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Separation of acenaphthene from coal tar. A. I. Kiprianov and M. M. Dashevskii. *Anilinokrasochnaya Prom.* 2, No. 8-9, 13-18(1932).—The results of lab. extns. of acenaphthene (I) from heavy coal-tar oils of various sources by fractional distn. in vacuo are described and tabulated. The final purification of high-percentage I can be made by crystn. from alc., and of the low-melting fractions by the method of Ger. pat. 277,110.

Chas. Blanc

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3RD AND 4TH ORDERS

PROCESSES AND PROPERTIES INDEX

Synthesis of alcamine acids by the cyanohydrin method. A. I. Kipriyanov and G. I. Kipriyanov. *J. Gen. Chem.* (U.S.S.R.) **2**, 585-9(1932).—The proposed term "*alcamino acid*" is constructed from alcamine (amino alc.) and amino acid to distinguish this type of aminohydroxy acids from that of serine. In the synthesis of alcamino acids by the interaction of a hydroxyalkyl halide and amino acid esters is usually obtained a mixt. of monohydroxyalkyl- and dihydroxyalkylamino acids, the sepn. of which is very difficult, and in the lower amino acids, such as glycocoll and alanine, is impossible (C. A. **21**, 2466; **22**, 3134; **26**, 108). Zelinskii and Stadnikov (*J. Russ. Phys. Chem. Soc.* **38**, 722; **40**, 790) produced amino acids from CO compds. with KCN and NH_3, while by using amines in place of NH_3 can be obtained amino acids substituted in the NH_2 group. It was found that by using amino alcs. instead of NH_3 with CO compds. and KCN are easily obtained good yields of alcaminonitriles which on sapon. give alcamino acids. Thus the HCl salt of ethanolamine (I), condensed at room temp. with CH_2O, Me_2CO, BzH and cyclohexanone (II), produced with liberation of heat 70% of alcamino acids synthesized for the 1st time. I condensed with II gave *hydroxyethylaminocyclohexanenitrile*, $C_6H_{10}(CN)NH(CH_2)_2OH$ (III), which on sapon. produced *hydroxyethylamino-1-cyclohexanecarboxylic acid*, $C_6H_{10}(CO_2H)NH(CH_2)_2OH$ (IV). In other cases the nitriles were not sepd. but directly sapond. to the acids. BzH gave with I *phenylhydroxyethylaminoacetic acid*, $C_6H_5CH(CO_2H)NH(CH_2)_2OH$ (V), Me_2CO, *dimethylhydroxyethylaminoacetic acid*, $Me_2C(CO_2H)NH(CH_2)_2OH$ (VI), and CH_2O, *hydroxyethylaminoacetic acid*, $CH_2(CO_2H)NH(CH_2)_2OH$ (VII). I, b. 170-2°, was prepd. by Knorr's method (Ger. pat. 97,102) and converted to the HCl salt with concd. HCl to neutral reaction to litmus, and used in soln. (48 g. in 100 cc.). V was prepd. when a mixt. of 3.3 g. KCN in 15 cc. H_2O, 5.4 g. BzH, 10.5 cc. I.HCl and 15 cc. MeOH was digested 1.5 days, the MeOH distd. off, the oil extd. with Et_2O, the Et_2O expelled, the oil dissolved in dil. HCl, any insol. matter extd. with Et_2O, then concd. by evapg., sapond. with concd. HCl, after 2 hrs. standing dild. with H_2O, concd. on the water bath, sepd. from NH_4Cl by treating with alc. and

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Et_2O, there was obtained 8.4 g. (71.8%) of V; HCl salt m. 178-91° in a sealed capillary tube (decompn.), sol. in H_2O and alc. About 65% of the free acid of V was sepd. by treating a concd. soln. of the salt with concd. NH_3 to neutral reaction, and the rest by the $Ag(OH)_2$ and H_2S method. V m. 217-8° in a sealed capillary tube, is poorly sol. in cold H_2O and alc., insol. in Et_2O. A yield of 7.25 g. ([illegible]8%) of III, m. 78-[illegible]°, was prepd. when a mixt. of 20 cc. soln. of I, 8.0 g. KCN, 12 g. II, b. 1[illegible]7°, and 50 cc. Et_2O was digested 1 day, the ether layer sepd., the aq. layer extd. with Et_2O, the combined ether exts. dried with K_2CO_3, the Et_2O expelled; white crystals from Et_2O, easily sol. in alc., sparingly sol. in H_2O. The HCl salt of III, m. 95.8°, was prepd. by passing dry HCl into III in Et_2O. The aq. layer of the reaction and the mother liquor from the sepn. of III were combined and hydrolyzed with HCl, the reaction mass was evapd. to dryness, the mineral salts were sepd. by recrystg. from alc., IV was sepd. from its HCl salt with NH_3, and the mother liquor subjected to similar operations produced in all 10 g. (41.9%) IV, (41.9%), or 75.7% of III and IV combined. IV, m. 252.4° in a sealed capillary tube, is sol. in H_2O, poorly sol. in alc., and insol. in Et_2O. VI was obtained in 6 g. yield (40%) by digesting 1 day a mixt. of 9.75 g. HCl salt of I, 6.5 g. KCN, 5.8 g. Me_2CO and 25 cc. H_2O, hydrolyzing with an equal vol. of concd. HCl on the water bath for 2 hrs. and sepg. the mineral salts as above. The sepn. of a cryst. HCl salt of VI being impossible, the free acid was obtained by the $Ag(OH)_2$ method. VI, m. 243.5° in a sealed capillary tube, is sol. in H_2O, little sol. in alc. and insol. in Et_2O. VII, m. 174-5°, was obtained in 5.7 g. yield (62.3%) when a soln. of 5 g. KCN was added dropwise in 3 hrs. with stirring and cooling to a mixt. of 5.7 g. HCl salt of I and 5.8 g. 40% CH_2O, and allowed to stand 1.5 hr. at room temp., an equal vol. of concd. HCl was added, let stand 12 hrs., digested 1.5 hrs. in a water bath, sepd. from KCl and NH_4Cl and worked up with $Ag(OH)_2$ as above; white crystals were obtained easily sol. in H_2O, slightly sol. in alc. and insol. in Et_2O.

Chas. Blanc

1α

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Use of polychlorobenzenes in the synthesis of dyes. III. Preparation of p-chlorophenol from p-dichlorobenzene. A. I. Kipriyanov and M. M. Dashevskii. *Ukrain. Khem. Zhur.* 7, Wiss.-tech. Abt. 78-86(1932); cf. *C. A.* 25, 5134.—The hydrolysis of p-$C_6H_4Cl_2$ with aq. NaOH gives a max. yield of 30% of p-C_6H_4ClOH (I); 2.5 mols. of alkali suffice for the complete removal of Cl. With NaOH-MeOH and a little Cu powder at 225° yields up to 85% are obtained, probably because of the insoly. of the C_6H_4ClONa formed in the medium. **IV. Preparation of p-aminophenol from p-dichlorobenzene.** A. I. Kipriyanov, G. I. Kipriyanov and M. M. Dashevskii. *Ibid.* 87-93.—The influence of various factors on the formation of p-$H_2NC_6H_4OH$ from (I) and aq. NH_3 in presence of $CuSO_4$ has been examd. The optimum yield (82.5%) was obtained by heating with 4 vols. of 33% NH_3 and 10% of $CuSO_4$ for 3 hrs. at 185°. **V. Preparation of pyrocatechol from polychlorobenzenes.** A. I. Kipriyanov and B. D. Suich. *Ibid.* 94-100.—o-$C_6H_4Cl_2$ is hydrolyzed to o-C_6H_4ClOH with 2.5 mols. of NaOH-MeOH at 225° in a rocking autoclave. The further hydrolysis to pyrocatechol by NaOH in presence of $CuSO_4$ gives yields up to 71%, provided a Cu- or Ag-lined autoclave is employed. $Ba(OH)_2$ and Na_2CO_3 are unsatisfactory hydrolytic agents. The concn. of alkali must not exceed 10%, but the temp. and duration of heating are of secondary importance.

