of the reaction of 2-hydroxyanthracene with iron chloride. I. B. Ioffe and L. S. Efros. *Trudy LKKhTI, Lab. Krasyashchikh Veshchestv* 1939, No. 7, 142-56; *Khim. Referat. Zhur.* 1939, No. 6, 98; cf. *C. A.* 33, 8604³.—Two parallel reactions take place with approx. the same velocity from the action of $FeCl_3$ on 2-hydroxyanthracene (I): the oxidation-condensation of 2 mols. of I at the expense of the α-positions with the formation of 2,2'-dihydroxy-1,1'-bianthryl which after formation is immediately further oxidized to 2-hydroxy-1,1',2',9-bianthrylene oxide, and the oxidation-condensation of 2 mols. of I at the expense of their ms-positions with the formation of 2,2'-dihydroxy-9,9'-bianthrone. The 1st process is the usual one for all derivs. of β-naphthol and yields a ruby-colored product which is sol. in benzene, producing a blood-red soln. with a yellow fluorescence (mol. wt. 1664, calcd. 384). The 2nd process, which is specific for anthracene compds., produces a brown product, very little sol. in most org. solvents, sol. in pyridine and insol. in alkali. It is acetylated with difficulty and it dyes wool in a brown color with Cr and Fe mordants.

W. R. Henn

1ST AND 2ND ORDERS

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Monosulfonic acids of phenanthrene. I. S. Ioffe. *Org. Chem. Ind.* (U. S. S. R.) 7, 374-6(1940).—The following method may be used to sulfonate phenanthrene and to sep. the isomeric monosulfonic acids. Heat 178 g. of phenanthrene gradually to the molten state and then heat to 105-110°. Mix with a stirrer, add from a funnel 150 g. of 92-94% H_2SO_4 in 30 min., regulating the temp. so that it will not rise above 120°, then maintain for 2 hrs. at 110-120° while stirring continuously. Pour into 1 l. of satd. salt soln., wash the vessel and stirrer with the same soln. (the total vol. should be about 1.6 l.), cool and filter. The filtrate is weakly colored, indicating complete absence of disulfo acids, and is discarded. Wash the light gray ppt. 3 times with satd. salt soln. and compress. The yield is 600-800 g. of paste, depending on the degree of compression. Transfer the paste into 1800 ml. of hot water, heat the mixt. to boiling, boil for 1 hr., cool gradually to 70°, maintain at 70° for 12 hrs., and filter through a heated funnel into a heated receiver, taking care that the temp. does not drop below 60°. The ppt. contains most of the 2-isomer and some unreacted phenanthrene and the filtrate (I) contains most of the 3-sulfonic acid and some 2-isomer. Transfer the ppt. into 2 l. of boiling water, add 5 g. of activated charcoal, boil for 1 hr., filter through a heated funnel, mix, evap. immediately to 200-300 ml., let stand for 12 hrs., filter and dry. The yield was 45-60 g. of pure salt. Boil I, add 10 g. of $BaCl_2$, boil for 15 min., filter, mix the filtrate and evap. to 1 l. and allow to crystallize in 12 hrs. Filter and dry. The yield was 150-170 g. of sufficiently pure salt. The Ba salts are a mixt. of salts of the 2- and 3-sulfo acids and may be converted to Na salts and sepd. in the usual manner. To convert the sulfo acids into the phenanthranol proceed as follows. Add a few ml. of water to 500 g. NaOH, heat to 280° to melt, add in small amts. 100 g. of 2-sulfonic acid obtained above during the course of 1 hr., raise the temp. to 300° and hold at 300° for 30 min. Pour the melt into 2 l. of water, add while heating HCl to a weakly alk. reaction, filter and add HCl to a weakly acidic reaction. Cool, filter and dry. The product m. 160-2° and the yield was 70% of the theoretical. 3-Phenanthranol is obtained under the same conditions except that 350-400 g. NaOH may be used instead of the 500 g. The product usually becomes tarry so that it should be purified by vacuum distn.

H. Z. Kamich

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

Ca ✓ 11A

Development of the chemistry of organic substances. I. S. Ioffe. *Uspekhi Khim.* 9, 819-38(1940).—Historical, with special emphasis on the road from the search for the elixir of life to the synthesis of vitamins and hormones.

F. H. Rathmann

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The interaction of diazo compounds with indophenols. I. S. Ioffe and B. K. Krichevtsov. *J. Gen. Chem.* (U. S. S. R.) 10, 1385-90(1940); cf. *C. A.* 34, 4730^{6}.—An indophenol, obtained by the condensation of p-NOC_6H_4OH with carbazole and having the formula 3-(p-$O:C_6H_4:N$)-$\underbrace{C_6H_3.C_6H_4.NH}$ (I), was used in glacial AcOH for the reaction with diazotized p-$NH_2C_6H_4SO_3H$, (II) at 10-5°. With no excess of II the reaction yielded after 2-3 hrs. 2 isomeric forms of phenylindophenolsulfonic acid, 2 (and 3)-(p-$HO_3SC_6H_4$)-4-$O:C_6H_3:N\underbrace{C_6H_3.C_6H_4.NH}$ (75%), and in the presence of excess of II it yielded after 5-6 hrs. the 2,5-bis-(sulfophenyl) deriv. The monoacid was insol. in water but sol. in aq. alk. solns. and the diacid was sol. in water and in aq. alk. solns. The soln. of I in acetone treated with diazotized p-$ClC_6H_4NH_2$ yielded 2 (and 3)-(p-ClC_6H_4)-4-$O:C_6H_3:N\underbrace{C_6H_3.C_6H_4.NH}$ and in the presence of an excess of the reagent the 2,5-bis(p-ClC_6H_4) deriv. Conclusions: The indophenols reacted with the diazo compds., decompg. them with the liberation of N and adding the aryl residue to the quinoid ring. The arylated indophenols were more colored than the original compds.

A. A. Podgorny

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Polycyclic xanthene and acridine dyes with condensed rings. A. K. Poraĭ-Koshits, I. S. Ioffe, L. S. Efros, V. I. Ivanova and A. D. Turevskiĭ. *J. Applied Chem.* (U. S. S. R.) 13, 1355-68(in German, 1368)(1940).—The method of Dilthey and Quint (*C. A.* 29, 1434^9; 32, 1112^4; Can. pat. 362,970; Swiss pat. 176,020) for the prepn. of carbenium compds. was rechecked and the tech. value of green and purple dyes appraised. For the prepn. of these dyes, it is recommended to fuse the initial reagents with an alkali bisulfate. The following derivs. of ms-phenylxanthene and ms-phenyldihydroacridine were prepd. by the condensation of m- and p-$O_2NC_6H_4CHO$ with HO and amino derivs. of naphthalene and anthracene

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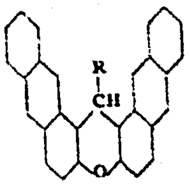
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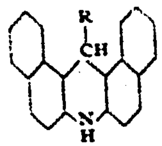
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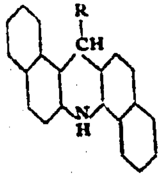
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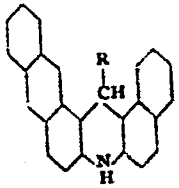
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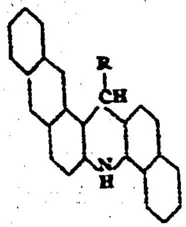
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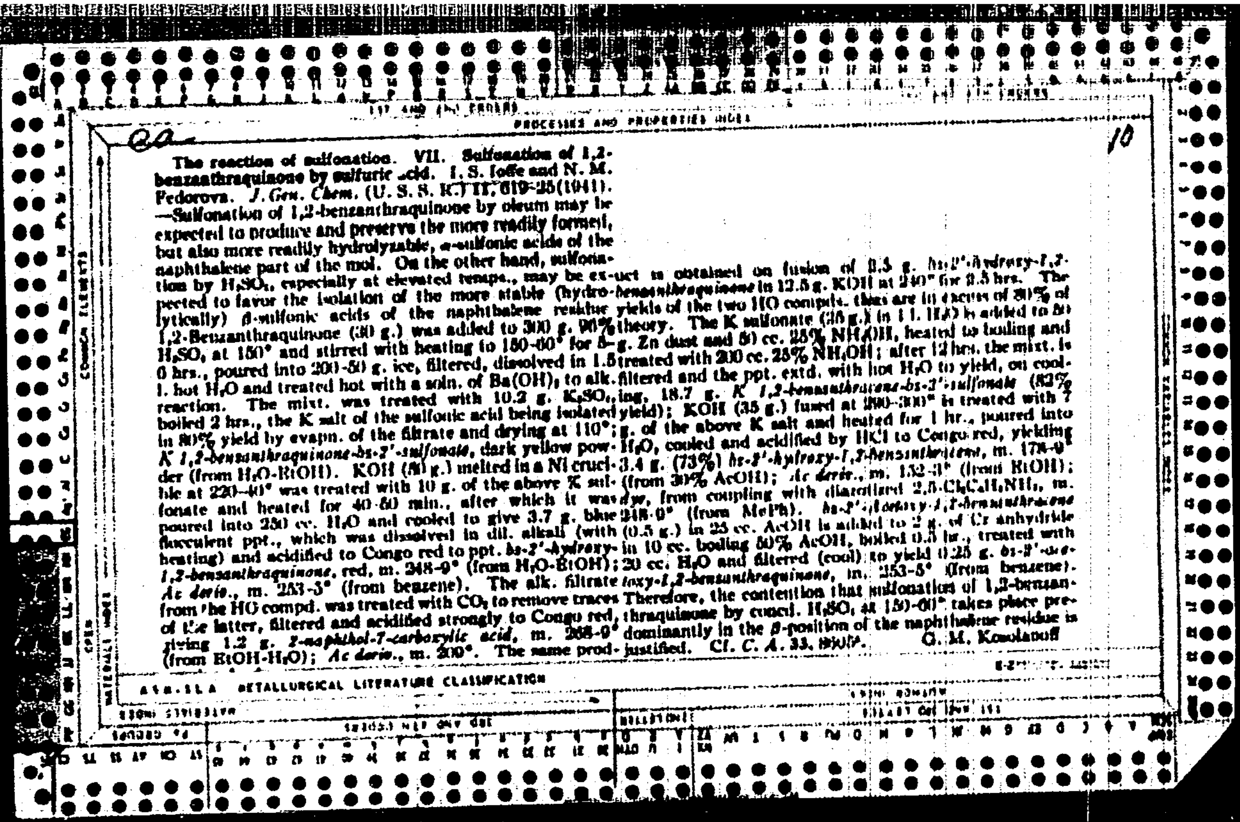
in glacial AcOH and H_2SO_4: *ms-(m-nitrophenyl)dinaphthoxanthene* (I, R = m-$O_2NC_6H_4$), m. 304° (uncor.); *p-nitrophenyl isomer* (II), m. 345°; *ms-(m-nitrophenyl)dibenzodihydroacridine* (III), m. 269–70°; *p-nitrophenyl isomer* (IV), m. above 330°, was oxidized with Br in C_6H_6 yielding a corresponding carbinol, m. 319–20° (III, with HO in place of H on the central C atom) and oxidation of IV yielded the *carbinol*, m. 294–5°. Fusing the above compds. with a mixt. of $AlCl_3$ and NaCl at 180° yielded the corresponding carbenium dyes. The condensation of the same reagents as for the prepn. of III but in naphthol (using mixts. of α-naphthylamino-β-naphthol or β-naphthylamino-α-naphthol) yielded an isomer of III, ms-(m-nitrophenyl)dibenzodihydroacridine (IV), m. 296°, oxidation of which with Br in PhCl yielded the *carbinol*, m. 284–5°. On applying the reaction to 2-hydroxyacridine (but not in naphthol) 2 isomeric *ms-(m-nitrophenyl)benzonaphthodihydroacridines* were obtained (V and VI), m. 282–4° and 311°. On fusing with an $AlCl_3$-NaCl mixt., only V yielded a carbenium dye. The dyes of the xanthene group have stronger basic properties than those of the acridine group. A. A. P.



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The reaction of sulfonation. VII. Sulfonation of 1,2-benzanthraquinone by sulfuric acid. I. S. Ioffe and N. M. Fedorova. *J. Gen. Chem.* (U. S. S. R.) 11, 619-25(1941).—Sulfonation of 1,2-benzanthraquinone by oleum may be expected to produce and preserve the more readily formed, but also more readily hydrolyzable, α-sulfonic acids of the naphthalene part of the mol. On the other hand, sulfonation by H_2SO_4, especially at elevated temps., may be expected to favor the isolation of the more stable (hydrolytically) β-sulfonic acids of the naphthalene residue. 1,2-Benzanthraquinone (30 g.) was added to 300 g. 96% H_2SO_4 at 150° and stirred with heating to 150-60° for 5-6 hrs., poured into 200-50 g. ice, filtered, dissolved in 1.5 l. hot H_2O and treated hot with a soln. of $Ba(OH)_2$ to alk. reaction. The mixt. was treated with 10.2 g. K_2SO_4, boiled 2 hrs., the K salt of the sulfonic acid being isolated in 80% yield by evapn. of the filtrate and drying at 110°; *K 1,2-benzanthraquinone-bz-2'-sulfonate*, dark yellow powder (from H_2O-EtOH). KOH (80 g.) melted in a Ni crucible at 220-40° was treated with 10 g. of the above K sulfonate and heated for 40-60 min., after which it was poured into 250 cc. H_2O and cooled to give 3.7 g. blue flocculent ppt., which was dissolved in dil. alkali (with heating) and acidified to Congo red to ppt. *bz-2'-hydroxy-1,2-benzanthraquinone*, red, m. 248-9° (from H_2O-EtOH); *Ac deriv.*, m. 253-5° (from benzene). The alk. filtrate from the HO compd. was treated with CO_2 to remove traces of the latter, filtered and acidified strongly to Congo red, giving 1.2 g. *2-naphthol-7-carboxylic acid*, m. 268-9° (from EtOH-H_2O); *Ac deriv.*, m. 200°. The same product is obtained on fusion of 0.5 g. *bz-2'-hydroxy-1,2-benzanthraquinone* in 12.5 g. KOH at 240° for 0.5 hrs. The yields of the two HO compds. thus are in excess of 80% of theory. The K sulfonate (25 g.) in 1 l. H_2O is added to 50 g. Zn dust and 50 cc. 25% NH_4OH, heated to boiling and treated with 200 cc. 25% NH_4OH; after 12 hrs. the mixt. is filtered and the ppt. extd. with hot H_2O to yield, on cooling, 18.7 g. *K 1,2-benzanthracene-bz-2'-sulfonate* (82% yield); KOH (35 g.) fused at 290-300° is treated with 7 g. of the above K salt and heated for 1 hr., poured into H_2O, cooled and acidified by HCl to Congo red, yielding 3.4 g. (73%) *bz-2'-hydroxy-1,2-benzanthracene*, m. 178-9° (from 30% AcOH); *Ac deriv.*, m. 152-3° (from EtOH); dye, from coupling with diazotized 2,5-$Cl_2C_6H_3NH_2$, m. 248-9° (from MePh). *bz-2'-Acetoxy-1,2-benzanthracene* (0.5 g.) in 25 cc. AcOH is added to 2 g. of Cr anhydride in 10 cc. boiling 80% AcOH, boiled 0.5 hr., treated with 20 cc. H_2O and filtered (cool) to yield 0.25 g. *bz-2'-acetoxy-1,2-benzanthraquinone*, m. 253-5° (from benzene). Therefore, the contention that sulfonation of 1,2-benzanthraquinone by concd. H_2SO_4 at 150-60° takes place predominantly in the β-position of the naphthalene residue is justified. Cf. *C. A.* 33, 8600[6]. G. M. Kosolapoff

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COMMON ELEMENTS

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Ioffe, I. S.: The Sulfonation of Organic Substances. Leningrad: Naval Med. Acad. 1944. 332 pp. R. 30. Reviewed in *Chem. Eng. News* 25, 2307 (1947).