B. C. A.

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Determination of β-naphthalenesulfonic acid. A. I. Kiprianov, S. M. Mikhlavskii and F. A. Bilenko. *Zavodskaya Lab.* 3, 414-16(1934).—The detn. of β-$C_{10}H_7SO_3H$ (I) and indirectly of α-$C_{10}H_7SO_3H$ (II) in a sulfonation mixt. is based on the insoly. of $(\beta\text{-}C_{10}H_7SO_3)_2Mg$ (III) and the soly. of $(\alpha\text{-}C_{10}H_7SO_3)_2Mg$ in a concd. soln. of $MgCl_2$ or $MgSO_4$. The method gives sufficiently accurate results for the control of sulfonation of $C_{10}H_8$ in the production of β-$C_{10}H_7OH$ with a considerable saving in time and labor as compared with the procedure of Euwes (C. A. 3, 2702). By pptg. III from a concd. soln. of 0.5-1 g. of the mixed acids with 80 cc. of 40% $MgCl_2$, washing the ppt. with 35% $MgCl_2$ and detg. S by the Eschka method, the values obtained are 1% low; this is probably caused by a partial hydrolysis of III by washing and is confirmed by somewhat high values for H_2SO_4 in the sulfonation mixt. The use of the time-consuming Eschka method can be avoided by substituting $MgSO_4$ for $MgCl_2$ as a precipitant. $MgSO_4.7H_2O$ heated at 135° gives the stable hydrate $MgSO_4.H_2O$ without the formation of a basic salt. Hence by drying a mixt. of $MgSO_4$ and III at 135° to a const. wt. and then detg. the sulfate ion, the percentage of $MgSO_4.H_2O$ and that of III by difference can be calcd. Dissolve 7.5 g. of the sulfonation mixt. in 100 cc. H_2O, filter, wash and weigh the insol. residue, dil. the filtrate to 250 cc., withdraw 50 cc. of the soln., add 2-3 cc. of methyl red soln., neutralize on a water bath with dry MgO, dissolve any excess of MgO with a few drops of dil. H_2SO_4, add, with stirring, hot satd. $MgSO_4$ (40 g. $MgSO_4.7H_2O$ in 10 cc. H_2O), digest 1 hr. in a boiling-water bath, let stand overnight at room temp., filter off the ppt. through a dried and weighed Schott crucible with a porous bottom with strong suction (do not wash the ppt.), use the filtrate for transferring the ppt. from the beaker to the filter, dry the crucible with the ppt. 2-3 hrs. at 100° and 3-4 hrs. at exactly 133.5° to a const. wt. and weigh; dissolve the ppt. in hot H_2O, dil. to 500-600 cc., acidify with HCl, det. SO_4 with $BaCl_2$ and calc. the percentage of $MgSO_4.H_2O$ and that of III by difference. H_2SO_4 in the sulfonation mixt. is detd. with $BaCl_2$ in a sep. sample. II is detd. indirectly by titrating the total acidity with 0.1 N NaOH against methyl red and then calcg. The results of 10 detns. of the same sulfonation mixt. are: I 56, 56.8, 56.6, 56.8, 56.6, 56.9, 56.6, 57.3, 56.9, 56.8, mean 56.7%, and II (calcd.) 13.4%. The accuracy, checked with an artificial mixt. of recrystd. Kahlbaum I and II, is 0.3-0.7% (high). The same sulfonation mixt. detd. by pptn. with $MgCl_2$ and detn. of S by the Eschka method gave from 55.8 to 56.8% I with an av. of 56.4%. C. B.

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3RD AND 4TH ORDERS

Determination of benzene-mono- and -disulfonic acids. A. I. Kipriyanov and E. D. Such. *Zavodskaya Lab.* 3, 633-5(1934).—Three g. of material is dissolved in 250 cc. of H_2O, H_2SO_4 is detd. in 25 cc., and total acidity in a second 25-cc. portion by titration with 0.1 N KOH (phenolphthalein). The titrated soln. is evapd. to dryness, and the residue of K salts is heated at 250° to const. wt. The percentage content of $PhSO_3H$ = 135.1(S − 0.0157A), and of $C_6H_4(SO_3H)_2$ = 119.8(0.0196A − S), where S is the wt. of K salts less that of K_2SO_4, and A is total acidity less that due to H_2SO_4.   B. C. A.

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Oxidation of acenaphthene to acenaphthenequinone. A. I. Kiprianov and M. M. Iushevskii. *J. Applied Chem.* (U. S. S. R.) 7, 944-9(1934). In the oxidation of the acenaphthene to acenaphthenequinone a considerable residue is obtained, insol. in Na_2CO_3 and $NaHSO_3$, which lowers the yield of the acenaphthenequinone. This residue is composed of an isomorphic mixt. of acenaphthenequinone and naphthalic acid anhydride. The low soly. of the latter in Na_2CO_3 and $NaHSO_3$ is probably due to the difference in the chem. properties of the consecutive mol. layers of the cryst. structure. The isomorphic mixt. may be sepd. by extg. with Na_2CO_3 and $NaHSO_3$ at elevated temps. and pressures or by treating the mixt. in hot $PhNO_2$ with the same substances; this raises the small yields of acenaphthenequinone.

A. A. Boehtlingk

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A·3

Alkamino-acids (hydroxyalkamino-acids); their synthesis and reactions. A. I. Kiprianov (Trav. Inst. Chim. Charkov, 1936, 1, 39—51).—A review of published papers. In [illegible] R. T.

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Ca

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Chlorination of methane. I. Preparation of carbon tetrachloride. A. I. Kirkanov and T. S. Kusner. *J. Applied Chem.* ~~(U. S. S. R.)~~ 8, 673-84(1935).—Up to 90% of CCl_4 was obtained when passing a mixt. of CH_4, HCl and Cl_2 through an activated C catalyst, at a reaction temp. of 525-30°. The ratio of the ingredients was Cl:HCl = 1:2. 100 l. Cl_2 can be handled hourly by 100 g. activated C, and the approx. ratio, depending upon the purity, of CH_4:Cl_2:HCl = 14:64:30 100 l. A detailed description of the exptl. procedure is presented.

A. A. Boehtlingk

ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION

BC

PROCESSES AND PROPERTIES INDEX

A-3

(A) Cyanine dyes from amino-derivatives of benzthiazole. (B) Cyanine dyes from isomeric dimethylbenzthiazoles. A. I. K[illegible] and [illegible] D. Sytnick (Trav. Inst. Chim. Charkov, 19[illegible], 2, 15—24, 25—32).—(A) *5-Dimethylamino-1-methylbenzthiazole*, m.p. 71°, prepared from 5-amino-1-methylbenzthiazole and p-$C_6H_4Me·SO_3Me$, or by a Jacobsen synthesis from $NPhMe_2$, yields a coloured 3-N- (I) and a colourless *5-N-methiodide*, both m.p. 202° (decomp.), and a 3-N- (II), m.p. 243°, and *5-N-ethiodide*, m.p. 146°; the yield of 3-N-derivative rises with increasing duration and temp. of reaction with the alkyl iodides. *5-Diethylamino-1-methylbenzthiazole*, b.p. 18[illegible]—19[illegible]°/15 mm. [*3-N-ethiodide* (III), m.p. 7[illegible]°], was prepared analogously. In pyridine (at the b.p.) $CH(OEt)_3$ and (I), or (II) yield *5:5'-bisdimethylamino-2:2'-dimethyl-* (IV), m.p. 244°, or *-2:2'-diethyl-thiocarbocyanine iodide* (V), and *5:5'-bisdiethylamino-2:2'-diethylthiocarbocyanine iodide* (VI) is prepared similarly from (III). The 8-*Me* derivative of (IV) is obtained when NMe_3 is added to the reaction mixture. The 8-*Me* derivatives of (V) and (VI) are prepared similarly to them, using $CMe(OEt)_3$ in place of $CH(OEt)_3$. 2-Iodoquinoline ethiodide and (I) in EtOH–KOH (1 hr. at the b.p.) yield *5-dimethylamino-1-methyl-2'-ethylthio-ψ-cyanine iodide*, m.p. 171°, whilst with quinoline methiodide *5-dimethylamino-1':2-dimethylthioisocyanine iodide*, m.p. 17[illegible]°, is obtained. Max. light absorption data are recorded for the above dyes. The dyes are valuable sensitisers of photographic emulsions.

(B) Thioacet-toluidide in aq. NaOH and aq. $K_3Fe(CN)_6$ at 7° yield *1:3-dimethylbenzthiazole*, b.p. 16[illegible]—163°/55 mm., the *ethiodide*, m.p. 150°, of which gives 3:3'-*dimethyl-* or 3:3':8-*trimethyl-2:2'-diethylthiocarbocyanine iodide* when heated with $CH(OEt)_3$ or $CMe(OEt)_3$, respectively. 2-Amino-4-methylthiolphenol and Ac_2O in C_6H_6 (at the b.p.; 2 hr.) yield *1:4-dimethylbenzthiazole*, b.p. 153—156°/25 mm., m.p. 34°, from the *ethiodide*, m.p. 195—196°, of which are prepared 4:4'-*dimethyl-* and 4:4':8-*trimethyl-2:2'-diethylthiocarbocyanine iodide*. The sensitising action of the isomeric dyes is unaffected by position of the Me, but the greatest bathochromic effect is given by the 4:4'-Me_2 derivatives. R. T.