OPEN

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Sulfonation reaction. VIII. Sulfonation of 1,2-benzanthraquinone with fuming H_2SO_4. I. S. Ioffe and N. M. Fedorova. *J. Gen. Chem.* (U. S. S. R.) 14, 88-95(1944) (English summary); cf. *C. A.* 35, 6953^{8}.—1,2-Benzanthraquinone (50 g.) was sulfonated by 150 g. 20% oleum at 20-5° for 4-5 days; the mixt. was treated with ice, the ppt. dissolved in 1 l. water and treated with hot $Ba(OH)_2$ to alk. reaction; the suspension was treated with a hot soln. of 17 g. K_2SO_4 and filtered; on cooling, the product (46% by wt.) seps. as the *K salt* of *4'-sulfo-1,2-benzanthraquinone* (identified by alk. fusion to the corresponding 4'-hydroxy-1,2-benzanthraquinone, with by-products: 1-naphthol-2-carboxylic acid, 1-naphthol and BzOH). The filtrate on concn. or treatment with alc. gave the *K salt* of *2'-sulfo-1,2-benzanthraquinone* as a dark yellow solid (identified by fusion with alk. to 2'-hydroxy-1,2-benzanthraquinone), in 13.6% yield. Evapn. of the filtrate to dryness gave impure products, contaminated with inorg. matter, which contained apparently some *disulfonation products of 1,2-benzanthraquinone.* Apparently, Semproni (*C. A.* 34, 410^{9}) and Cason and Fieser (*C. A.* 34, 7900^{9}) failed to detect the 2'-isomer because of its high soly. The K salt of 4'-sulfo-1,2-benzanthraquinone is readily reduced to the *K salt* of *4'-sulfo-1,2-benzanthrone* by Zn dust in dil. NH_4OH; the product forms fine needles which are very difficultly sol. in H_2O and are recovered by heating the reaction mixt. with K_2SO_4 soln. and filtering while hot. Fusion with KOH at 300° gave 90% *4'-hydroxy-1,2-benzanthrone*, m. 230-1° (from benzene); *Ac deriv.*, m. 193-4° (from EtOH). Oxidation of the Ac compd. with Cr oxide in AcOH gave *4'-acetoxy-1,2-benzanthraquinone*, m. 202-3° (from benzene). **IX. Dynamics of the sulfonation of 1,2-benzanthraquinone.** *Ibid.* 96-101.—It was shown that variation of the sulfonation conditions (acid concn., temp. and duration) changes the ratio between 2'- and 4'-sulfo-1,2-benzanthraquinones; in those cases in which desulfonation may be expected, the 4'-isomer is obtained in smaller amts. or is not formed at all (as in the use of 96% H_2SO_4 for 60 hrs. at 100° or for 6 hrs. at 160°), with correspondingly higher yields of the 2'-isomer. This corresponds in general to sulfonation of naphthalene. Treatment of the 4'-isomer with 96% H_2SO_4 yields up to 80% of 2'-isomer (at 160° for 6 hrs.). It was shown that the desulfonation reaction rate for the 4'-isomer is 15 times greater than for the 2'-isomer. The K salts of the 4'- and 2'-isomers, resp., have the following solubilities (g./l.) in water: at 20°, 2.4, 8.5; at 100°, 12.5, 77.2.

O. M. Kosolapoff

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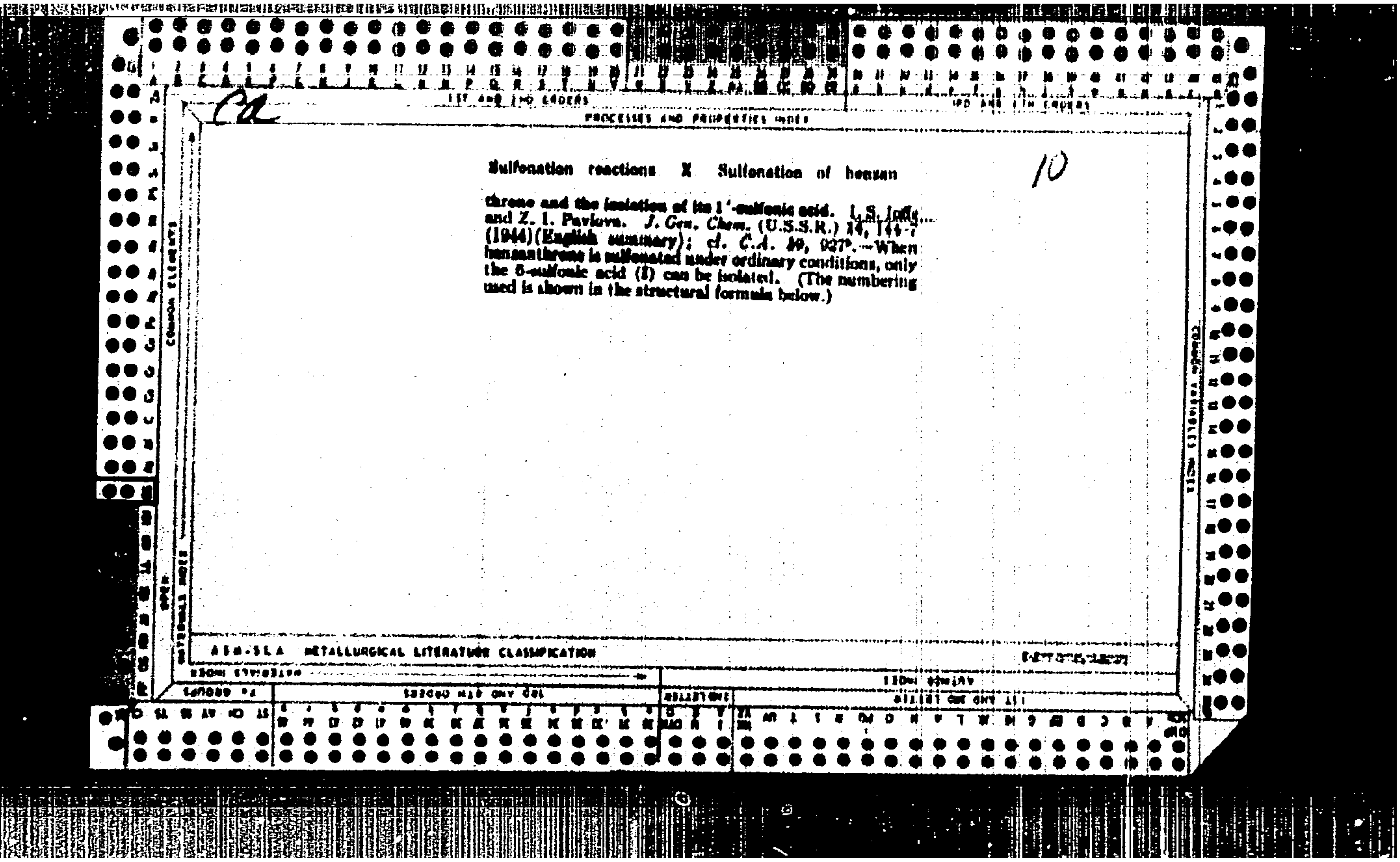

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Sulfonation reactions X. Sulfonation of benzanthrone and the isolation of its 1'-sulfonic acid. I. S. Ioffe and Z. I. Pavlova. *J. Gen. Chem.* (U.S.S.R.) 14, 144-7 (1944)(English summary); cf. *C.A.* 39, 927^9.—When benzanthrone is sulfonated under ordinary conditions, only the 6-sulfonic acid (I) can be isolated. (The numbering used is shown in the structural formula below.)

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Acetylation of aromatic amines with acetic anhydride in the presence of water. I. S. Ioffe. *J. Gen. Chem.* (U.S.S.R.) 14, 812-15(1944)(English summary).—It was shown that numerous aromatic amines may be readily acetylated by Ac_2O in aq. medium. $PhNH_2$ (47 g.) is well emulsified by stirring in 140 cc. water and rapidly treated with [illegible] g. Ac_2O; the mass warms up and rapidly changes to a thick suspension of AcNHPh, which is filtered on cooling and washed with cold water; yield of over [illegible], m. 114°. Yields of over 80% are obtained under similar conditions from "aniline water," contg. 31 g. $PhNH_2$ per l. Yields of better than 80% are obtained with *o*- and *p*-$H_2NC_6H_4Me$, 1- and 2-$H_2NC_{10}H_7$; MeHNPh, *m*- and *p*-$(H_2N)_2C_6H_4$ give yields of 70-80%. EtHNPh gave a 80% yield. *p*-$H_2NC_6H_4NMe_2$ gave a low yield of the Ac deriv., probably because of good soly. of the latter in water. O. M. Kosolapoff

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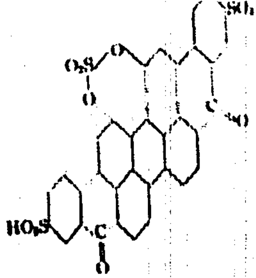
Sulfonation reaction. XI. Sulfonation of violanthrone. I. S. Ioffe, E. P. Kekkonen, and L. A. Kalika. *J. Gen. Chem.* (U.S.S.R.) 14, 816-21(1944)(English summary); cf. *C.A.* 39, 2288², 4507⁴.--Violanthrone (10 g.) in 100 g. 100% H_2SO_4 was heated to 100° for 8 hrs.; on cooling, the mass was treated with 100 cc. concd. HCl and the ppt. filtered off and purified by repptn. from water by strong HCl; *6,6'-violanthronedisulfonic acid* so obtained is a deep blue powder, sol. in water and EtOH. The *Na salt* is readily sol., the *Ba salt* poorly sol. in water. The above acid (5 g.) in 100 cc. 90% H_2SO_4 was treated with 10 g. MnO_2 at 0° for 6 hrs., after which the mixt. was held at 0° for 24 hrs., poured on ice, and the ppt. dissolved in Na_2CO_3 soln., and treated with hydrosulfite to reduce the diketo compd.; the blue soln. was blown with air to oxidize the leuco compd. and the green soln. was acidified with HCl to yield a green ppt. of *2,2'-dihydroxy-6,6'-violanthronedisulfonic acid*. The same compd. was prepd. by sulfonation of 2,2'-dihydroxyviolanthrone by 20% oleum at 20°; it is a green solid, poorly sol. in water and dyes fibers green. Violanthrone (10 g.) was added to 100 g. 20% oleum and heated to 100-70° for 8 hrs.; after treatment with HCl there was obtained the sulfate of *2,2'-dihydroxy-6,6'-violanthronedisulfonic acid*



as a violet powder with bronze luster. The same product is obtained by treatment of 2,2'-dihydroxyviolanthrone

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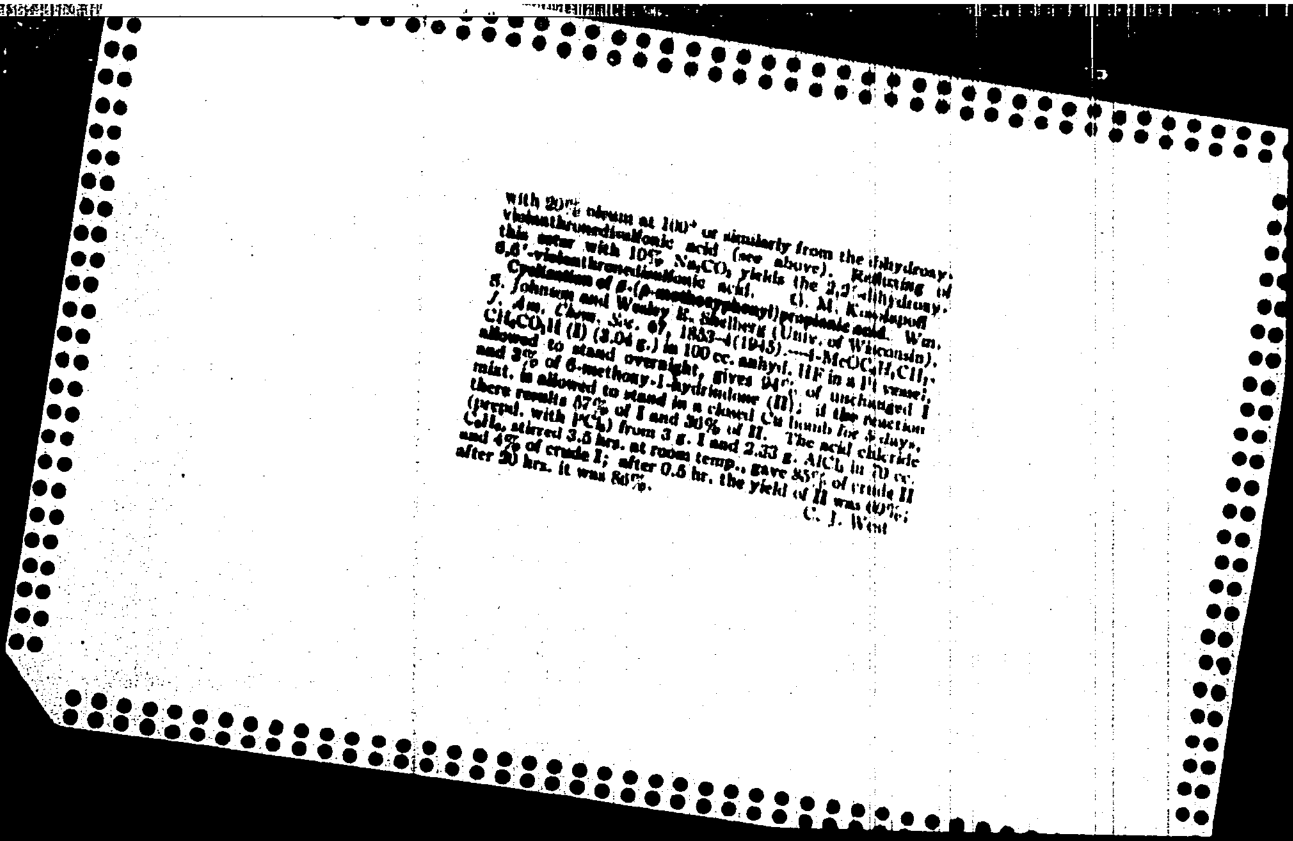

with 20% oleum at 100° or similarly from the dihydroxyviolanthronedisulfonic acid (see above). Refluxing of this ester with 10% Na_2CO_3 yields the 2,2'-dihydroxy-6,6'-violanthronedisulfonic acid. G. M. Kosolapoff

Cyclization of β-(p-methoxyphenyl)propionic acid. Wm. S. Johnson and Wesley E. Shelberg (Univ. of Wisconsin). *J. Am. Chem. Soc.* 67, 1853-4(1945).—4-$MeOC_6H_4CH_2CH_2CO_2H$ (I) (3.04 g.) in 100 cc. anhyd. HF in a Pt vessel, allowed to stand overnight, gives 94% of unchanged I and 3% of 6-methoxy-1-hydrindone (II); if the reaction mixt. is allowed to stand in a closed Cu bomb for 5 days, there results 67% of I and 30% of II. The acid chloride (prepd. with PCl_5) from 3 g. I and 2.33 g. $AlCl_3$ in 50 cc. C_6H_6, stirred 3.5 hrs. at room temp., gave 85% of crude II and 4% of crude I; after 0.5 hr. the yield of II was 60%; after 20 hrs. it was 80%. C. J. West

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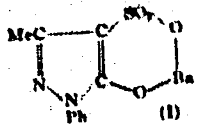
Sulfonation reaction. XII. Sulfonation of 1-phenyl-3-methyl-5-pyrazolone. I. S. Ioffe and E. Ya. Khavin. *J. Gen. Chem.* (U.S.S.R.) 14, 823-4(1944)(English summary).—Sulfonation of 1-phenyl-3-methyl-5-pyrazolone by $H_2SO_4.H_2O$ below 10°, followed by neutralization by BaO, gave the *Ba deriv.* (I) of enolized *1-phenyl-3-methyl-5-*



(I)

pyrazolone-4-sulfonic acid. The 4-sulfonic acid is very labile and is readily cleaved by HNO_3 or diazonium salts, while heating with 95% H_2SO_4 transforms it to the 4'-sulfonic acid, which is formed under all but the mildest conditions of sulfonation of the initial pyrazolone (Mollenhof, *Ber.* 25, 1041(1892)). G. M. Kosolapoff

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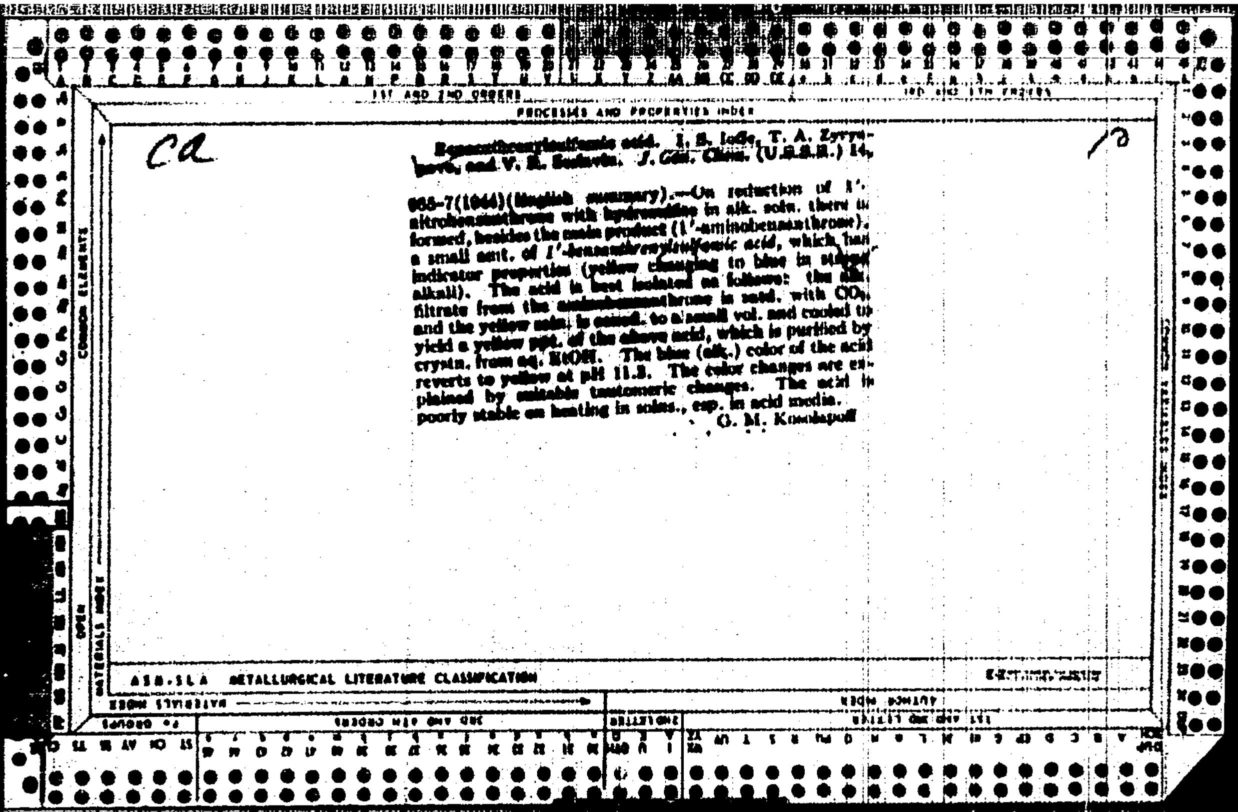

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Benzanthronylsulfamic acid. I. S. Ioffe, T. A. Zyryanova, and V. S. Sudavin. *J. Gen. Chem.* (U.S.S.R.) 14, 965-7(1944)(English summary).—On reduction of 1'-nitrobenzanthrone with hydrosulfite in alk. soln. there is formed, besides the main product (1'-aminobenzanthrone), a small amt. of *1'-benzanthronylsulfamic acid*, which has indicator properties (yellow changing to blue in strong alkali). The acid is best isolated as follows: the alk. filtrate from the aminobenzanthrone is satd. with CO_2, and the yellow soln. is concd. to a small vol. and cooled to yield a yellow ppt. of the above acid, which is purified by crystn. from aq. EtOH. The blue (alk.) color of the acid reverts to yellow at pH 11.3. The color changes are explained by suitable tautomeric changes. The acid is poorly stable on heating in solns., esp. in acid media.

G. M. Kosolapoff

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Sulfonation reaction. XIII. Reaction of tertiary aliphatic aromatic amines with chlorosulfonic acid. I. S. Ioffe and S. S. Bravina. *J. Gen. Chem.* (U.S.S.R.) 14, 965-73(1944)(English summary); cf. *C.A.* 39, 2269.—Addn. of $PhNMe_2$ to an equimol. amt. of $ClSO_3H$ yields mainly the anhydro salt, with evolution of HCl and gradual thickening of the mixt.; the product contains only traces of the salt of p-$Me_2NC_6H_4SO_3H$. Reversal of the addn., however, leads to HCl evolution and thickening of the mixt. only in the initial stage of addn., with the final product contg., in addn. to the anhydro salt, large amts. of the salt of the p-$Me_2NC_6H_4SO_3H$. The result is explainable by the action of the anhydro salt as a sulfonating agent.

G. M. Kosolapoff

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Nitro and amine derivatives of dibenzopyrene. I. S. Ioffe and L. S. Efros (1st Leningrad Med. Inst.). *J. Gen. Chem.* (U.S.S.R.) 16, 111-16(1946).—Dibenzopyrene (6.04 g.) was dissolved with warming in 1200 cc. $PhNO_2$ and treated, at 25-30°, dropwise with 0.4 g. HNO_3 (d. 1.52) in 10 cc. $PhNO_2$; after 4 hrs. the solvent was concd. to yield 4.9 g. *5-nitrodibenzopyrene*, m. 268-72° (from $PhNO_2$); boiling with $PhNHNH_2$ for 15 min. gave *5-aminodibenzopyrene* (I), m. about 310° (from PhCl); *Ac deriv.*, m. about 350° (from $PhNO_2$). Dibenzopyrene (3.02 g.) in 100 cc. $PhNO_2$, treated with 1.4 g. HNO_3 (d. 1.52), gave, in 5 hrs., 3 g. *5,10-dinitrodibenzopyrene*, m. 346-8° (decompn.; from $PhNO_2$); this, heated for 15 min. with boiling $PhNHNH_2$, gave *5,10-diaminodibenzopyrene*, m. 360-8° (from $PhNO_2$); *di-Ac deriv.*, m. 440°. Nitration of I in $PhNO_2$ gave *5-nitro-10-acetylaminodibenzopyrene*, m. 318-20° (from $PhNO_2$); reduction by boiling with $PhNHNH_2$ gave *5-amino-10-acetylaminodibenzopyrene*, m. about 357° (from $PhNO_2$), which on acetylation gave a product identical with that obtained by acetylation of the diamine described above. G. M. Kosolapoff

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Hydroxy derivatives of triphenylmethane. I. S. Ioffe. U.S.S.R. 68,312, Apr. 30, 1947. HCl gas is passed through a mixt. of an aromatic aldehyde 1 and phenol 2 mols. The reaction products are sufficiently pure and can be used directly for the production of the corresponding *hydroxyfuchsin dyes.* M. Hosch

Purification of hydroxyfuchsone dyes. I. S. Ioffe. U.S.S.R. 69,404, Oct. 31, 1947. To facilitate the sepn. of these dyes from their bisulfite solns., the process is carried out in the presence of a satd. soln. of NaCl. Cf. C.A. 43, 3627a. M. Hosch

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Sulfonation reaction. XIV. Sulfonation of 1-phenyl-3-methyl-5-pyrazolone and preparation and properties of sulfonic acids of phenylmethylpyrazolone. I. B. Ioffe and Z. Ya. Khavin. *J. Gen. Chem.* (U.S.S.R.) 17, 523-7(1947)(in Russian); cf. *C.A.* 40, 2847^{9}.—1-Phenyl-3-methyl-5-pyrazolone (I) (10 g.) in 60 g. 90% H_2SO_4 was heated 1.5 hrs. at 200-20° until the reaction was complete (a few drops of the mixt. in 3-4 cc. H_2O is treated with several drops of $NaNO_2$ and 2-3 cc. Et_2O and shaken; completion of the reaction is shown by a colorless Et_2O layer and intensely yellow aq. layer), poured into 100 g. ice, and filtered after standing until pptn. was complete, giving 92% *1-p-sulfophenyl-3-methyl-5-pyrazolone*, difficultly sol. in cold H_2O, sol. in hot H_2O, forms in hot aq. soln. with $BaCO_3$ the *Ba salt*, which is sol. in H_2O but can be recrystd. from aq. EtOH. The acid or the Ba salt with $NaNO_2$ gives the water-sol. nitroso deriv. $p-O_2NC_6H_4N_2Cl$ gives an orange-yellow azo dye which is fairly sol. in H_2O and in alkalies with a red color. The free acid reduces NH_3-Ag_2O and gives with $FeCl_3$ a red color which fades on heating or acidification with HCl. It is stable to hydrolysis; heating to 100-20° with 24% HCl does not affect it. I (10 g.), thoroughly dry, was added slowly to 30 g. 20% oleum and the soln. kept several days at 10-15° (end of reaction shown by treating a few drops with 3-4 g. ice, shaking with Et_2O, and treating the Et_2O layer with $NaNO_2$ and acid, which should give a barely yellow color); after pouring on 100 g. ice, keeping the temp. below 2-3°, the soln. was neutralized with $BaCO_3$, filtered, concd. to 100 cc., again filtered, treated hot with EtOH until crystn. began, and cooled, giving 60% *1-phenyl-3-methyl-5-pyrazolone-4-sulfonic acid* as white scales; *Ba salt*, silvery crystals, contains 5.5 moles H_2O and cannot be completely dehydrated without decompn., is sol. in H_2O, poorly sol. in dil. EtOH; $AgNO_3$ gives an insol. *Ag salt*; $FeCl_3$ gives a blue-violet color; $NaNO_2$ in acid soln. causes loss of $BaSO_4$ and gives 4-nitroso-1-phenyl-3-methyl-5-pyrazolone, m. 157-8° (from H_2O); reaction with $p-O_2NC_6H_4N_2Cl$ in the presence of NaOAc also causes loss of $BaSO_4$ and gives a dye, m. 198-9° (from C_6H_6), which is identical with the product of similar coupling of I. The free acid loses the SO_3 group as easily as does the Ba salt. I (10 g.) was slowly added to 50 g. 20% oleum with cooling, then heated on a steam bath 2 hrs. (test as above should give an almost colorless Et_2O layer), poured slowly with cooling into 200 g. ice, the cooled soln. neutralized with $BaCO_3$, filtered, and the filtrate evapd. to 60 cc. and treated with EtOH to give 78.7% of the *Ba salt of 1-p-sulfophenyl-3-methyl-5-pyrazolone-4-sulfonic acid*; on crystn. from dil. EtOH this is obtained as colorless needles, sol. in H_2O, more sol. in dil. EtOH than the Ba salt of the 4-sulfonic acid; it contains $6H_2O$ and cannot be completely dehydrated without decompn.; treatment with $AgNO_3$ gives an insol. *Ag salt*; with $FeCl_3$ it gives a red color; $NaNO_2$ in acid soln. splits off the 4-sulfo group and gives a nitroso compd. identical with that of the *p*-sulfo deriv.; $p-O_2NC_6H_4N_2Cl$ also cleaves a 4-sulfo group and gives an azo dye identical with that from the *p*-sulfo acid. Heating with acids leads to ready loss of the 4-sulfo group. The $NaNO_2$ reaction with the Ba salts of the above acids is quant. and may be used as a basis for their analytical estn.