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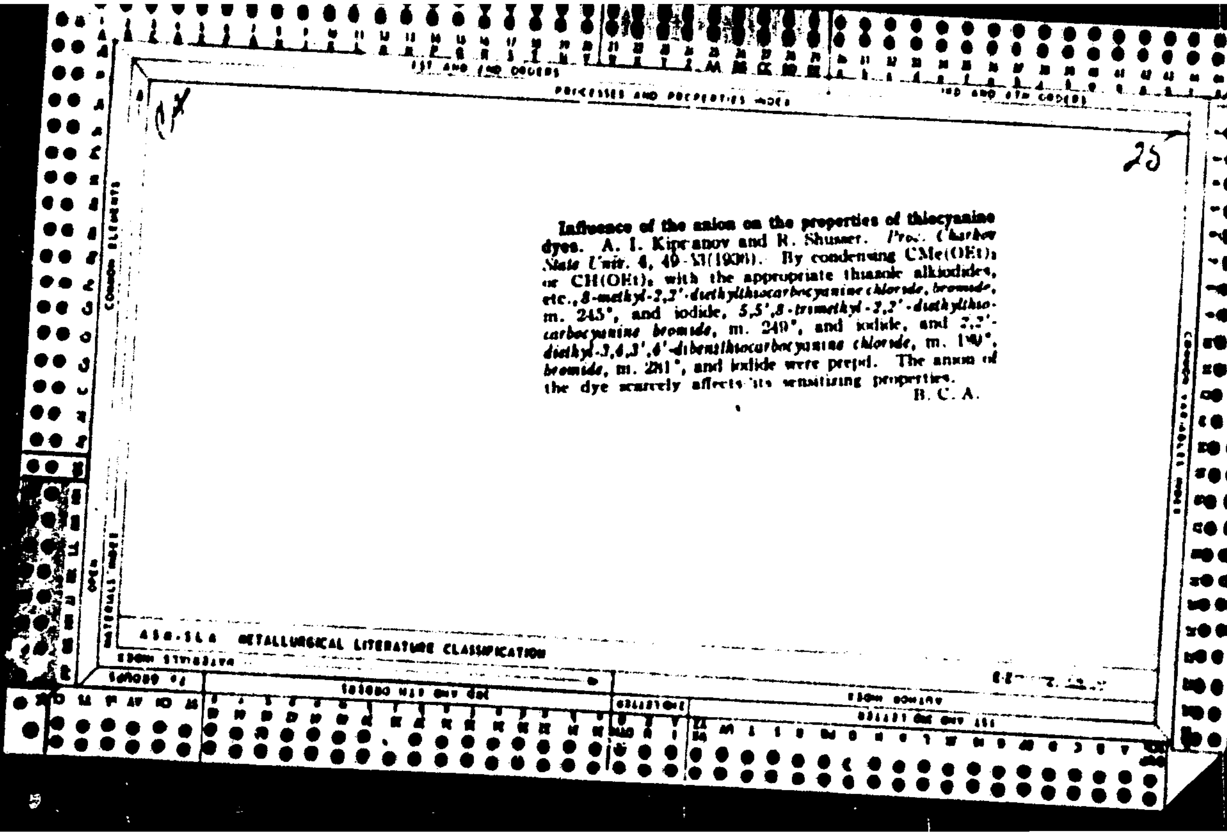

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Influence of the anion on the properties of thiocyanine dyes. A. I. Kiprianov and R. Shusser. *Proc. Charkov State Univ.* 4, 49–53(1936). By condensing CMe(OEt)$_3$ or CH(OEt)$_3$ with the appropriate thiazole alkiodides, etc., *8-methyl-2,2'-diethylthiocarbocyanine chloride, bromide*, m. 245°, and iodide, *5,5',8-trimethyl-2,2'-diethylthiocarbocyanine bromide*, m. 249°, and iodide, and *2,2'-diethyl-3,4,3',4'-dibenzthiocarbocyanine chloride*, m. 190°, *bromide*, m. 281°, and iodide were prepd. The anion of the dye scarcely affects its sensitizing properties.

B. C. A.

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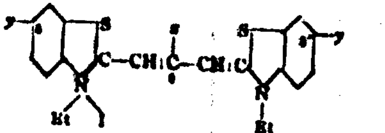
Cyanine dyes. I. Thiocarbocyanines. A. I. Kiprianov, Z. P. Sytnik and E. D. Sych. *J. Gen. Chem.* (U. S. S. R.) 6, 42-9(1936).—Eleven dyes of the general formula



were synthesized in which x is H, Me, OMe or Ph and y is H, Me or OEt. Attempts to prep. the 8-Ph and 5,5'-di-EtO derivs. were unsuccessful. The general synthetic method used was condensation of the quaternary salts of the heterocyclic bases contg. a reactive Me group with esters of ortho acids. All 3 benzothiazoles were prepd. by Jacobson's method which consists in fusing the Ac derivs. of the aromatic amines with P_2S_5 and oxidation of the resulting thioamides with $K_3Fe(CN)_6$. The yield of thioamides has been increased from 30 to 50-60% by introducing better control of the fusion temp. Unpurified P_2S_5 was used. Thiophenacetin m. 117° (from AcOH) (according to Sachs and Loewy, m. 99-100°; cf. *Ber.* 37, 876). A new compd., *1-methyl-4-ethoxybenzothiazole* (I), m. 57.5°. Increased yields of some of the esters are reported: $HC(OEt)_3$, 45%; $MeC(OEt)_3$, 60% (cf. *Ber.* 15, 116; *C. A.* 23, 943). The max. absorptions observed in alc. for y = H, Me and OEt, resp., are as follows: x = H, 5580, 5680, 5710; Me, 5390, 5430, 5540; OMe, 5360, 5420, 5540; Ph, 5600, —, —. Substituents in the 8-position, regardless of their nature, increase the sensitizing action of the thiocarbocyanines. A finely divided mixt. of 33 g. P_2S_5 and 54 g. PhNHAc was heated on a water bath with continuous stirring until the whole mass was molten and then for 5 min. more. Extn. of the cooled melt with successive portions of 8% aq. NaOH until the alk. ext. no longer was rendered turbid by acidification, addn. of dil. H_2SO_4 to the combined exts. to incipient pptn. and pptn. with CO_2 gave 60-65% of impure thioacetanilide, m. 75-8°, suitable for the prepn. of 1-methylbenzothiazole (II). P_2S_5 was prepd. by melting together P and S in theoretical proportions. *p*-Thioacetotoluide was prepd. by an analogous method at 130° in 55% yield. Thiophenacetin, 50% yield, m. 113-14°. The yields of benzothiazoles and their ethiodides were: II, b_{16} 125°, 60%, ethiodide, m. 191°, 90%. 1,5-Dimethylbenzothiazole (III), distd. in vacuo, 80%; ethiodide, m. 166-70°, 84%. I, m. 57.5° (from alc.), b_{16} 135-40°, 35%; ethiodide, m. 161-2° (from alc.), 85%. In the prepn. of $HC(OEt)_3$, the higher yield is obtained by adding the $CHCl_3$ to a gently boiling

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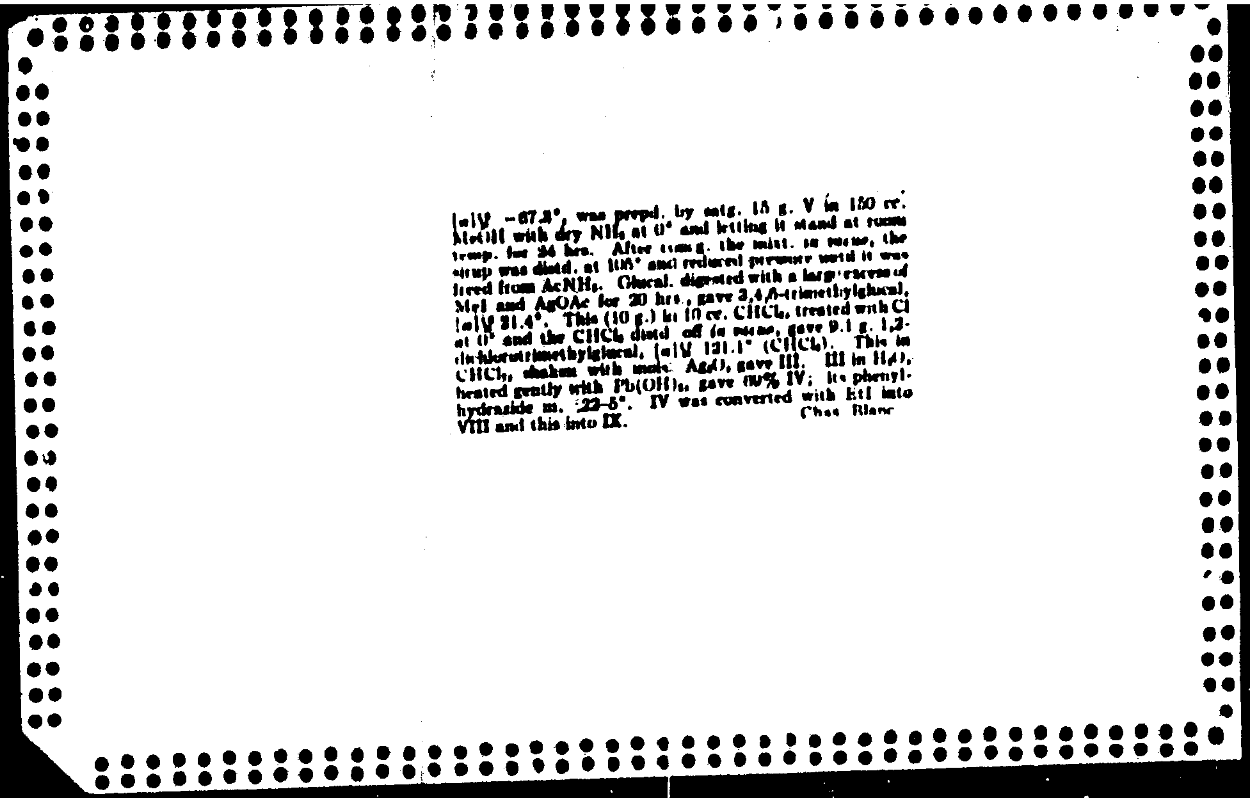

[α]$_D^{20}$ −67.3°, was prepd. by satg. 15 g. V in 150 cc. MeOH with dry NH$_3$ at 0° and letting it stand at room temp. for 24 hrs. After evapg. the mixt. in vacuo, the sirup was dried. at 105° and reduced pressure until it was freed from AcNH$_2$. Glucal. digested with a large excess of MeI and AgOAc for 20 hrs., gave 3,4,6-trimethylglucal, [α]$_D$ 21.4°. This (10 g.) in 10 cc. CHCl$_3$, treated with Cl at 0° and the CHCl$_3$ distd. off in vacuo, gave 9.1 g. 1,2-dichlorotrimethylglucal, [α]$_D$ 121.1° (CHCl$_3$). This in CHCl$_3$, shaken with moist Ag$_2$O, gave III. III in H$_2$O, heated gently with Pb(OH)$_2$, gave 60% IV; its phenylhydrazide m. 122-5°. IV was converted with EtI into VIII and this into IX.