G. M. Kosolapoff

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

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Sulfonation reaction. XV. Sulfonation of 1-phenyl-3-methyl-5-pyrazolone and the influence of reaction conditions on the yield of sulfonation products and their mutual transformations. I. S. Ioffe and Z. Ya. Khavin. *J. Gen. Chem.* (U.S.S.R.) 17, 528-37(1947)(in Russian).—It was shown in part XIV (*C.A.* 42, 903a) that sulfonation of 1-phenyl-3-methyl-5-pyrazolone (I) can be made to yield 3 products, depending on conditions: the 4-sulfo (II), the 1-*p*-sulfophenyl (III), and the 4-sulfo-1-*p*-sulfophenyl (IV) derivs. Since this was in contradiction with Mollenhoff's results (*Ber.* 25, 1941(1892)) a new series of expts. were carried out showing that M.'s isolation of only III was due to hydrolysis of the sulfo group in the 4-position during quenching of his reaction mixt. with ice without adequate provision for cooling. Sulfonation in oleum leads to IV by 2 routes: formation of II and III which then undergo further sulfonation; II is formed predominantly and is subject to fairly rapid sulfonation even at low temps.

Sulfonation with H_2SO_4 leads to III through a complex series of steps: the primary products are similar to those produced by oleum; these lead to the formation of IV in later stages of the reaction as well as to accumulation of III through hydrolysis of II by H_2O, III being stable to such hydrolysis. IV then substantially loses the 4-sulfo group by similar hydrolysis and the over-all reaction is the formation of III. I (10 g.) added with external cooling to 30 g. 20% oleum in small portions and allowed to stand 7-10 days at 10-15° and hydrolyzed by pouring slowly into 100 g. externally cooled ice, followed by neutralization with $BaCO_3$, gave 66% of the Ba salt (V) of II; the mother liquor on further treatment with EtOH gave 17% IV (as the Ba salt (VI)) and a small amt. of V. However, when 10 g. I in 50 g. 20% oleum was heated to 100° 1.5-2 hrs., cooled, and the soln. divided into (*a*) which was rapidly poured into 100 cc. H_2O (without cooling), allowed to cool, and yielded 85% III, and (*b*) which was carefully poured on 100 g. ice with external cooling; the soln. remained clear and, after neutralization by $BaCO_3$, filtration of the $BaSO_4$ and addn. of EtOH

with HCl, giving 61% 5-hydroxy-6-methoxy-8-nitro-
quinoline (III), m. 203° (decompn.). III, m. 210-11°
(decompn.), is also obtained in 95% yield when 100 g. II
is refluxed with 50 cc. HCl in 1 l. H_2O 6 hrs. The Ag salt of
III refluxed with MeI in MeOH 4 hrs. gives 8.5% II, light
yellow needles, m. 123-5°. Slow addn. of 41 g. III to 150
cc. $POCl_3$ at 80°, refluxing the mixt. 1.5 hrs., and pouring
it into 700 cc. concd. NH_4OH and ice give 95% 5-chloro-
6-methoxy-8-nitroquinoline (IV), m. 203.5-5°. Heating
4.77 g. IV with $CH_2(OH)CH_2ONa$ in $(CH_2OH)_2$ 7 hrs.
and pouring the cooled mixt. into 350 cc. H_2O give 5-(2-
hydroxyethoxy)-6-methoxy-8-nitroquinoline (V), bright yel-
low solid, m. 122-3° (*Ac deriv.* m. 70-1°). V is also ob-
tained in 32% yield by heating 2.4 g. IV in 90 cc. $(CH_2$-
$OH)_2$ with 0.06 g. 85% KOH in 10 cc. H_2O at 165°. Re-
duction of 7.1 g. V in abs. EtOH with PtO_2 at 40 lb. in 35
min. gives 81% *5-(2-hydroxyethoxy)-6-methoxy-8-amino-*
quinoline (VI), m. 103-4° (*picrate* m. 174-6°). An inti-
mate mixt. of 9.53 g. VI and 12.0 g. $Et_2NCH_2(CH_2)_4CH_2Br$
is heated 12 hrs. at 115-25° and 2 hrs. at 125-35° in a N
atm., giving *2-[8-(6-diethylaminohexylamino)-6-methoxy-*
5-quinolyloxy]ethanol, unstable yellow oil, [illegible] 165-6°.
Heating 2 g. II with 30 cc. concd. HCl in a sealed tube 6
hrs. at 120° gives 1.4 g. *5,6-dihydroxy-8-nitroquinoline*.
HCl, m. 233-4° (sealed tube, decompn.). Nitration of 17
g. m-ClC_6H_4NHAc in 30 cc. Ac_2O and 9 g. AcOH at 0°
to −5° with 10 g. HNO_3 (d. 1.42) in 9 cc. AcOH gives
60% 2-nitro-5-chloroacetanilide, m. 117-18°, saponif. with
MeONa in MeOH to 90% 2,5-$(NO_2)ClC_6H_3NH_2$, m. 127.5-
8°, which is converted into 5-chloro-8-nitroquinoline
(VII) according to Fourneau, *et al.* (*C.A.* 24, 5300).
Treatment of 3 g. VII with 3 g. MeONa in MeOH 6 hrs.
at 55-60° and overnight at room temp. gives 83% 5-
methoxy-8-nitroquinoline (VIII), yellow crystals, m. 119.5-
20°. Refluxing 1 g. VIII with 50 cc. H_2O and 3 cc. concd.
HCl gives 80% *5-hydroxy-8-nitroquinoline* (IX), compact
orange crystals, m. 201° (decompn.). IX is also formed in
45% yield by refluxing VII with KOH in EtOH and H_2O
[illegible] almost 100% yield, m. 111-11.5°). Heptyl-
[illegible]

which gives a blue color in alkali. 2-Amino-5-phenylthia-
zole under these conditions gives 9% 2-nitro-5-phenyl-
thiazole, m. 123-4°, which gives no color in alkali.

H. M. Leicester

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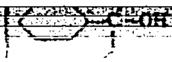


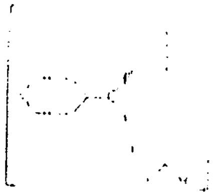
[illegible] crude product obtained [illegible] of AmOAc, [illegible] cooled, treated with 0.5 l AmOAc, and with [illegible] and the [illegible]

4/1

[illegible] less soln. [illegible] tered. Na [illegible] colorless flakes of the carbonyl [illegible] yellow and [illegible] even in [illegible] on at [illegible] The anhydrous [illegible]

[illegible] NaOAc [illegible]

soln. is carried by the ion VI [illegible] all, this [illegible]



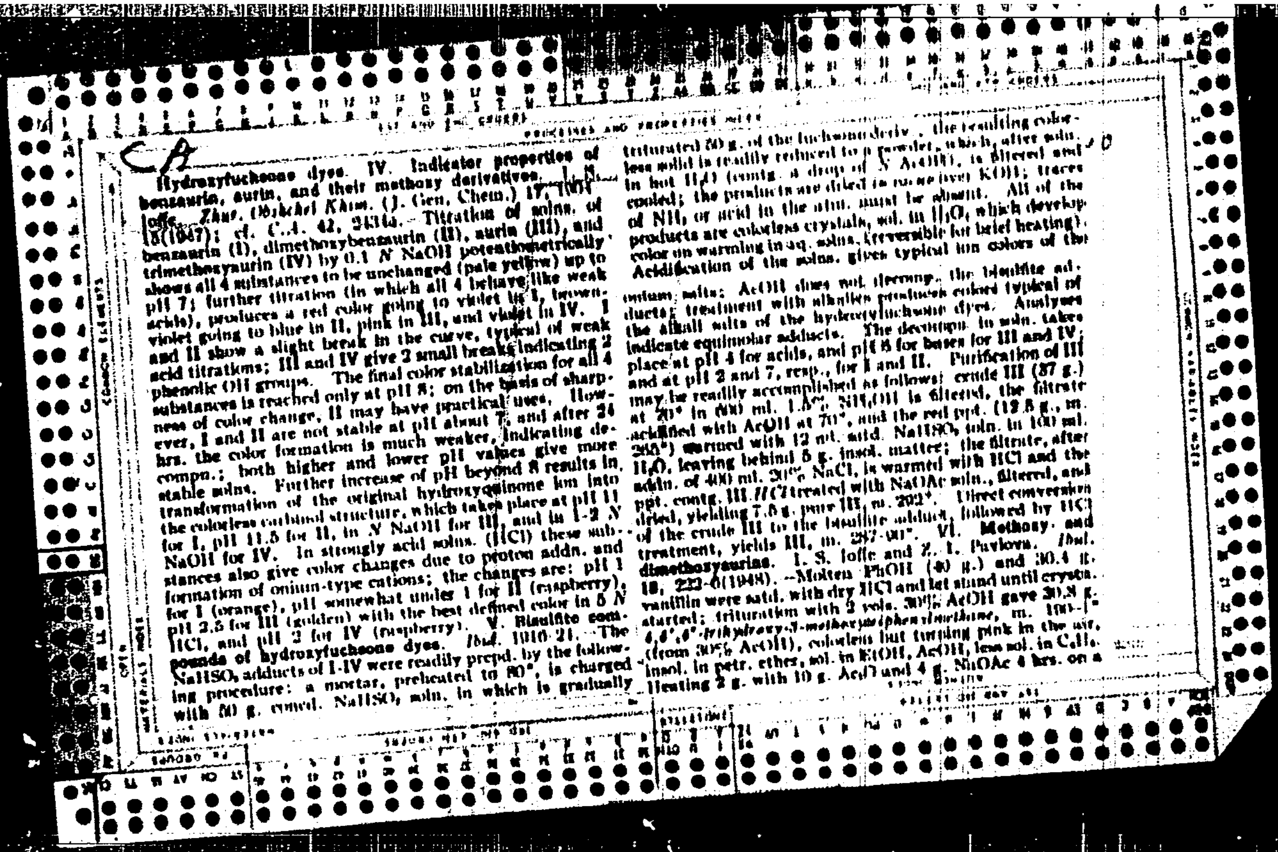
(VII)

[illegible]

IOFFE, I. S.

"Investigation in the Field of the Oxyfuchsone Dyes. II. Preparation of 4', 4''-Dioxy-3,3',3('-Trimetoxyfuchsone (Rubrophene)" (p. 1376)

SO: Journal of General Chemistry, (Zhurnal Obshchei Khimii), 1947, Vol. 17, No. 7



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Hydroxyfuchsone dyes. IV. Indicator properties of benzaurin, aurin, and their methoxy derivatives. I. S. Ioffe. *Zhur. Obshchei Khim.* (J. Gen. Chem.) 17, 1904-18(1947); cf. *C.A.* 42, 2834a.—Titration of solns. of benzaurin (I), dimethoxybenzaurin (II), aurin (III), and trimethoxyaurin (IV) by 0.1 *N* NaOH potentiometrically shows all 4 substances to be unchanged (pale yellow) up to pH 7; further titration (in which all 4 behave like weak acids), produces a red color going to violet in I, brown-violet going to blue in II, pink in III, and violet in IV. I and II show a slight break in the curve, typical of weak acid titrations; III and IV give 2 small breaks indicating 2 phenolic OH groups. The final color stabilization for all 4 substances is reached only at pH 8; on the basis of sharpness of color change, II may have practical uses. However, I and II are not stable at pH about 7, and after 24 hrs. the color formation is much weaker, indicating decompn.; both higher and lower pH values give more stable solns. Further increase of pH beyond 8 results in transformation of the original hydroxyquinone ion into the colorless carbinol structure, which takes place at pH 11 for I, pH 11.5 for II, in *N* NaOH for III, and in 1-2 *N* NaOH for IV. In strongly acid solns. (HCl) these substances also give color changes due to proton addn. and formation of onium-type cations; the changes are: pH 1 for I (orange), pH somewhat under 1 for II (raspberry), pH 2.5 for III (golden) with the best defined color in 5 *N* HCl, and pH 2 for IV (raspberry). **V. Bisulfite compounds of hydroxyfuchsone dyes.** *Ibid.* 1916-21.—The $NaHSO_3$ adducts of I-IV were readily prepd. by the following procedure: a mortar, preheated to 80°, is charged with 50 g. concd. $NaHSO_3$ soln. in which is gradually triturated 50 g. of the fuchsone deriv., the resulting colorless solid is readily reduced to a powder, which, after soln. in hot H_2O (contg. a drop of *N* AcOH), is filtered and cooled; the products are dried in vacuo over KOH; traces of NH_3 or acid in the atm. must be absent. All of the products are colorless crystals, sol. in H_2O, which develop color on warming in aq. solns. (reversible for brief heating). Acidification of the solns. gives typical ion colors of the onium salts; AcOH does not decomp. the bisulfite adducts; treatment with alkalies produces colors typical of the alkali salts of the hydroxyfuchsone dyes. Analyses indicate equimolar adducts. The decompn. in soln. takes place at pH 4 for acids, and pH 8 for bases for III and IV, and at pH 2 and 7, resp., for I and II. Purification of III may be readily accomplished as follows: crude III (87 g.) at 20° in 600 ml. 1.5% NH_4OH is filtered, the filtrate acidified with AcOH at 70°, and the red ppt. (12.5 g., m. 285°) warmed with 12 ml. satd. $NaHSO_3$ soln. in 100 ml. H_2O, leaving behind 5 g. insol. matter; the filtrate, after addn. of 400 ml. 20% NaCl, is warmed with HCl and the ppt. contg. III.*HCl* treated with NaOAc soln., filtered, and dried, yielding 7.5 g. pure III, m. 292°. Direct conversion of the crude III to the bisulfite adduct, followed by HCl treatment, yields III, m. 287-90°. **VI. Methoxy- and dimethoxyaurins.** I. S. Ioffe and Z. I. Pavlova. *Ibid.* 18, 223-6(1948).—Molten PhOH (40 g.) and 30.4 g. vanillin were satd. with dry HCl and let stand until crystn. started; trituration with 2 vols. 30% AcOH gave 30.8 g. *4,4',4''-trihydroxy-3-methoxytriphenylmethane*, m. 190-1° (from 30% AcOH), colorless but turning pink in the air, insol. in petr. ether, sol. in EtOH, AcOH, less sol. in C_6H_6. Heating 2 g. with 10 g. Ac_2O and 4 g. NaOAc 4 hrs. on a

steam bath gave the [illegible] *c deriv.*, colorless needles, m.
112° (from EtOH). *p*-HOC_6H_4CHO (12.2 g.) and 20 g.
guaiacol in 20 ml. AcOH satd. with dry HCl, allowed to
stand several days and the red mass taken up in 10%
NaOH, dild. to 2 l. with water, filtered, and acidified with
HCl, gave 30 g. *4,4',4''-trihydroxy-3,3'-dimethoxytri-*
phenylmethane, m. 175-5.5° (from 30% AcOH), sol. in
EtOH, Et_2O, AcOH, AmOAc, less sol. in C_6H_6 or petr. ether;
tri-Ac deriv., colorless, m. 120-1°. The condensation
product of 40 g. PhOH and 30.4 g. vanillin taken up in 150
ml. AmOAc, treated with 40 ml. AmOAc satd. with dry
HCl, the mixt. treated with 17.5 g. fresh AmONO
with stirring over 2-3 hrs., stirred 4 hrs., and let stand
overnight gave 70% *3-methoxyaurin-HCl*, purified by
heating to 80° with 35 ml. satd. $NaHSO_3$ soln. and 100
ml. H_2O, pouring into 400 ml. boiling 30% NaCl soln.,
treating with charcoal, filtering, adding 50 ml. concd. HCl
dropwise to the hot filtrate, and collecting the product
and washing it with water; the pure product, bronze-tinted
crystals, decomp. 180°, can be crystd. from AcOH. This
HCl salt (12 g.), on addn. to 5 g. NaOAc in water, gives
an oil, which on boiling crystallizes and yields *hydroxy-*
fuchsone, m. 274-5°, red crystals with bronze-like tint,
can be crystallized from EtOH or AcOH; heating with
Ac_2O and NaOAc gives the *tri-Ac deriv.*, yellowish, m.
108-9° (from EtOH), which probably is based on the
carbinol structure. 4,4',4''-Trihydroxy-3,3'-dimethoxy-
triphenylmethane (5 g.) in 25 ml. AmOAc treated with 4
ml. AcOAm satd. with HCl, stirred 6 hrs., and let stand
overnight gave 3.2 g. *3,3'-dimethoxyaurin-HCl*, which,
purified as above, decomp. 165-70°; treatment with Na-
OAc as above gave the *free dye*, red, m. 226-8° (from
EtOH); *tri-Ac deriv.*, colorless, m. 124°. G. M. K.

IOFFE, I. S.

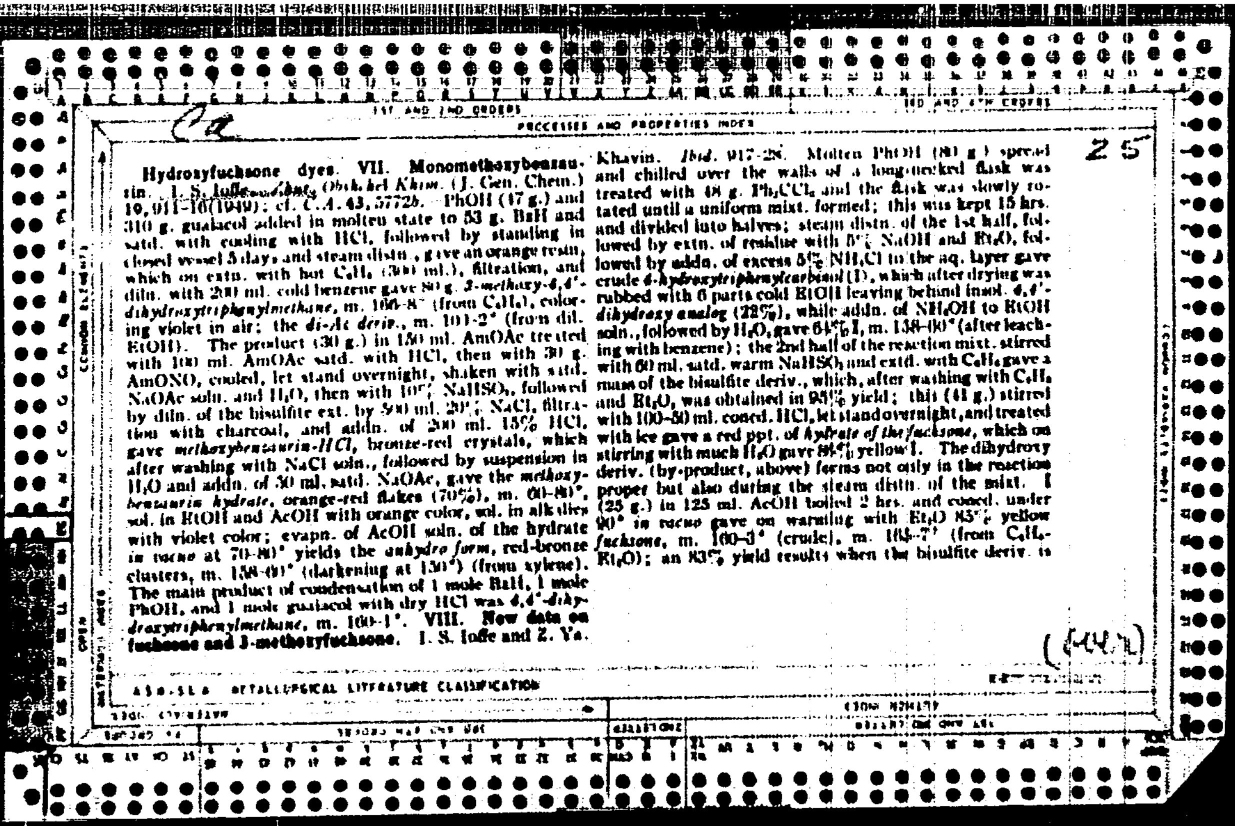
Ioffe, I. S., Pavlova, Z. I., "Research in the Field of Oxyfuchsone Dyes. VI. Methoxy- and Dimethoxyaurins." (p. 222)
(Nav Med Acad imeni Leningard)

SO: Journal of General Chemistry, (Zhurnal Obshchei Khimii), 1948, Volume 18, no. 2

IOFFE, I. S.

22972 Issledovaniye v ob oblasti oksifuksonovykh krasiteley. (Soobshch) 9. I. S. Ioffe i A.F. Sukhina. Stroyenie i tsvetnost' oksimetoksifuksonov. Zhurnal obshchey khimii, 1949, Vyp. 6, C. 1169-76. Bibliogr: 9 Nazv.

SO: LETOPIS' NO. 31, 1949



1ST AND 2ND ORDERS

PROCESSES AND PROPERTIES INDEX

3RD AND 4TH ORDERS

Ca

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Hydroxyfuchsone dyes. VII. Monomethoxybenzaurin. I. S. Ioffe. *Zhur. Obshchei Khim.* (J. Gen. Chem.) 19, 911-16(1949); cf. *C.A.* 43, 5772*b*. PhOH (47 g.) and 310 g. guaiacol added in molten state to 53 g. BzH and satd. with cooling with HCl, followed by standing in closed vessel 5 days and steam distn., gave an orange resin, which on extn. with hot C_6H_6 (300 ml.), filtration, and diln. with 200 ml. cold benzene gave 80 g. *3-methoxy-4,4'-dihydroxytriphenylmethane*, m. 166-8° (from C_6H_6), coloring violet in air; the *di-Ac deriv.*, m. 101-2° (from dil. EtOH). The product (30 g.) in 150 ml. AmOAc treated with 100 ml. AmOAc satd. with HCl, then with 30 g. AmONO, cooled, let stand overnight, shaken with satd. NaOAc soln. and H_2O, then with 10% $NaHSO_3$, followed by diln. of the bisulfite ext. by 500 ml. 20% NaCl, filtration with charcoal, and addn. of 200 ml. 15% HCl, gave *methoxybenzaurin-HCl*, bronze-red crystals, which after washing with NaCl soln., followed by suspension in H_2O and addn. of 30 ml. satd. NaOAc, gave the *methoxybenzaurin hydrate*, orange-red flakes (70%), m. 60-80°, sol. in EtOH and AcOH with orange color, sol. in alkalies with violet color; evapn. of AcOH soln. of the hydrate *in vacuo* at 70-80° yields the *anhydro form*, red-bronze clusters, m. 158-60° (darkening at 130°) (from xylene). The main product of condensation of 1 mole BzH, 1 mole PhOH, and 1 mole guaiacol with dry HCl was *4,4'-dihydroxytriphenylmethane*, m. 160-1°. **VIII. New data on fuchsone and 3-methoxyfuchsone.** I. S. Ioffe and Z. Ya. Khavin. *Ibid.* 917-28. Molten PhOH (80 g.) spread and chilled over the walls of a long-necked flask was treated with 48 g. Ph_2CCl_2 and the flask was slowly rotated until a uniform mixt. formed; this was kept 15 hrs. and divided into halves; steam distn. of the 1st half, followed by extn. of residue with 5% NaOH and Et_2O, followed by addn. of excess 5% NH_4Cl to the aq. layer gave crude *4-hydroxytriphenylcarbinol* (I), which after drying was rubbed with 6 parts cold EtOH leaving behind insol. *4,4'-dihydroxy analog* (22%), while addn. of NH_4OH to EtOH soln., followed by H_2O, gave 64% I, m. 158-60° (after leaching with benzene); the 2nd half of the reaction mixt. stirred with 600 ml. satd. warm $NaHSO_3$ and extd. with C_6H_6 gave a mass of the bisulfite deriv., which, after washing with C_6H_6 and Et_2O, was obtained in 95% yield; this (41 g.) stirred with 100-50 ml. concd. HCl, let stand overnight, and treated with ice gave a red ppt. of *hydrate of the fuchsone*, which on stirring with much H_2O gave 96% yellow I. The dihydroxy deriv. (by-product, above) forms not only in the reaction proper but also during the steam distn. of the mixt. I (25 g.) in 125 ml. AcOH boiled 2 hrs. and concd. under 90° *in vacuo* gave on warming with Et_2O 85% yellow *fuchsone*, m. 160-3° (crude), m. 165-7° (from C_6H_6-Et_2O); an 83% yield results when the bisulfite deriv. is

(442)

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

boiled 4 hrs. with AcOH as above. The bisulfite deriv. is obtained by shaking an alc. soln. of the fuchsone with warm satd. $NaHSO_3$ soln. and diln. to 50% with hot H_2O (I does not undergo this reaction); it is also obtained on addn. of $NaHSO_3$ soln. to AcOH soln. of fuchsone or I; either I or fuchsone in excess cold concd. HCl yields the brown *HCl salt*, which with satd. $NaHSO_3$ soln. (enough to neutralize residual acid) also gives the same bisulfite deriv. Warm alc. soln of fuchsone is decolorized by a few drops of aq. NH_4OH and on diln. gives I; the same results on boiling with *N* NaOH and diln. with NH_4Cl soln., or on boiling with 40% AcOH, or on soln. in concd. HCl and diln. Cooled HCl soln. of fuchsone-HCl is rapidly hydrolyzed by ice yielding voluminous *red fuchsone hydrate*, m. 59-62°, which on long standing in water yields I; the hydrate is stable only in acid media. Ph_3CCl (192 g.) and 240 g. guaiacol let stand 3 weeks gave a red mass which was divided in halves: the 1st half was steam distd., powd., and extd. with *N* NaOH and the soln. treated with CO_2 giving 64% *4-hydroxy-3-methoxytriphenylcarbinol* (II), m. 158-9° (from C_6H_6); the 2nd half was stirred on a steam bath with excess satd. $NaHSO_3$ soln., shaken with warm H_2O and benzene, and the bisulfite deriv. (80%) was ground with concd. HCl and the red soln. of 3-methoxyfuchsone-HCl was hydrolyzed by ice after 24 hrs. giving voluminous *red hydrate*, which on stirring with H_2O gave 78% *yellow* II, m. 116-18°, pure m. 157-9° (colorless) (from C_6H_6). II (25 g.) boiled 4-5 hrs. with 150 ml. AcOH and evapd. *in vacuo* gave on extn. with warm Et_2O 87% *3-methoxyfuchsone*, m. 130-3°; the same was obtained in 50% yield by boiling the bisulfite deriv. with AcOH, evapn., washing with Et_2O, and extn. with hot C_6H_6; the bisulfite deriv. forms under the same conditions as that of fuchsone itself and forms a tetrahydrate. The carbinol deriv. of 3-methoxyfuchsone: action of NH_4OH or alkali on fuchsone give colorless II, m. 157-9°, while boiling 3-methoxyfuchsone with 40% AcOH yields *yellow carbinol deriv.*, m. 147°, and hydrolysis of 3-methoxyfuchsone-HCl gives *yellow hydrate*, m. 116-18°, on standing, while the immediate hydrolysis product is a deep-pink solid. Benzhydrol (30 g.), 45 g. PhOH, and 10 ml. AcOH satd. in the cold with HCl and kept several days, steam distd., and treated with C_6H_6 gave *4-hydroxytriphenylmethane* (73%), m. 108-10° (from dil. AcOH); *Ac deriv.*, m. 82-4°. A similar reaction with 100 g. guaiacol gave 40% *4-hydroxy-3-methoxytriphenylmethane*, m. 103-5° (from C_6H_6); *Ac deriv.* m. 116-18° (from EtOH).

G. M. Kosolapoff

IOFFE, I. S.

IA 67/49T50

USSR/Chemistry - Dyes
Fuchsone
May 49

"Research in the Field of Oxyfuchsone Dyes: VII, Monomethoxybenzaurin," I. S. Ioffe, Chair of Org Chem, Nav Med Acad, 6 pp

"Zhur Obshch Khim" Vol XIX, No 5

Synthesized 3-methoxy-4,4 -dioxytriphenylmethane to obtain 3-methoxybenzaurin. It is extracted in a crystalline form by the passage of dry hydrogen chloride gas over a saturated mixture containing proportionally 1 mole of benzaldehyde, 1 mole of phenol, and 5 moles of guaiacol. The tri-phenylmethane derivative, with a melting point of

67/49T50

USSR/Chemistry - Dyes (Contd)
May 49

166-168°, remains after the acetyl derivative melts off at 100-102°. It is then oxidized in an amyl-acetate solution of amylnitrite to produce the 3-methoxybenzaurin, which has a low melting point in the hydrate form and melts at 158-160° in the anhydride form. Alkali solutions of this dye are violet; strong hydrochloric acid solutions, raspberry; and in the nonionized form, it forms light yellow solutions similar to the solutions of benzaurin and its di-methoxy derivative. Submitted 23 Feb 48.