Chas. Blanc

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Synthesis of benzothiazole and its μ-alkyl-substitution products. A. I. Kiprianov, Z. P. Suitnik and N. I. Grigor'eva. *J. Gen. Chem.* (U. S. S. R.) 6, 212-5 (1936). — The improved method of production of benzothiazole (I) and μ-alkyl derivs. is based on that of [illegible] (*Ber.* 12, [illegible]). In the prepn. of o-H[illegible] (II) by interaction of o-$O_2NC_6H_4Cl$ with Na_2S_2 and reduction of the $(o\text{-}O_2NC_6H_4S)_2$ (III) to II, 80% $(H_2NC_6H_4S)_2Zn$ (IV) was obtained by treating III with 10 parts of 20% AcOH, 10 parts of concd. HCl and 1 part of Zn dust for 1 hr. and pptg. IV in the filtrate with NaOAc. A considerable saving of AcOH and Zn with 90% II resulted by treating alternately in small portions 5 g. III in 30 g. of 100% AcOH with 8 g. Zn dust and 20 cc. HCl within 25 min. and pptg. IV by dilg. the filtrate with 3 parts of water. The method of reduction of III and acetylation of II in 1 operation with formation of 80% μ-methylbenzothiazole consists of reduction of III in 100% AcOH as described above, followed by refluxing of the reaction mixt. with 10 g. Ac_2O and 20 cc. C_6H_6 for 3 hrs. and steam distn. of the alkalized mixt. I and its derivs. were obtained by refluxing a mixt. of IV with a corresponding acid and steam distg. the alkalized reaction mixt.: I (80%), from 5 g. IV and 25 cc. HCO_2H for 5 hrs.; ethylbenzothiazole (72%), from 20 g. IV and 60 g. $EtCO_2H$ for 18 hrs.; propylbenzothiazole (80%), from 5 g. IV and 20 g. $PrCO_2H$ for 6 hrs.; butylbenzothiazole (59%), from 35 g. IV and 110 g. $BuCO_2H$ for 20 hrs. These compds. were identified as [illegible] compds. by boiling with HCl.

Chas. Blanc

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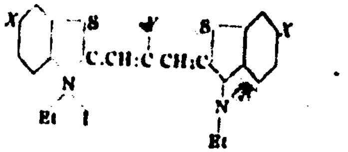
Relation between the structure and optical and photographic properties of cyanine dyes. II. Thiocyanines with substituents containing sulfur. A. I. Kiprianov, Z. P. Suitnikov and E. D. Sukh. *J. Gen. Chem.* (U. S. S. R.) 6, 576-81(1936); cf. *C. A.* 30, 4809^4, 4862^8.—The function of S in the thiocyanine dyes in producing the sensitizing and stabilizing properties was studied by synthesizing and testing thiocyanine derivs. contg. S in the substituents in addn. to the S in the heterocycles. Five dyes were produced of the general formula:



where *X* and *Y* are substituents contg. S (a thioalkyl as the simplest group). The results show that S substituents have no sp. effect on the sensitizing and stabilizing properties of thiocyanine dyes. In the synthesis of the dyes several new methods and compds. were developed and identified. A diazo soln. from 8.2 g. amino-1-methylbenzothiazole, m. 122° (Sheppard, *Bull. soc. franc. phot.* 12, 382(1925)), and 3.5 g. $NaNO_2$ is treated with 12 g. of cryst. NaOAc and then poured, with stirring, into 8 g. K xanthate in 50 cc. H_2O at 70°. The oily xanthate is extd. with Et_2O and, after drying and freeing from the Et_2O, it is boiled with 8 g. KOH in 50 cc. alc. for 3 hrs., the alc. is distd. off and the residue is shaken with 6.2 g. Me_2SO_4 in 100 cc. H_2O, giving 5.1 g. methyl-1-methylbenzothiazole (I). EtI deriv. (II), m. 215°, resulted in 2.2 g. yield from 5.1 g. I and 5 g. EtI by heating the mixt. in a sealed tube at 100° for 4 hrs. II (0.9 g.) with 0.8 g. $HC(OEt)_3$ in 5 g. of dry C_5H_5N is digested in an oil bath for 3 hrs., giving 75% dye, *3,3'-diethyl-5,5'-methylmercaptothiocarbocyanine iodide*. II (0.4 g.) and 0.4 g. $MeC(OEt)_3$ in 3 g. C_5H_5N heated for 1.5 hrs. gave 50% *3,3'-diethyl-5,5'-dimethylmercapto-8-methylthiocarbocyanine iodide*. MeSH is obtained in 80% yield when a NaSH soln. (from 160 g. NaOH in 600 cc. H_2O satd. with H_2S) is slowly treated, with stirring, with 126 g. Me_2SO_4 (1 hr.) under a condenser cooled with ice and water. Me_2S, b. 38°, is retained in the reaction flask, while gaseous MeSH is conducted through a $CaCl_2$ U-tube and is condensed by a freezing mixt. EtSH, b. 37°, is similarly prepd. in 70% yield with the condenser fed with H_2O at 40–50°, retaining Et_2S, b. 92°, in the flask. *$MeSCH_2CN$*, b_{50} 74.5°, resulted in 56% yield when a soln. of 37.5 g. MeSH with 18 g. Na in 230 cc. of abs. alc. was slowly introduced, with stirring, into 59 g. $ClCH_2CN$ in alc. The filtrate from NaCl was freed from the alc. and the residue redistd. *$MeSCH_2CO_2Et$*, 174-6°, is prepd. in 33.6% yield from an equimol. mixt. of $ClCH_2CO_2Et$ and MeSNa in alc. by dilg. it with H_2O and redistg. the oil. A mixt. of 34 g. of the ester with 61 g. of 23% NH_4OH after standing for 24 hrs. gave 67.5% *$MeSCH_2CONH_2$*, b. 104°. *$MeSCH_2C(:NH)OEt$* (III) is prepd. in 95.5% yield by conducting 10 g. of dry HCl into 22.5 g. $MeSCH_2CN$ in 15 cc. of abs. alc. After 4-5 hrs. III.HCl is filtered off and decompd. with KOH. *$MeSCH_2C(OEt)_3$* (IV),

0V21

b$_{15}$ 78-81°, resulted in 25% yield from 10 g. III.HCl in 15
cc. of abs. alc. after standing for 7 days. The filtrate
from NH_4Cl is freed from the alc. and the residue redistd.
$EtSCH_2CN$, b$_{15}$ 104-5° (88.5% yield) (16 g.) in 7.3 g. alc.
treated with 7 g. HCl at -15° gave 80% *$EtSCH_2C$-*
(:NH)OEt (V), b$_{15}$ 103-4°. *3,3'-Diethyl-8-methylmer-*
captomethylthiocarbocyanine iodide resulted in 24% yield
from 1-methylbenzothiazole-EtI (VI) and 3.9 g. III in 10
cc. of abs. alc. by heating 1 hr. The same dye is obtained
from VI and IV in 22% yield. *3,3'-Diethyl-8-ethylmer-*
captomethylthiocarbocyanine iodide (11% yield) resulted
from 3 g. VI and 5.4 g. V. *3,3'-Diethyl-5,5'-dimethyl-8-*
methylmercaptomethylthiocarbocyanine iodide (11% yield)

is prepd. from IV and 1,5-dimethylbenzothiazole (Bernth- ✓
sen, *Ann.* 251, [illegible](1889)).
Chas. Blanc

PROCESSES AND PROPERTIES INDEX

Np

10

Reaction of ethanolamine with aldehydes and malonic
acid. A. I. Kiprianov and T. S. Kinner. *J. Gen. Chem.*
(U. S. S. R.) 6, 641-4(1936).—Previously it was shown
that the condensation of $H_2NCH_2CH_2OH$ (I) with alde-
hydes or ketones and HCN results in alkamino acids (*C. A.*
27, 1618). Rodionov (*C. A.* 21, 1257; 23, 1882) has
shown that the condensation of aldehydes with NH_3 and
$CH_2(CO_2H)_2$ (II) gives goods yield of β-amino acids, and
that the substitution of $EtNH_2$ for NH_3 gives poor results.
Attempts to synthesize alkamino acids by this reaction by
substituting I for NH_3 and alkylamines gave neg. results.
Refluxing 8 g. BzH, 9 g. II and 6.1 g. I in 50 cc. alc. on a
water bath for 5 hrs. gave 61% cinnamic acid (III) and no
amino acids. A similar mixt., obtained by cooling with
water, was allowed to stand overnight at room temp.,
giving 63% $PhCH:C(CO_2H)_2.H_2N(CH_2)_2OH$ (IV), m.
135-6° (decompn.), and not $PhCH(NHCH_2CH_2OH)CH$-
$(CO_2H)_2$, according to the Rodionov reaction of condensa-
tion with NH_3 or an amine. Under these conditions fur-