67/49T50

IOFFE, IS S.

FA 67/49T49

USSR/Chemistry - Dyes May 49
Fuchsone

"Research in the Field of Oxyfuchsone Dyes: VIII, New Data on Fuchsone and 3-Methoxyfuchsone," I. S. Ioffe, Z. Ya. Khavin, Chair of Org Chem, Nav Med Acad, 11 3/4 pp

"Zhur Obshch Khim" Vol XIX, No 5

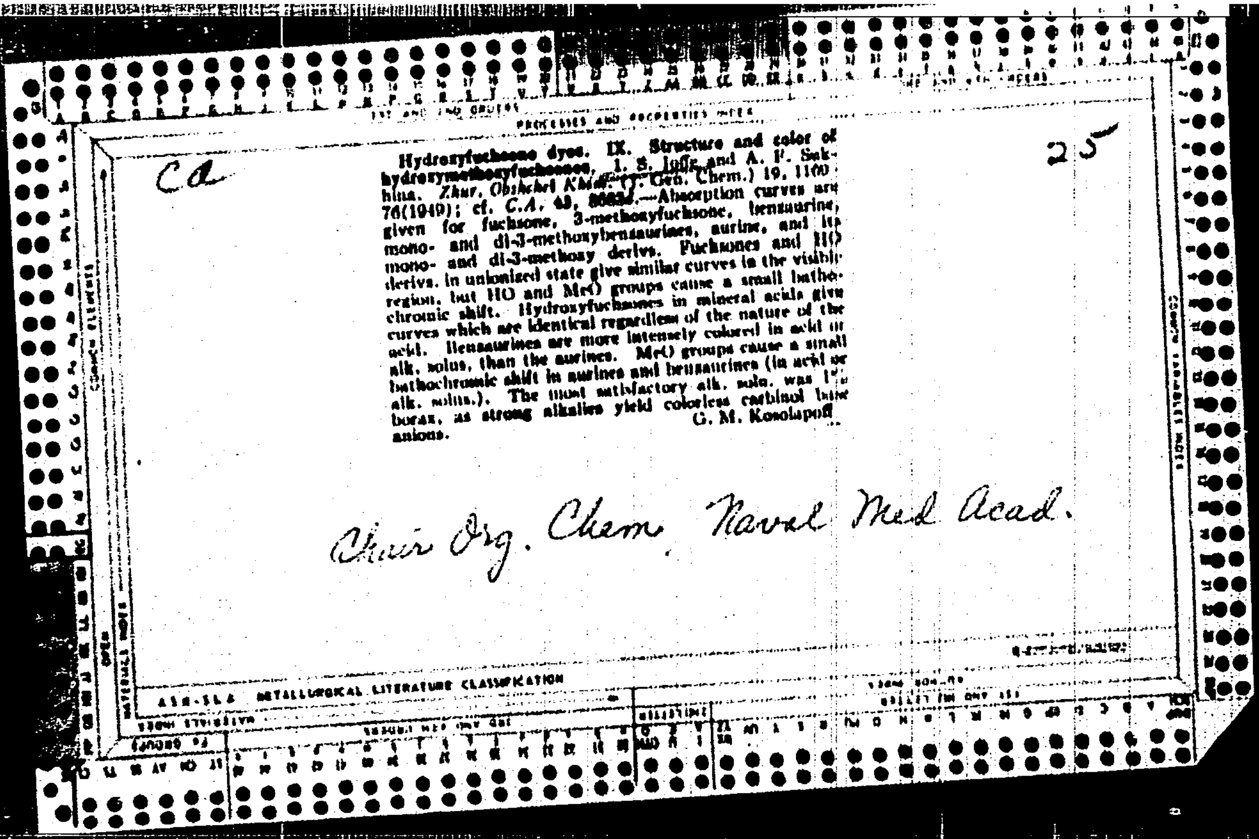
Describes a "new method" for the dehydration of oxy-triarylcarbinols to produce "good yields" of fuchsone and 3-methoxy-fuchsone, determining that 4,4'-dioxy-tetraphenylmethane is also accumulated in the process. Also describes a "new and easier"

[redacted] 67/49T49

USSR/Chemistry - Dyes (Contd) May 49

method for extracting oxy-triaryl-carbinols or fuchsones from products of the reaction of benzophenonechloride with phenols, and in addition a "new method" for obtaining oxy-triarylmethanes, based on the activity of benzhydrol with phenols in the presence of dry hydrogen chloride gas. Submitted 23 Feb 48.

[redacted] 67/49T49



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Hydroxyfuchsone dyes. IX. Structure and color of
hydroxymethoxyfuchsones. I. S. Ioffe and A. F. Suk-
hina. *Zhur. Obshchei Khim.* (J. Gen. Chem.) 19, 1100-
76(1949); cf. *C.A.* 43, 8663d.—Absorption curves are
given for fuchsone, 3-methoxyfuchsone, benzaurine,
mono- and di-3-methoxybenzaurines, aurine, and its
mono- and di-3-methoxy derivs. Fuchsones and HO
derivs. in unionized state give similar curves in the visible
region, but HO and MeO groups cause a small batho-
chromic shift. Hydroxyfuchsones in mineral acids give
curves which are identical regardless of the nature of the
acid. Benzaurines are more intensely colored in acid or
alk. solns. than the aurines. MeO groups cause a small
bathochromic shift in aurines and benzaurines (in acid or
alk. solns.). The most satisfactory alk. soln. was 1%
borax, as strong alkalies yield colorless carbinol base
anions. G. M. Kosolapoff

Chair Org. Chem. Naval Med Acad.

IOFFE, I. S.

Ioffe, I. S. & Khavin, Z. Ya. - "Interaction of methylenic bases of the thiazole series with alkyl halides." (p. 145)

SO: Journal of General Chemistry, (Zhurnal Obshchei Khimii), 1950, Vol. 20, No. 1

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Hydroxyfuchsone dyes. X. So-called tautomerism of hydroxytriarylcarbinols. I. S. Ioffe and Z. Ya. Khavin (Naval Med. Acad., Leningrad). *Zhur. Obshchei Khim.* (J. Gen. Chem.) 20, 158-70(1950); cf. *C.A.* 43, 9451b.—Crit. examn. of exptl. data indicates that Gomberg's school is in error in its defense of "desmotropy" of hydroxytriarylcarbinols (*C.A.* 7, 3507; 10, 52, 53). Heating such compds. as 3-methoxy-4-hydroxytriphenylcarbinol to 75° in porcelain boats in glass app. gave loss of 1 H_2O only in 50 hrs. from the colored form, while the colorless form lost but 0.6% of its wt.; however, continued heating gave continued wt. loss and formation of sublimable decompn. products; in addn. the "dehydrated" product on treatment with $NaHSO_3$ soln. gave a ppt. of the initial carbinol, while authentic 3-methoxyfuchsone gave a colorless soln. Spectroscopic data of Gomberg and Anderson (*C.A.* 23, 3457) indicate that the so-called "desmotropes" are probably mixts. of colorless carbinols with fuchsones. Although crystn. of 4-hydroxytriphenylcarbinol and 3-methoxy-4-hydroxytriphenylcarbinol from AcOH of various concns. (40, 60, 80%) gives products of different colors and m.ps., quant. colorimetry of their solns. in C_6H_6 merely indicates different amts. of admixture (0.1-1.1%) of corresponding fuchsone to the carbinol, and not individually different substances. This is supported by isolation of similar materials upon crystn. of fuchsones from dil. AcOH of the same concns., i.e. hydration of fuchsones occurring in this case gives mixts. similar to those obtained by dehydration of the carbinols, both reactions being feasible in dil. AcOH. Treatment of such products from 4-hydroxytriphenylcarbinol with dry C_6H_6 suffices to separate the fuchsone impurity; similar sepn. is possible by treatment with $NaHSO_3$ soln., when the fuchsones dissolve in the form of adducts, while the carbinols are unchanged. G. M. Kosolapoff

CA 25

Hydroxyfuchsone dyes. XI. Oxidative alkaline decomposition of hydroxyfuchsone dyes of benzaurine group. I. S. Ioffe. *Zhur. Obshchei Khim.* (J. Gen. Chem.) 20, 346-55(1950); cf. C.A. 44, 5598c.—Aeration of alk. solns. of hydroxyfuchsone dyes gives the corresponding substituted benzophenones. The reaction permitted identification of Bartolotti's compd. (*Gazz. chim. ital.* 27, 288(1897)), m. 131-2° (from BzCl and guaiacol) as *4-methoxy-3-hydroxybenzophenone*. Only the colored monomeric anions of the dyes are oxidizable; solns. in the form of undissocd. hydroxyquinone derivs. or colorless carbinols are stable to aeration, and the ease of oxidation rises with increased concn. of alkali, although an increase of oxidation-stable carbinol form gives a superficial appearance of lesser overall reactivity; low temp. and higher alk. concn. both tend to shift the equil. to the carbinol side. The effect of alkali was confirmed on solns. of 1% Na_2CO_3 and 0.1-5.0% NaOH with aurin, trimethoxyaurin, benzaurin, and dimethoxybenzaurin. Passage of air through 5 g. benzaurin in 250 ml. 1% NaOH on a water bath until red-brown color forms, followed by addn. of 10 ml. AcOH and 2 ml. $NaHSO_3$ soln. gave 1.5 g. *4-hydroxybenzophenone*, m. 134-5°; benzoate, m. 112.5° (from EtOH). Similar reaction with 3,3'-dimethoxybenzaurin gave *3-methoxy-4-hydroxybenzophenone*, m. 97-8°. Treatment of this or the 4,3-analog with Me_2SO_4 and 10% NaOH gave *3,4-dimethoxybenzophenone*, m. 99-100° (from dil. EtOH). G. M. Kosolapoff

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Hydroxyfuchsone dyes. XII. Acidic transformations of methoxyfuchsone derivatives. L. S. Ioffe (Naval Med. Acad., Leningrad). *Zhur. Obshchei Khim.* (J. Gen. Chem.). **20**, 539-40(1950); cf. *C.A.* **44**, 6130*i*.—Fuchsones contg. a MeO group ortho to the CO link undergo an irreversible change on heating with acids; the products are colorless substances, with the same empirical compn., which are the result of ring closure to *meso*-phenylfluorene derivs.; the distn. of such products with Zn dust should yield *meso*-phenylfluorene, but this has not been accomplished as yet, and the evidence is indirect. Heating 10 g. 3-methoxyfuchsone with 100 ml. 15% HCl 1-2 hrs. yields 10 g. brown transformation product, purified by soln. in EtOH and addn. of $NaHSO_3$ soln., followed by extn. with Et_2O and crystn. from 60% EtOH, 30% AcOH, or C_6H_6. The purified product forms colorless needles, m. 173-4°. poorly sol. in cold aq. alkalies; the product, $C_{20}H_{15}O(OH)$, yields a *monoacetate*, m. 176°, with Ac_2O-pyridine. 3,3'-Dimethoxybenzaurin similarly boiled with 10% HCl yields a colorless product, $C_{21}H_{16}O_2(OH)_2$, m. 199-201° (from EtOH and AcOH), which forms a *diacetate*, m. 227-9° (from AcOH), identical with that formed by heating 3,3'-dimethoxybenzaurin-HCl with Ac_2O and AcCl 2 hrs. on a steam bath. Boiling 3,3',3''-trimethoxyaurin with 10% HCl 2-3 days gave 5-6 g. *transformation product*, which was finally purified by boiling in C_6H_6 with Zn dust and AcOH, when it was obtained in 0.5-1.5 g. yield, m. 236-40°; its *acetylation product* m. 204-6° (from EtOH). The MeO groups in all the aurins investigated are intact in the transformation products, which are believed to contain the OH groups in the para position, relative to the central C atom. The Ac deriv. of the last compd. was identical with the acetylation product of rubrocol (cf. Rkilin and Postovskii, *C.A.* **42**, 152*g*), but the structure proposed by R. and P. is questionable.

G. M. Kosolapoff

IOFFE, I. [Ed.]

[Using engineer Kovalev's method in oil well drilling and operation] Opyt primeneniia metoda inzhenera Kovaleva v burenii i dobyche nefti. 1951. 58 p. (MIRA 8:8)

1. Moscow. TSentral'nyy nauchno-issledovatel'skiy institut mekhanizatsiy truda v neftyanoy promyshlennosti. Byuro tekhniko-ekonomicheskoy informatsii.
(Oil well drilling)

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Hydroxyfuchsone dyes. XIII. Acetylation of hydroxymethoxyfuchsones. I. S. Ioffe. *Zhur. Obshchei Khim.* (*J. Gen. Chem.*) 21, 1916-20(1951); cf. *C.A.* 45, 3600h, 6385e.—Hydroxyfuchsone dyes with MeO groups ortho to hydroxyl or keto groups are acetylated normally forming corresponding acetoxytriphenylcarbinols, which are hydrolyzed by acids or bases to colored salts of the original hydroxyfuchsone dyes. The acetylation in the presence of HCl leads to 2 reactions simultaneously: one yields the above products while the second reaction leads to acid isomerization of the original dyes with subsequent acetylation of the probably formed hydroxyfluorene derivs. The concept of free radical dimers, as representative of the 2nd set of products (above), as postulated by Ridlin and Postovskii (*C.A.* 42, 152g), is in error. *3,3'-Dimethoxybenzaurine*, Ac$_2$O, and NaOAc refluxed 6 hrs. give 65% of an *acetylation product*, m. 136-8° (from EtOH), whose solns. are colorless in org. solvents, while mineral acids give violet color; hot aq. alkali gives blue color; boiling the Ac deriv. with Zn-AcOH yields a product that no longer gives color with acids or alkalies; analysis of the Ac deriv. indicates the compn. $C_{21}H_{18}O_4(Ac)_2$. Acetylation with AcCl-Ac$_2$O gives a small amt. of a *substance*, m. 229-32°, identical with the product of acid *isomerization* of 3,3'-dimethoxybenzaurine, and the mother liquor yields the product, m. 136-8°, described in above expt. Acetylation of *3,3',3''-trimethoxyaurine* with Ac$_2$O-NaOAc gives 60% product, m. 168°, corresponding to the normal *triacetate*; heated with acids or alkalies it gives violet color of rubrosol salts. Acetylation with AcCl-Ac$_2$O gave the above product and a less sol. product, m. 206-8°, identical to the Postovskii-Ridlin product, unchanged by acids; alkalies on heating yield a colorless soln.