$O.CH:CH.CH:CCH(CO_2H)_2.NH_2$-
fural gave 76.5%
$(CH_2)_2OH$ (V), m. 137° (decompn.); salicylaldehyde gave
76% of the I salt of coumarincarboxylic acid (VI), m. 196-
7° (decompn.), and piperonal 84% of a corresponding
cryst. compd., which could not be recrystd. These con-
densation products are not β-aminodicarboxylic acids
capable of splitting off of CO_2 with the formation of β-
aminocarboxylic acids, because on heating they cleave CO_2

and I, giving the derivs. of III. Thus IV on heating gave
III, and by decompn. in H_2O with dil. H_2SO_4 there resulted
76% $PhCH:C(CO_2H)_2$, m. 195° (decompn.) (cf. Knoe-
venagel, *Ber.* 31, 2596(1898)). V with dil. HCl gave 95%

$O.CH:CH.CH:CCH:C(CO_2H)_2$, m. 197° (decompn.)
(Knoevenagel, *loc. cit.*). VI with dil. HCl gave 91%
coumarincarboxylic acid, m. 187-8° (cf. Stuart, *J. Chem.*
Soc. 49, 358(1886)). On the addn. of equimol. amts. of I
to $PhCH:C(CO_2H)_2$ and its derivs. in alc. there are formed
compds. identical with the condensation products of I
with aldehydes and II.

Chas. Blanc

Mercurial derivatives of o-cresotic acid. A. Lespagnol
and D. Bar. *Bull. soc. chim.* [5], 3, 1107-14(1936).—By
an application to the study of the Hg derivs. of o-cresotic
acid of the methods used to establish the constitution of
the analogous compds. of $o\text{-}HOC_6H_4CO_2H$, it has been
shown that there is only 1 basic Hg cresotate and that it
contains the Hg atom in the benzene ring para to the
phenolic OH. A soln. of 30 g. yellow HgO in 20 cc.
AcOH was dild. to 100 cc. and boiled free from excess
AcOH, cooled, filtered and added to a soln. contg. 40 g. Na
cresotate. The ppt. was filtered off and washed, yielding
a true Hg salt, $[MeC_6H_3(OH)CO_2]_2Hg$ (I). In boiling
solns., I is decompd. to the basic *Hg cresotate* (II), Me-

$C_6H_2(OH).CO.O.Hg$. Treatment of 20 g. II with 7.4 g.
KCN in 100 cc. H_2O gave a series of fractions of crystals in
9.9, 2.5, 7.7 and 4.1 g. yields which, by analysis, only. in

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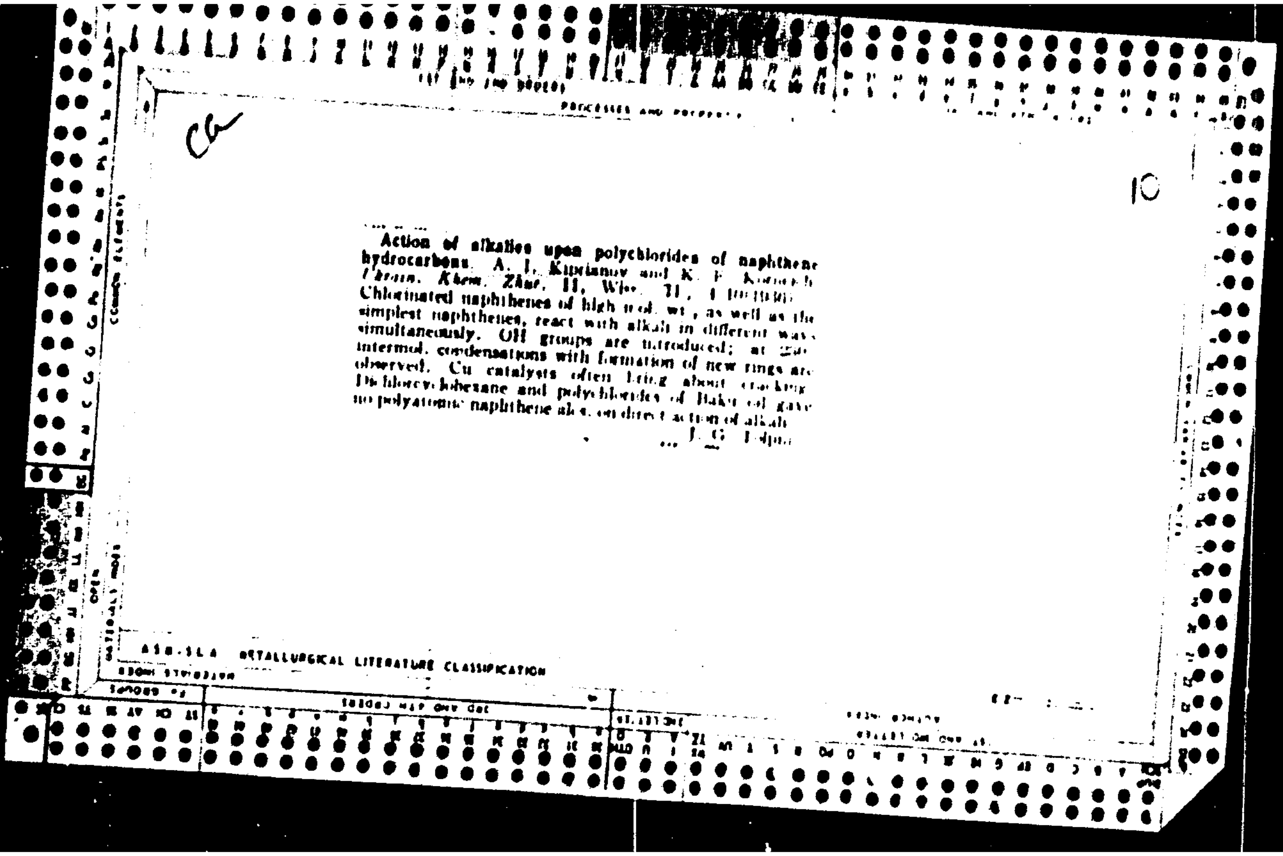
H_2O and behavior on nitration, proved to be identical
samples of *K cyanomercuricresotate*, $MeC_6H_2(OH)(HgCN)$-
CO_2K (III). Nitration of III or II by boiling with HNO_3
produced 3,2,6-$Me(HO)(NO_2)C_6H_2CO_2H$ (IV). The con-
stitution of IV was proved by reduction to the correspond-
ing aminocresotic acid (V), m. 308°, by the aid of $Na_2S_2O_4$.
Diazotization of V yielded 3,2,6-$Me(HO)_2C_6H_2CO_2H$, m.
215°, which was decarboxylated, by heating, to 1,4-di-
hydroxytoluene, m. 125°. Decarboxylation of V at 300°
under reduced pressure yielded 1-hydroxy-4-aminotoluene,
m. 175°. From the established constitution of IV and the
assumption that, in nitration, the group NO_2 takes the
place of the radical HgCN, a structure for III is postulated
from which II is arrived at by the splitting out of KCN.
The decompn. of I in boiling soln. takes place by cleavage
to II and *o*-cresotic acid.

C. R. Addinall



PROCESSES AND PROPERTIES

Ca

10

Action of alkalies upon polychlorides of naphthene hydrocarbons. A. I. Kuprianov and K. F. Koroch. *Ukrain. Khem. Zhur.* 11, Wiss. Tl., [illegible] Chlorinated naphthenes of high mol. wt., as well as the simplest naphthenes, react with alkali in different ways simultaneously. OH groups are introduced; at 250° intermol. condensations with formation of new rings are observed. Cu catalysts often bring about cracking. Dichlorocyclohexane and polychlorides of Baku oil gave no polyatomic naphthene alcs. on direct action of alkali.

J. G. Tolpin

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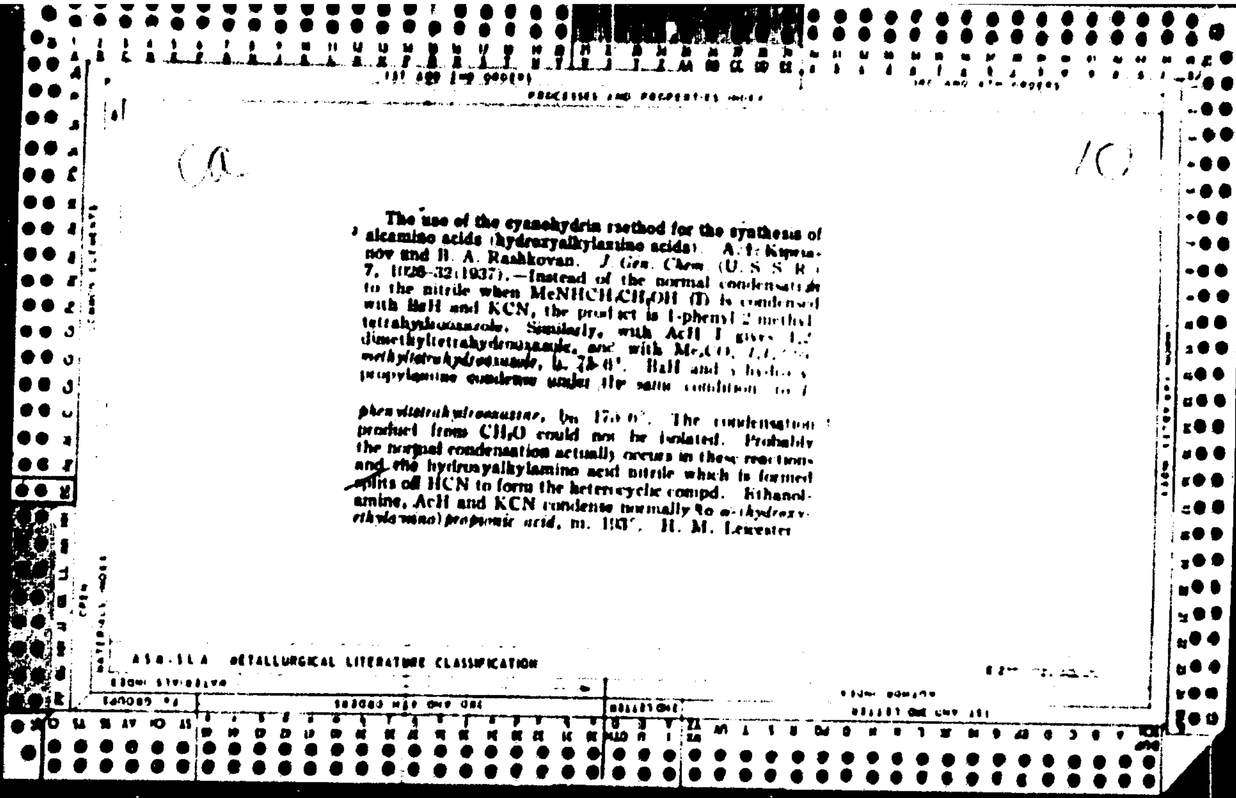

PROCESSES AND PROPERTIES INDEX

CA

10

The use of the cyanohydrin method for the synthesis of alcamine acids (hydroxyalkylamino acids). A. I. Kiprianov and B. A. Rashkovan. *J. Gen. Chem.* (U.S.S.R.) 7, 1026-32(1937).—Instead of the normal condensation to the nitrile when $MeNHCH_2CH_2OH$ (I) is condensed with BzH and KCN, the product is 1-phenyl-2-methyltetrahydrooxazole. Similarly, with AcH I gives 1,2-dimethyltetrahydrooxazole, and with Me_2CO, *1,1,2-trimethyltetrahydrooxazole*, b. 75-6°. BzH and γ-hydroxypropylamine condense under the same condition to *1-phenyltetrahydrooxazine*, b. 175-6°. The condensation product from CH_2O could not be isolated. Probably the normal condensation actually occurs in these reactions and the hydroxyalkylamino acid nitrile which is formed splits off HCN to form the heterocyclic compd. Ethanolamine, AcH and KCN condense normally to *α-(hydroxyethylamino)propionic acid*, m. 183°. H. M. Leicester

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CA

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The N-alkyl- and the N-arylmorpholones (2-ketotetrahydro-1,4-oxazines). A. I. Kiprianov, A. P. Tiselsko and I. K. Ushenko. *Trudy Khar'kov. Gosudarst. Univ.* 3, 45-52(1938); *Khim. Referat. Zhur.* 2, No. 4, 54-5(1939). —By boiling the alkyl- and the arylaminoethanols with $ClCH_2CO_2Na$ were obtained Me, Et, Pr, iso-Pr, iso-Am, $PhCH_2$, Ph and o- and p-MeC_6H_4 derivs. of morpholone. In case of the aryl derivs. morpholones are formed directly

$$ArNHCH_2CH_2OH + ClCH_2CO_2Na \rightarrow \overline{CH_2.CH_2.NAr.CH_2.CO.O} + NaCl + H_2O \text{ (I)}.$$

In case of the alkylaminoethanols the hydroxyalkylamino acids are formed first and are dehydrated to the corresponding alkylmorpholones by distn. in vacuo. The alkylmorpholones are easily hydrolyzed. By the action of concd. NH_3 on the arylmorpholones the amino acids, N-aryl-N-β-hydroxyethylaminoacetic acids, were obtained. The product of the condensation of N-phenylmorpholone with Michler's ketone was obtained in the form of an amorphous iodide. Its probable structure is $Me_2NC_6H_4CR{:}C_6H_4{:}\dot{N}Me_2 + I^-$ $(R = p\text{-}\underline{CH_2.CH_2.O.CO.CH_2.N}C_6H_4\text{-})$ (II). For the prepn. of N-methylmorpholone 17 g. of $ClCH_2CO_2H$ in 35 cc. of water are neutralized with concd. NaOH, boiled for 7 hrs. with 13.5 g. of $MeNHCH_2CH_2OH$, evapd. on a water bath and the residue distd. in vacuo. The yield was 8.4 g., colorless liquid, b_{14} 100-2°, b. 231° (Knorr, *Ann.* **307**, 199 (1899).) A yield of 14 g. of N-ethylmorpholone (14 g. from 15.6 g. of $EtNHCH_2CH_2OH$ (Knorr and Schmidt, *Ber.* **31**, 1073(1898)), colorless mobile liquid, b_9 97-9.5°. By hydrolysis was obtained N-ethyl-N-β-hydroxyethylaminoacetic acid, colorless crystals. A yield of 8 g. of N-propylmorpholone was obtained from 17 g. of propylethanolamine, b_{11} 130-4°, as a dense colorless liquid. N-Propyl-N-β-hydroxyethylaminoacetic acid is a non-crystg. sirup. The Cu salt $(C_7H_{14}O_3N)_2Cu.3H_2O$ forms dark blue needles. A yield of 2.5 g. of N-isopropylmorpholone was

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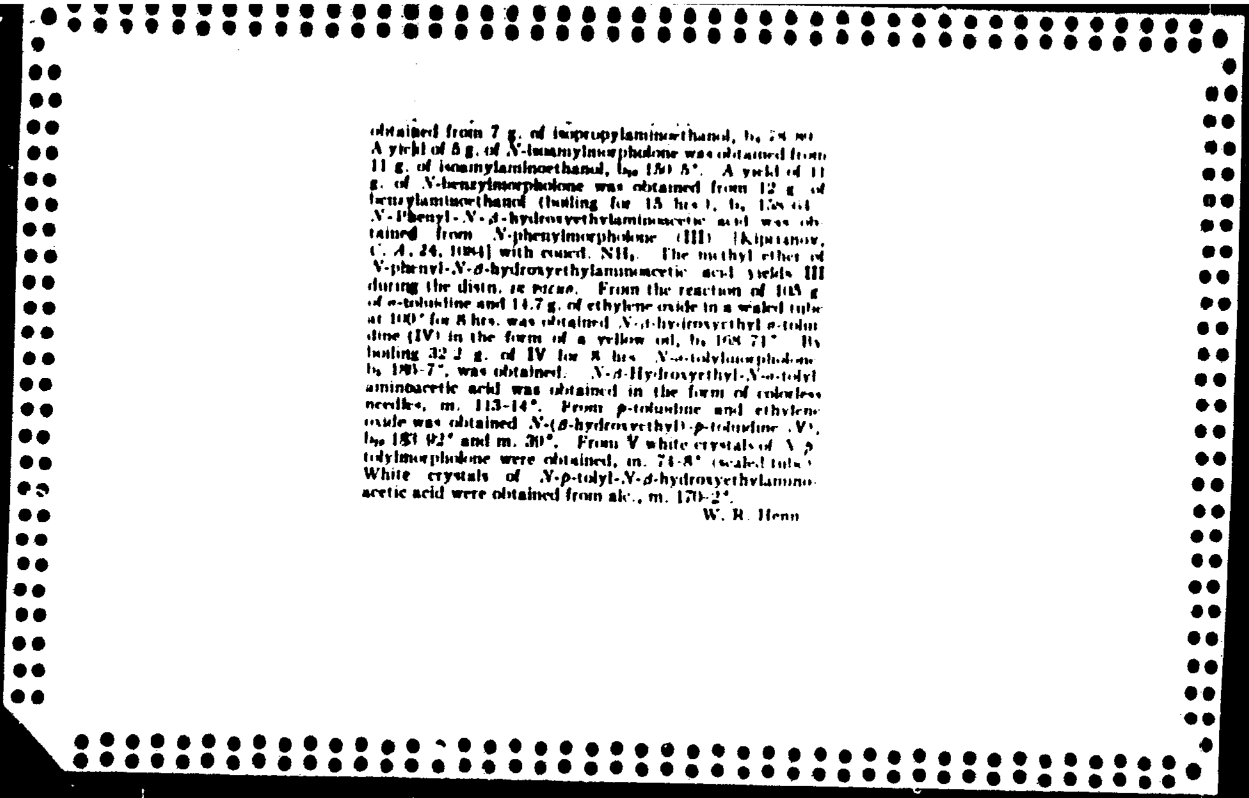