G. M. Kosolapoff

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**Hydroxyfuchsone dyes. XIV. Structure of the bisulfite
derivatives of hydroxyfuchsone dyes.** L. S. Ioffe (Naval
Med. Acad., Leningrad). *Zhur. Obshchei Khim.* (J. Gen.
Chem.) 21, 1514-17(1951); cf. *C.A.* 45, 10500h.—Alk.
hydrolysis of acetyl derivs. of hydroxyfuchsone dyes, which
are the Ac derivs. of the carbinol derivs., results in forma-
tion of colorless salts of the carbinols. Similar hydrolysis
of the bisulfite derivs. of hydroxyfuchsone dyes leads directly
to the colored salts of the dyes. Hence, the bisulfite derivs.
are not the sulfite esters of the carbinols as proposed by
Bayer (*Ber.* 39, 57(1906)) but are the result of reaction of
the bisulfite with the carbonyl group of the dye and should

be regarded as the α-hydroxysulfonic acids. Thus, the
bisulfite deriv. of 3,3'-dimethoxybenzaurine in H_2O treated
in the cold with 5% NaOH gives immediately a blue color,
which disappears only slowly and reappears on warming.
Similar treatment of the Ac deriv. gives murkiness, which
goes over to a colorless soln., which acquires a weak blue
color only after long standing, which is intensified by heat-
ing, but disappears on cooling. G. M. Kosolapoff

IOFFE, I. S.

"Hydroxyfuchsone dyestuffs. XV. Acetoxyfuchsones." (p. 1677)

SO: Journal of General Chemistry (Zhurnal Obshchei Khimii) 1951, Vol 21, No 9.

IOFFE, I. S.

Ioffe, I. S., Bolen'kii, B. G.- "Investigation of hydroxyfuchsone dyes. XVI. 2-Hydroxyfuchsone." (p. 1437)

SO: Journal of General Chemistry, (Zhurnal Obshchei Khimii), 1952, Vol. 22, No. 8

IOFFE, I. S.

CATALYSTS

Chemical Abst.
Vol. 48 No. 3
Feb. 10, 1954
Organic Chemistry

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4

Quinones. II. Reaction of p-benzoquinone with acylaminosulfinic acids. I. S. Ioffe. Zhur. Obshchei Khim. 23, 125-6(1953).—A hot soln. of [illegible] g. p-$AcNHC_6H_4SO_2H$ in 800 ml. H_2O, was filtered, brought to the b.p. and treated gradually with 11 g. p-benzoquinone, causing a temporary orange-yellow color, with pptn. of colorless product; after 15 min. boiling the colorless soln. was filtered yielding 20 g. $C_{14}H_{13}O_5NS$, m. 282-5° (from AcOH or EtOH). This product is *4-acetamido-2',5'-dihydroxydiphenyl sulfone* (I). Heated on water bath with Ac_2O and pyridine 1 hr. it gave *4-acetamido-2',5'-diacetoxydiphenyl sulfone*, 64%, m. 182-4° (from aq. EtOH); on soln. in alkalies and subsequent acidification the 2 Ac groups are lost and the original material, m. 283°, is regenerated. Similar reaction of p-methoxycarbonylaminobenzenesulfinic acid gave 67% *4-methoxycarbonylamino-2',5'-dihydroxydiphenyl sulfone* (II), 210-11° (from H_2O), very stable to hot mineral acids, but hydrolyzed with hot alkalies. I refluxed with 10% HCl and evapd. gave 83% *4-amino-2',5'-dihydroxydiphenyl sulfone*, m. 175-6° (from aq. EtOH); the same is obtained by hydrolysis of I in hot 10% NaOH. II similarly yields this substance by hydrolysis with 10% NaOH. The amino deriv. yields the *tri-Ac deriv.*, m. 150-2°, when heated with Ac_2O-pyridine, while mere Ac_2O yields the *N-Ac deriv.* identical with above described. The *amino deriv.* forms *HCl salt*, m. 208-10°, which hydrolyzes rather readily in aq. soln.

O. M. Kosolapoff

1-31-54

Ioffe, I. S.

Quinone series. II. Chloromethoxyquinones. I. S. Ioffe and A. F. Sukhina. *Zhur. Obshchei Khim.* 23, 295-9 (1953); cf. *C.A.* 48, 1300e.—Methoxylation of chloro-*p*-benzoquinone with MeOH-$ZnCl_2$ leads not only to introduction of MeO group, but also to displacement of the Cl by a 2nd MeO group. To 6 g. vanillin in 40 ml. 4% NaOH was rapidly added 40 ml. 6% H_2O_2, and the dark brown soln. treated after 1 hr. with 8 ml. 20% H_2SO_4 (8 ml.), chilled, then treated at −3° with 40 g. $Na_2Cr_2O_7$ in 75 ml. 20% H_2SO_4 over 2 hrs., followed by 2 hrs. at 0°, giving 3.0 g. (71%) *methoxy-p-benzoquinone*, m. 144° (from EtOH). Direct chlorination of vanillin in $CHCl_3$ gave 3,4,5-Cl(HO)-*(MeO)*C_6H_2*CHO*, m. 165°, which (6 g.) in 40 ml. 4% NaOH treated as described above with 40 ml. 6% H_2O_2 30-40 min., acidified with 20% H_2SO_4, and chilled gave a ppt. of 6-*chloro-2-methoxyhydroquinone*, m. 140°; the mixt. can be directly oxidized with $Na_2Cr_2O_7$ at −5° as described, yielding 77% *6-chloro-2-methoxy-p-benzoquinone*, orange, m. 188-9° (from EtOH). Similar treatment of 2,4,5-Cl(HO)-(MeO)C_6H_2CHO gave 60% *5-chloro-2-methoxy-p-benzoquinone*, yellow, m. 172-3° (from EtOH), less sol. in AcOH and EtOH than the 6-Cl analog. The yield of 2,5-dimethoxy-*p*-benzoquinone by the Bückel method [*Ber.* 34, 3334(1901)] is increased beyond 33% by addn. of oxidizing agents to the reaction mixt. and thus reducing the consumption of the starting material in oxidation-reduction reactions failed and the yields were even lower than without such addns. ($FeCl_3$, PbO_2). III. Chlorination of methoxyquinone. *Ibid.* 299-303.—Passage of HCl into methoxy-*p*-benzoquinone (I) in $CHCl_3$ gave a blue-violet ppt., free of Cl, m. 238-40° (from $PhNO_2$), also formed on addn. of mineral acids to I in AcOH. The product has been described earlier (Erdtman, *C.A.* 28, 1337⁸). Thus I dimerizes in the presence of mineral acids. Passage of Cl through I in $CHCl_3$ yields a *dichloride*, which yellows at 100° and

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decomp. 120°, losing HCl and yielding an orange melt,
which resolidifies and m. 158–63°, being transformed to 6-
chloro-2-methoxy-p-benzoquinone. Thus introduction of a
MeO group reduces the stability of quinone dichlorides.
Benzoquinone dichloride m. 146° without decompn., and
only at 170–80° does it slowly lose HCl, yielding an unstable
monochloroquinone (cf. Dimroth, *et al.*, *C.A.* 20, 1004).
Chlorination of methoxy-p-benzoquinone must be done with
pure Cl, for even traces of HCl lead to dimerization men-
tioned above. The heating of the methoxyquinone di-
chloride is best done by spreading the substance in a thin
layer in a dish and heating to 120° in a thermostat. Al-
though its decompn. can lead to 2 isomeric chloromethoxy-p-
benzoquinones, the product actually obtained is the pure
chloro-2-methoxy isomer, m. 173°. The yield reaches 70%.
The methoxyquinone dichloride is also unstable on heating in
various solvents. Thus in hot aq. EtOH it loses HCl and
yields up to 80% *6-chloro-2-methoxy-p-benzoquinone*, m.
159°. Addn. of the dichloride to hot AcOH gave *6-chloro-
2-methoxybenzoquinone*, m. 172–3°, also formed in hot dry
Me_2CO but in aq. AcOH and aq. Me_2CO the 6-Cl analog is
formed. In hot H_2O the dichloride also yields the 6-Cl
deriv. Heating the dichloride in aromatic hydrocarbons
under dry conditions gives different results; the substance is
not decompd. in boiling xylene for over 1 hr., while hot
C_6H_6 can be used as recrystn. solvent; the dichloride thus
purified m. 120° (decompn.). A trace of H_2O immediately
yields 6-chloro-2-methoxy-p-benzoquinone. G. M. K.

IOFFE, I. S.

"Investigation of quinones. Part 3. Chlorination of methoxy-quinone." Ioffe, I. S., Sukhina, A. F. (p. 299)

SO: Journal of General Chemistry (Zhurnal Obshchei Khimii) 1953, Volume No. 23, No. 2.

IOFFE, I. S.

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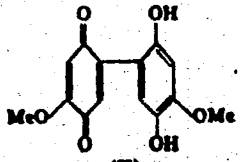
Organic Chem

✓ Quinone series. IV. Transformation of methoxyquinone under the influence of acids. I. S. Ioffe and A. F. Sukhina. *Zhur. Obshchei Khim.* 23, 1370-6(1953); cf. *ibid.* 295; Erdtman, *C.A.* 28, 1337⁶.—In contrast with other quinones, methoxyquinone (I), under the action of mineral acids, forms a condensation product with formation of a biphenyl link in a position para to the MeO group. Thus 10 g. I in 100 ml. warm AcOH, poured into 2 l. 1% HCl, gradually yields a blue ppt., which after 48 hrs. amounts to 95% II, m. 230° (crude), m. 236° (from pyridine), which is generally but sparingly sol. in org. solvents.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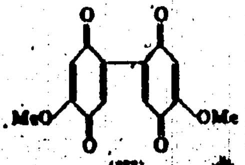
(III)

Reduction of 3 g. II with 3 g. Zn dust in refluxing AcOH gave, upon filtration, diln., and treatment with dil. NaHSO₃, a 60% yield of [5,2,4-(HO)₂MeOC₆H₂]₂, decomp. 210° (from dil. EtOH); *tetra-Ac deriv.* from Ac₂O-pyridine, m. 1[illegible]-7° (from EtOH). II (5 g.) agitated with 5 g. chromic acid in 300 ml. H₂O gave III, m. 212-14° (from AcOH). I (1 g.) in 10 ml. AcOH treated with 20 ml. concd. HCl gave after 48 hrs. 75% *5,5'-dihydroxy-4,4'-dimethoxy-3-chlorodiphenyl oxide*, m. [illegible]-1° (from AcOH), colorless, the diacetate (Ac₂O-pyridine), m. [illegible]-1° (from AcOH); also obtained in 95% yield from II in warm AcOH with concd. HCl, the blue color of II being discharged at 65-70°. III (5 g.) in 25 ml. AcOH refluxed with 25 ml. concd. HCl gave [illegible]% *5,5'-dihydroxy-4,4'-dimethoxy-3,3'-dichlorodiphenyl oxide*, m. [illegible]-6° (from AcOH); diacetate, m. [illegible]-3° (from AcOH). G. M. Kosolapoff

IOFFE, I. S.

CATALYST

Chemical Abst.
Vol. 48 No. 3
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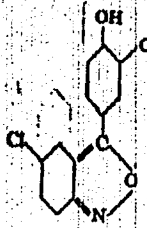
Dyes and Textile Chemistry

(2) Chem.

Hydroxyfuchsone dye series. XVII. Condensation of isomeric nitrobenzaldehydes with guaiacol. I. S. Ioffe and B. G. Belen'kii. *Zhur. Obshchei Khim.* 23, [illegible] cf. C.A. 42, 2431h; 43, 8083g; 47, 866a.—m-$O_2NC_6H_4CHO$ (21 g.) and 38 g. guaiacol, satd. with dry HCl (3.5 g.) and kept in the cold 10 days in a closed flask, gave a mass of solid product, which was extd. several times with hot 2% Na_2CO_3. The crude product treated with 60% EtOH and finally crystd. from 50% EtOH gave *3''-nitro-3,3'-dimethoxy-4,4'-dihydroxytriphenylmethane*, m. 141.5°. The yield of crude product is 60.5% after the extn. with 60% EtOH; yield of pure product is unstated. The crude product (5 g.), after the Na_2CO_3 treatment, was taken up in 50 ml. AmOAc and satd. with dry HCl, followed by a stream of N oxides (from $NaNO_2$-H_2SO_4) while maintaining the HCl stream. After 2 hrs. the mixt. was allowed to stand overnight, it deposited 68.5% crude *3''-nitro-3,3'-dimethoxy-4-hydroxyfuchsone-HCl*. With pure starting material the yield is 98%. The product is violet with green sheen and has no definite m.p. The HCl salt ground with excess 25% KOAc and 4 parts H_2O and allowed to stand overnight gave a ppt. of the hydrate form of the fuchsone, red solid. The latter (4.0 g.) heated with 60 ml. AcOH and cooled, gave 50.5% *free fuchsone*, red-orange, m. 239-9.5° (from AcOH); it is sol. in aq. acids and bases, giving red-violet soln. in acids and blue in bases. p-$O_2NC_6H_4CHO$ (4.9 g.) and 9.8 g. guaiacol satd. with dry HCl (0.7 g.) and kept in the cold 15 days, then treated with hot H_2O, gave crude yellowish leuco base, m. 50-60°, which (5 g.) was treated in AmOAc with HCl and N oxides as above, yielding 66% *4''-nitro-3,3'-dimethoxy-4-hydroxyfuchsone-HCl*, violet, without definite m.p. The latter (3.6 g.) with aq. KOAc gave the brick-red *hydrate* form of the *fuchsone* (3 g.), which crystd. from AcOH gave 48% *free* *fuchsone*, red, m. 235-5.5°; sol. in acids with violet color, in bases with blue-green color. When 5 g. p-$O_2NC_6H_4CHO$ and 9 g. guaiacol were satd. with 1.1 g. dry HCl and kept 3 weeks there was formed a viscous orange mass. This kept overnight under 15 ml. 70% EtOH and dried gave 2.92 g. golden-yellow crystals, which could be crystd. from various org. solvents; on recrystn. from AcOH it m. 181.5°. The product failed to undergo oxidation under the conditions used for the cases described above. Its compn. was $C_{14}H_{10}ClNO_3$ (I) indicating the condensation of 1 mol. of aldehyde with 1 mol. of guaiacol and simultaneous chlorination of a ring. When the product was reduced with HCl-Zn dust and the filtrate was diazotized and coupled with 2-$C_{10}H_7OH$, a red dye was formed; with H-acid the dye was red-violet. The results indicate that I had the structure II, apparently formed by rearrangement of the intermediate 3,4-$(MeO)(HO)C_6H_3CH(OH)(C_6H_4NO_2$-$p)$.