obtained from 7 g. of isopropylaminoethanol, b$_{4}$ 78-80°. A yield of 5 g. of N-isoamylmorpholone was obtained from 11 g. of isoamylaminoethanol, b$_{10}$ 150-5°. A yield of 11 g. of N-benzylmorpholone was obtained from 12 g. of benzylaminoethanol (boiling for 15 hrs.), b$_{3}$ 158-61°. N-Phenyl-N-β-hydroxyethylaminoacetic acid was obtained from N-phenylmorpholone (III) [Kipriyanov, C. A. 24, 1094] with concd. NH$_3$. The methyl ether of N-phenyl-N-β-hydroxyethylaminoacetic acid yields III during the distn. in vacuo. From the reaction of 103 g. of o-toluidine and 14.7 g. of ethylene oxide in a sealed tube at 100° for 8 hrs. was obtained N-β-hydroxyethyl-o-toluidine (IV) in the form of a yellow oil, b$_{5}$ 168-71°. By boiling 32.2 g. of IV for 8 hrs. N-o-tolylmorpholone, b$_{5}$ 190-7°, was obtained. N-β-Hydroxyethyl-N-o-tolylaminoacetic acid was obtained in the form of colorless needles, m. 113-14°. From p-toluidine and ethylene oxide was obtained N-(β-hydroxyethyl)-p-toluidine (V), b$_{10}$ 151-92° and m. 30°. From V white crystals of N-p-tolylmorpholone were obtained, m. 74-8° (sealed tube). White crystals of N-p-tolyl-N-β-hydroxyethylaminoacetic acid were obtained from alc., m. 170-2°.

W. R. Henn

1ST AND 2ND ORDERS

PROCESSES AND PROPERTIES INDEX

CA

10

The substitution of hydrogen by the methyl group in the polymethylene chromophore of cyanine dyes. A. I. Kiprianov and N. G. Grigor'eva. *Trudy Khar'kov. Gosudarst. Univ.* **3**, 51-60(1938); *Khim. Referat. Zhur.* **2**, No. 4, 86-8(1939).—In order to observe the influence of the Me group as a substituent in different positions of the chromophores of the thiacyanines, investigations were made of thiacyanines proper, thiacarbocyanines and thiadicarbocyanines. (In the following formulas

$$R = \overset{S\text{—}C\text{—}}{\underset{C_6H_4.NMeI}{|\quad\ \ \|}},\ R' = \overset{\text{—}C\text{—}S}{\underset{NEt.C_6H_4}{|\quad\ \ |}}\ \text{and}\ R'' = \overset{S\text{—}C\text{—}}{\underset{C_6H_4.NEtI.)}{|\quad\ \ \|}}$$

7-Methylthiacyanine, RCMe R' (I), was obtained by the condensation of the methiodide of 1-methylmercaptobenzothiazole (II) with the methiodide of 1-ethylbenzothiazole (III) (Brit. pat. 424,559, *C. A.* **29**, 4500^9). 7-Methylthiacarbocyanine, $R''\overset{1}{C}Me\cdot\overset{8}{C}H\overset{1'}{C}H{:}R'$ (IV), was obtained from R''CH CHNPhAc (V) (Brit. pat. 344,402) and III, 8-methylthiacarbocyanine by the method of Hamer (*C. A.* **23**, 1903; **24**, 1379), the 7-methylthiadicarbocyanine ($R''\overset{1}{C}Me.\overset{8}{C}H\overset{9}{C}H{:}\overset{8'}{C}H\overset{7'}{C}H{:}R'$) (VI) from R''CH CHCH CHNHPh (VII) (Fr. pat. 774,028, *C. A.* **29**, 2100^9) and III, 8-methylthiadicarbocyanine (VIII), from the acetal of the tetraldehyde and 1-methylbenzothiazole-EtI (IX), and 9-methylthiadicarbocyanine according to Brit. pat. 390,908 (*C. A.* **27**, 4749). The absorption curves were detd. for all dyes in a König-Martens spectrophotometer. The max. of absorption of I coincides with the curve of the unsubstituted thiacyanine. The max. of IV approaches the max. of the unsubstituted thiacarbocyanine while the absorption curve of 8-Me deriv. is moved into the short-wave region. All curves of the thiadicarbocyanines are very close to each other. The Me group has weakly bathochromic properties. For the prepn. of 2-methyl-2'-ethylthiacyanine iodide, $C_{19}H_{19}N_2S_2I$, 1 g. of II, 1 g. of 1-methylbenzothiazole-EtI and 1 g. of AcONa (anhyd.) in 20 cc. of ethanol were boiled for 1 hr. From alc. were obtained yellow needles, m. 270.5°. For the prepn. of 2,7-dimethyl-2'-ethylthiacyanine iodide, $C_{20}H_{21}N_2S_2I$, 1 g. of III, 1 g. of II and 1 g. of AcONa were heated for 1 hr. in 25 cc. of abs. ethanol. From alc. the m. p. was 278-80° (decompn.)

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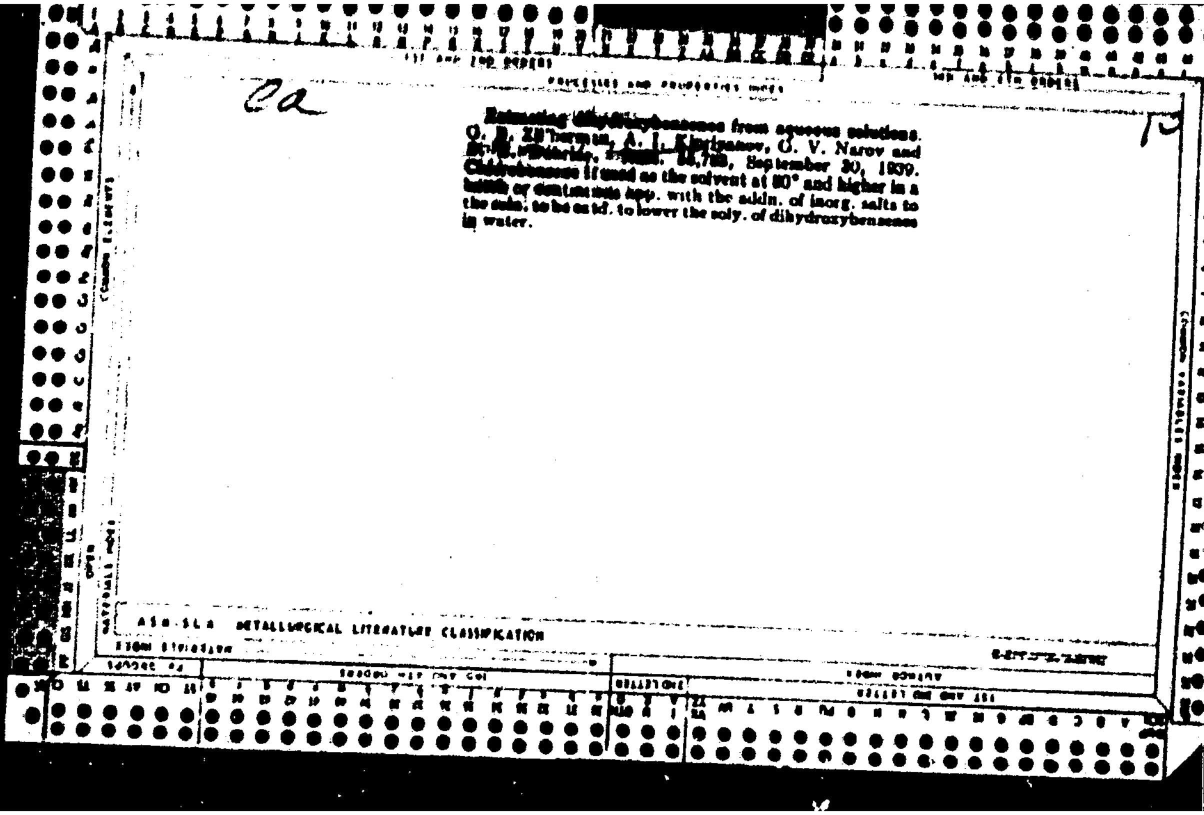
with a yield of 24%. For the prepn. of 2,2'-diethyl-7-methylthiacarbocyanine iodide, $C_{22}H_{23}N_2S_2I$ (IV), 0.6 g. of V and 0.5 g. of III were heated for 1 hr. in 3 cc. of pyridine. Fine blue-green crystals were obtained in 16.2% yield. For the prepn. of 2,2'-diethyl-7-methylthiadicarbocyanine iodide (VI) 0.1 g. of VII and 0.1 g. of III were boiled for 5 min. in 85 cc. of abs. alc. with 15 drops of piperidine. Fine green crystals with a yield of 11.5% were obtained. For the prepn. of 2,2'-diethyl-8-methylthiadicarbocyanine iodide (VIII) 0.5 g. of IX and 0.2 g. of tetrolaldehyde were heated for 20 min. to boiling in 10 cc. of pyridine. The pyridine was evapd. off and green crystals with a yield of 3% were obtained. W. R. Henn



PROCESSES AND PROPERTIES INDEX

Ca

Extracting dihydroxybenzenes from aqueous solutions. O. B. Zil'berman, A. I. Kipriyanov, G. V. Narov and [illegible]. Russ. 56,7[illegible], September 30, 1939. Chlorobenzene is used as the solvent at 80° and higher in a batch or continuous app. with the addn. of inorg. salts to the soln. to be extd. to lower the soly. of dihydroxybenzenes in water.