(II)

G. M. Kosolapoff

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IOFFE, I.S.; SUKHINA, A.F.

[redacted]

Research in the field of quinones. Part 5. Chlorination of 2,5-dimethoxyquinone. Zhur.ob.khim. 23 no.10:1752-1757 O '53. (MLRA 6:11)
(Quinone)

Ioffe, I.S.

Hydroxyfuchsone dyes. XVIII. Halogen derivatives of 3,3'-dimethoxybenzaurine. I. S. Ioffe and B. G. [illegible] *Zhur. Obshchei Khim.* 23, 1630-4(1953); cf. *C.A.* 48, 168[illegible].—Passage of dry HCl into 0.03 mole aldehyde and 0.12 mole guaiacol, followed by storage of the mixt. 1 week at room temp. in a closed vessel, treatment with hot H_2O and extn. with hot 10% aq. Na_2CO_3 gave 65-80% of the following *leucobases*, which were purified by soln. in EtOH and crystn. from EtOH or AcOH: *3,3'-dimethoxy-4,4'-dihydroxytriphenylmethane* (halogen shown): *2''-chloro*, decomp. 1[illegible]-30°; *3''-chloro*, decomp. 130-40°; *4''-chloro*, m. 130-3°; *2''-bromo*, decomp. 120-30°; *3''-bromo*, decomp. 130-3°; *4''-bromo*, m. 126-7°. These leucobases in AmOAc were satd. with dry HCl, then treated over 2 hrs. with a stream of N oxides containing NO_2, yielding a ppt. of the *HCl salt* of the dye in 100% yield: *3,3'-dimethoxy-4-fuchsone* (halogen shown): *2''-chloro*, m. 164-6°; *3''-chloro*, m. 147-8°; *4''-chloro*, m. 203°; *2''-bromo*, m. 171-2°; *3''-bromo*, m. 143-4°; *4''-bromo*, m. 202-5°. These salts are hydrolyzed by H_2O, yielding the hydrated forms of the hydroxyfuchsones; boiling these with AcOH, followed by distn. of the solvent *in vacuo*, gave the anhydro forms of the dyes, which were purified by crystn. from dry C_6H_6 or AcOH; these were, resp.: *o-chloro*, orange-yellow, purple in acids, blue-violet in alkalies; *m-chloro*, orange-red, violet in acids, blue in alkalies; *p-chloro*, red, red-purple in acids, blue in alkalies; *o-bromo*, yellow-orange, violet in acids, blue-violet in alkalies; *m-bromo*, red, purple in acids, blue-violet in alkalies; *p-bromo*, red, purple in acids, blue in alkalies. G. M. K.

Ioffe, I. S.

USSR/Chemistry - Dyes

Card 1/1 Pub. 151 - 30/38

Authors : Ioffe, I. S., and Belen'kiy, B. G.

Title : Investigation of oxyfuchsone dyes. Part 19.- Effect of nitro-group and halogens on the indication properties of 3,3-dimethoxybenzaurin derivatives

Periodical : Zhur. ob. khim. 24/2, 343-352, Feb 1954

Abstract : The effect of nitro-groups and halogens in the benzene nucleus of 3,3'-dimethoxybenzaurin on the indicating properties of dyes was investigated. It was found that the presence of these substitutes weakens the basic properties of dyes, their ability to form onic cations in strong acid media and reduces the stability of the cations. The presence of halogens in o-position relative to the central carbon atom, screens the latter and produces steric hindrances even during hydration of the dyes. The effects of the electron-acceptor and electron-donor nitro-groups on the conversion of 3,3'-dimethoxybenzaurin derivatives into carbinol compounds are discussed. Four USSR references (1947-1953). Tables; graphs.

Institution : ...

Submitted : July 28, 1953

Ioffe, I. S.

USSR/Chemistry - Dyes

Card 1/1 Pub. 151 - 31/38

Authors : Ioffe, I. S., and Belen'kiy, B. G.

Title : Investigation of oxyfuchsone dyes. Part 20.- Effect of nitro-groups and halogens on the colority of 3,3'-dimethoxybenzaurin derivatives

Periodical : Zhur. ob. khim. 24/2, 353-361, Feb 1954

Abstract : The effect of substitutes on the colority of 3,3'-dimethoxybenzaurin derivatives containing nitro-groups and halogens in the benzene nucleus, was investigated. It was established that the presence of these substitutes has a definite effect of the colority of dyes in nonionized state, and in ionized state only in strongly acid and alkaline solutions. Nitro-groups and halogens cause a deepening of the color and onium cation of the dye in a strongly acid solution and a deepening of the dye anion in an alkaline solution. The conditions leading to maximum bathochromic effects of the nitro-groups and halogens are discussed. Ten references: 7-USSR; 1-USA and 1-English; 1-S. African (1900-1954). Tables; graphs.

Institution : ...

Submitted : July 28, 1953

Ioffe, I. S.

USSR/Chemistry - Condensation products

Card 1/1 : Pub. 151 - 26/37

Authors : Ioffe, I. S., and Khavin, Z. Ya.

Title : Investigation of quinones. Part 6.-Condensation of p-benzquinone with alpha-amino acids

Periodical : Zhur. ob. khim. 24/3, 521-527, Mar 1954

Abstract : Investigations showed that the reaction of p-benzquinone with alpha-amino acids is followed by oxidizing cleavage of the amino-acid and consequent formation of products of their condensation with p-benzquinone. The condensation products obtained from p-benzquinone with glycine and from p-benzquinone with alpha-alanine are listed. The physico-chemical properties of these condensation products are described. Ten references: 3-USA; 3-German; 1-Polish; 1-English; 1-Japanese and 1-French (1910-1950).

Institution : .....

Submitted : July 28, 1953

Ioffe, I. S.

USSR/Chemistry - Reaction processes

Card 1/1 : Pub. 151 - 27/37

Authors : Ioffe, I. S., and Khavin, Z. Ya.

Title : Investigation of quinones. Part 7.-Reaction of chlorine derivatives of p-benzoquinone with glycine esters

Periodical : Zhur. ob. khim. 24/3, 527-532, Mar 1954

Abstract : The reaction of chloroquinones with amines and with non-substituted quinone was investigated. The formation of a diamino-quinone derivative having both amino-groups in p-position relative to each other is described. The mechanisms and tendencies of such a chloroquinone reaction and its dependence upon the number of halogen atoms are discussed. Ten references: 5-German; 4-French and 1-USSR (1881-1954).

Institution : .....

Submitted : July 28, 1953

Ioffe I.S.

USSR .

Quinones. VIII. Condensation of p-benzoquinone with
sulfanilamides. I. S. Ioffe, N. A. Filippova, and Z. Ya.
Khavin. *Zhur. Obshchei Khim.* 24, 702-6(1954); cf. C.A. 2
48, 13053*f*.—Addn. of 2.2 g. p-benzoquinone in 100 ml. hot
H_2O to 2.4 g. sulfapyridine in 100 ml. EtOH followed by
refluxing 3 hrs. gave 2.08 g. *2,5-disulfapyridino-p-benzo-*
quinone, m. above 300°. Similarly sulfathiazole gave *2,5-*
disulfathiazolo-p-benzoquinone, m. above 300°, while sulfa-
pyrimidine gave *2,5-disulfapyrimidino-p-benzoquinone*, C- 1/2
$H_{20}O_6N_8S_2$, m. above 300°. p-Benzoquinone in 2 l. warm
H_2O was added to 3.5 l. cold H_2O and 0.3 l. satd. NaCl; when
the soln. reached room temp. it was treated with 9 g. sul-
fanilamide in 100 ml. EtOH and after 3 days at room temp.
gave 5 g. *2-sulfanilamido-p-benzoquinone*, purified by extn.
with hot EtOH in which the bis-analog was insol. while
diln. of the alc. ext. with H_2O gave the pure 2-sulfanilamido-
p-benzoquinone. Similarly was prepd. *2-sulfapyridino-p-*
benzoquinone, sol. in EtOH and AcOH. In soln. both the
mono-derivs. are slowly transformed into insol. substances,
possibly polymerization or condensation products. IX.
Reaction of methoxyquinones with amines. I. S. Ioffe and
6. F. Sokhina. *Ibid.* 706-9.—To hot soln. of 5 g. 2-meth-
oxy-p-benzoquinone (I) in 75 ml. EtOH was added 1.5 g.
$PhNH_2$ and the mixt. refluxed 2 hrs. and cooled, yielded 3.5
g. red *2-methoxy-5-anilino-p-benzoquinone*, m. 100° (from
50% EtOH). This (1 g.) in 50 ml. hot AcOH treated with 1

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IOFFE, I.S.

g. $PhNH_2$ and refluxed 2 hrs. gave after hot filtration and cooling 1.2 g. red *2,5-dianilino-p-benzoquinone*, m. above 300° (from $PhNO_2$); the same can be obtained in 1 step by using excess $PhNH_2$. I (5 g.) in 75 ml. hot EtOH treated with 2.5 g. sulfanilamide and refluxed 2 hrs. gave 3 g. *2-methoxy-5-sulfanilamido-p-benzoquinone*, red-brown, m. 279-81° (from AcOH); on heating in AcOH it changes to 2,5-disulfanilamidobenzoquinone. Similarly I and sulfapyridine gave *2-methoxy-5-sulfapyridino-p-benzoquinone*, red, decomp. 273° (from 80% AcOH); sulfathiazole similarly gave red *2-methoxy-5-sulfathiazolo-p-benzoquinone*, decomp. 215-7° (from 60% AcOH). To 1 g. 2,6-dimethoxy-p-benzoquinone in 75 ml. hot AcOH was added 1 g. $PhNH_2$ and after 2 hrs. refluxing the mixt. gave 1 g. 2,6-dianilino-p-benzoquinone, m. above 300°. When 1 g. 2,6-dimethoxy-p-benzoquinone in 75 ml. hot AcOH was treated with 0.3 g. $PhNH_2$ and refluxed 2 hrs. there was formed after concn. and diln. with H_2O 0.8 g. 2-methoxy-6-anilino-p-benzoquinone, m. 160°. G. M. Kosolapoff

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IOFFE, I. S.

USSR/Chemistry

Card 1/1

Authors : Ioffe, I. S. ; and Sukhina, A. F.

Title : Investigation of quinones. Part 9.- Reaction of methoxyquinones with amines.

Periodical : Zhur. Ob. Khim. 24, Ed. 4, 705 - 709, April 1954

Abstract : The reaction of methoxyquinones with amines shows two trends: 1) addition of the amino radical to the non-substituted carbon atom of the quinoid nucleus and 2) displacement of the methoxyl group by the amino group. The amino radical subjected to the effect of the methoxyl group rapidly attaches itself to the non-substituted carbon atom provided the latter is in para-position relative to the amino group. Displacement of methoxyl group by still another amino radical at an aniline surplus is already much slower. Six references; 5 USSR since 1946; 1 English 1946; 2 German since 1891. Chemical formulas.

Institution : ......

Submitted : July 28, 1953

IOFFE, Isaak Solomonovich; KHAVIN, Z.Ya., redaktor; ERLIKH, Ye.Ya., tekhnicheskiy redaktor

[Organic chemistry] Organicheskaia khimiia. Izd-vo khim. lit-ry, 1956. 438 p. (MIRA 9:7)
(Chemistry, Organic)

5 (3)

AUTHORS: Ioffe, I. S., Zal'manovich, M. Z. SOV/79-29-8-51/81

TITLE: N-Substituted Amides of Salicylic Acid and Its Derivatives. I. Arylides of 3,5-Dichloro- and 5-Nitrosalicylic Acid

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 8, pp 2682 - 2685 (USSR)

ABSTRACT: Some arylides of salicylic acid are highly active disinfectants (Ref 1) (e.g. the "Anabial"). Particular attention is due to the synthesis of the parent compound of this group, the salicylanilide, by condensation of aniline with esters of the salicylic acid, e.g. with salol (Ref 8), where phenol is separated. This "salol method" is recommended as a general method of synthesizing various arylides of salicylic acid by heating salol with amines (Ref 10), in the medium of an inert solvent, e.g. trichlorobenzene. The experiments carried out by the authors, however, indicated that the solvent decreases the yield and only complicates the process. This reaction is shown to proceed quite smoothly when a mixture of salol and amine is fused together at 150-180° in an equimolar ratio, in which case at the beginning of the reaction the low-melting

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N-Substituted Amides of Salicylic Acid and Its Derivatives. I. Arylides of 3,5-Dichloro- and 5-Nitrosalicylic Acid

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salol acts as a solvent, and later on the resultant phenol. After termination of the reaction (1-2 hours) the phenol is removed by distillation, and the arylamide is purified from the alkaline solution by precipitation with acid and recrystalization from alcohol. In this way, yields of 80-95% were obtained in different arylides such as m-anisidide (Ref 8), n-phenetidide (Ref 9), o-nitroanilide and others (Refs 1,11,9). This method was also used for derivatives of salicylanilide with substituents in the salicyloyl nucleus. Different chlorine derivatives of the salicylanilide have so far been obtained by chlorination of this compound (Refs 12-14), while the degree of chlorination depends on the reaction conditions, and mixtures of different chlorinated chlorine derivatives are formed. The authors obtained easily the chlorine derivatives of salicylanilide in a pure state by fusing together the salol (and, accordingly, the chlorine salts) with aniline or chloro anilines. In this way, the 4'-chloro salicylanilide and 2',5'-dichloro salicylanilide (Ref 9) were obtained from

Card 2/3

N-Substituted Amides of Salicylic Acid and Its Derivatives. I. Arylides of 3,5-Dichloro- and 5-Nitrosalicylic Acid

SOV/79-29-8-51/81

salol, and the 3,5,4'-trichloro salicylanilide and 3,5,2',5'-tetrachloro salicylanilide (Ref 1) from 3,5-dichloro salol. Tables 1 and 2 present further arylides of the 3,5-dichloro salicylic acid and 5-nitrosalicylic acid synthesized in the same way. There are 2 tables and 16 references, 2 of which are Soviet.

ASSOCIATION: Voyenno-meditsinskaya akademiya imeni S. M. Kirova (Military Medical Academy imeni S. M. Kirov)

SUBMITTED: July 19, 1958

Card 3/3