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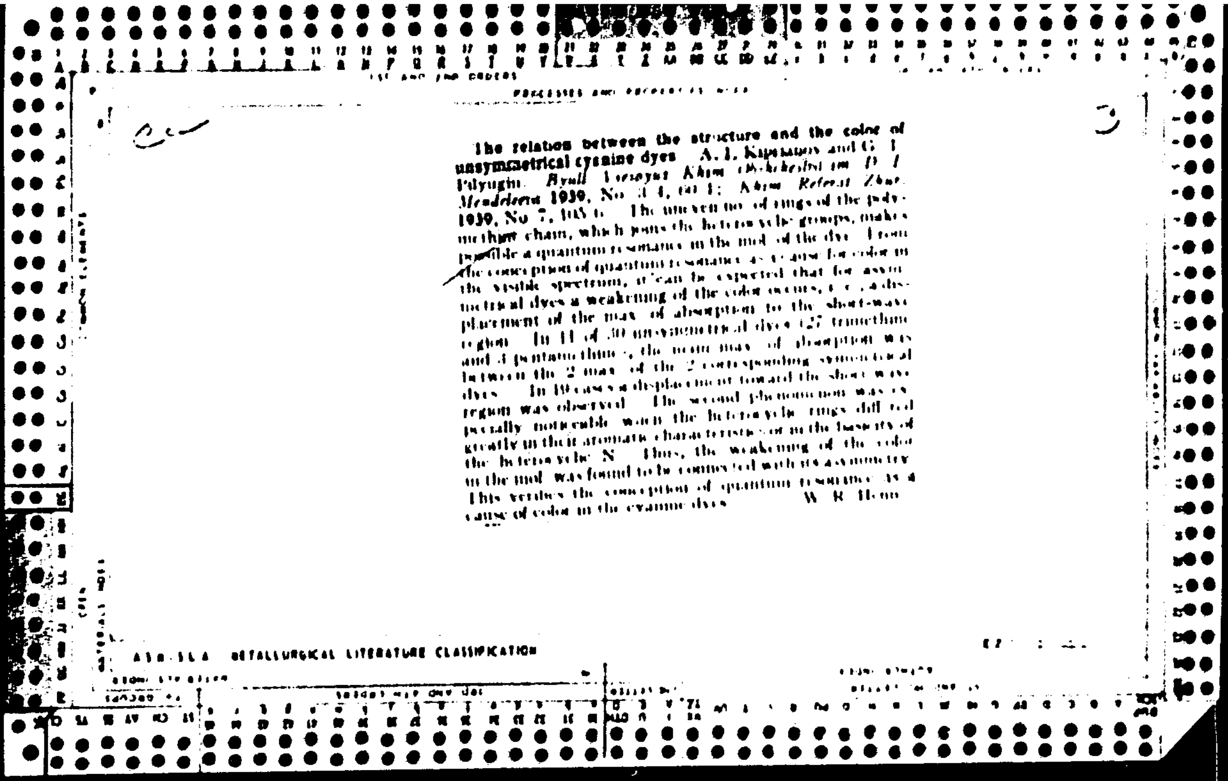

PROCESSES AND PROPERTIES INDEX

The relation between the structure and the color of unsymmetrical cyanine dyes A. I. Kiprianov and G. I. Pilyugin. *Byull. Vsesoyuz. Khim. Obshchestva im. D. I. Mendeleeva* 1939, No. 3-4, 60-1; *Khim. Referat. Zhur.* 1939, No. 7, 105-6. The uneven no. of rings of the polymethine chain, which joins the heterocyclic groups, makes possible a quantum resonance in the mol. of the dye. From the conception of quantum resonance as a cause for color in the visible spectrum, it can be expected that for asymmetrical dyes a weakening of the color occurs, i. e., a displacement of the max. of absorption to the short-wave region. In 11 of 30 unsymmetrical dyes (27 trimethine and 3 pentamethine), the main max. of absorption was between the 2 max. of the 2 corresponding symmetrical dyes. In 19 cases a displacement toward the short-wave region was observed. The second phenomenon was especially noticeable when the heterocyclic rings differed greatly in their aromatic characteristics or in the basicity of the heterocyclic N. Thus, the weakening of the color in the mol. was found to be connected with its asymmetry. This verifies the conception of quantum resonance as a cause of color in the examined dyes. W. R. Henn

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1

12

Hydroxystyryl derivatives of quaternary heterocyclic salts. A. I. Kiprianov and V. K. Petrun'kin. *J. Gen. Chem.* (U. S. S. R.) 10, 600-12(1940).—Condensation of *p-hydroxybenzaldehyde* with quaternary salts of *2,4-dimethylthiazole*, *2-methyl-4-phenylthiazole*, *2-methylbenzothiazole*, in the presence of pyridine yields the following yellow or orange compds.: *1-ethyl-2-(4-hydroxystyryl)-4-methylthiazolium iodide* (I), m. 237-8°, absorption max. 480 mμ; *2-hydroxystyryl isomer* (II), m. 215°, absorption max. 394 mμ; *1-ethyl-2-(4-hydroxystyryl)-4-phenylthiazolium iodide* (III), m. 222-3° (decompn.), absorption max 400 mμ; *1-ethyl-2-(4-hydroxystyryl)benzothiazolium iodide* (IV), m. 246°, absorption max. 420 mμ, and *2-hydroxystyryl isomer* (V), m. 241° (decompn.), absorption max. 410 mμ. With *quinaldine*, the reaction has to be carried out in abs. alc. in the presence of piperidine when there are formed *1-ethyl-2-(4-hydroxystyryl)quinolinium iodide* (VI), m. 252-3°, and the *2-hydroxystyryl isomer* (VII), m. 198-200°. The above salts of the hydroxystyryl compds. yield on treatment with alkali lye the corresponding bright orange or deep red bases such as VIII $2H_2O$ from I, m. 178° (decompn.), IX $2H_2O$ from II, m. 173°, X from III, m. 150-5° (decompn.), XI from V, m. 140-55° (decompn.) and XII from VII, m. 160-3° (decompn.). The base obtained from VI which is not intensively colored is rather unstable and has not been investigated further. When IV was treated with alkali lye, the expected base was not obtained, since the base was very sensitive toward alkali and was decompd. immediately. When IV was treated with $NaHCO_3$, however, a mol. compd. of IV and the corresponding base XIII was obtained, m. 219-20° (decompn.). *2-(4-Dimethylaminostyryl)-1-ethyl-4-methylthiazolium iodide*, m. 241° (decompn.), absorption max. 470 mμ, was prepd. from 2,4-dimethyl-1-ethylthiazolium iodide and 4-dimethylaminobenzaldehyde on boiling in the presence of pyridine and piperidine. Detailed data are given on the absorption of the salts of the hydroxystyryl compds. and the corresponding bases in various solvents such as alc., $CHCl_3$, pyridine and water.

SEE OTHER SIDE

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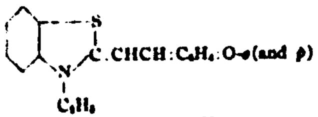
$\mathrm{S.CH{:}CMe.NEt.C\ CHCH{:}C_6H_4{:}O}$-*p* (and *o*)

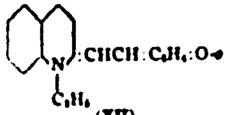
(VIII) and (IX)

$\mathrm{S.CH{:}CPh.NEt.C{:}CHCH{:}C_6H_4{:}O}$-*o*

(X)



(XI) and (XIII)



(XII)

Gertrude Berend

CA

The effect of solvent upon the color of organic dyes. A. I. Kiprianov and V. K. Petrun'kin. *J. Gen. Chem.* (U.S.S.R.) 10, 613-19 (1940).—From a comparison of the structures of the colored bases of hydroxystyryl derivs. of quaternary heterocyclic salts with those of other dyes (tetramethyldiaminofuchsone, some derivs. of indigo, etc.) it is concluded that the color changes in those dyes in which there is possible a resonance between nonpolar structure and bipolar-ion structure. The mesomeric structure of the dye mol. approaches one or other form, depending on the dielec. const. of the solvent. A. A. Podgorny

Inst. Chem., Khar'kov State U.

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

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The absorption spectra of cyanine dyes in the ultraviolet region. A. I. Kiprianov and V. K. Petrun'kin. *J. Gen. Chem.* (U. S. S. R.) 10, 620 (1940). The absorption spectra of 7 sym. carbocyanines and of 7 quaternary salts of heterocyclic bases from which the carbocyanines were prepd. (salts of quinaldine, 2-methylbenzothiazole, 2-methylbenzoxazole, 2,3-dimethylbenzoselenazole, 2,3,3-trimethylindolenine, 2,4-dimethylthiazole and 2-methylthiazoline) were investigated in the ultraviolet region. The absorption curves of dyes and corresponding salts were nearly similar in form and location. The ultraviolet absorption lines, together with the lines of the visible region, shifted toward the red with increase of the length of the polymethine chromophore of the cyanine dyes from benzothiazole to seven methine groups. The ultraviolet absorption of these dyes is conditioned by shifting of electrons in the heterocyclic rings.

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PROCESSES AND PROPERTIES INDEX

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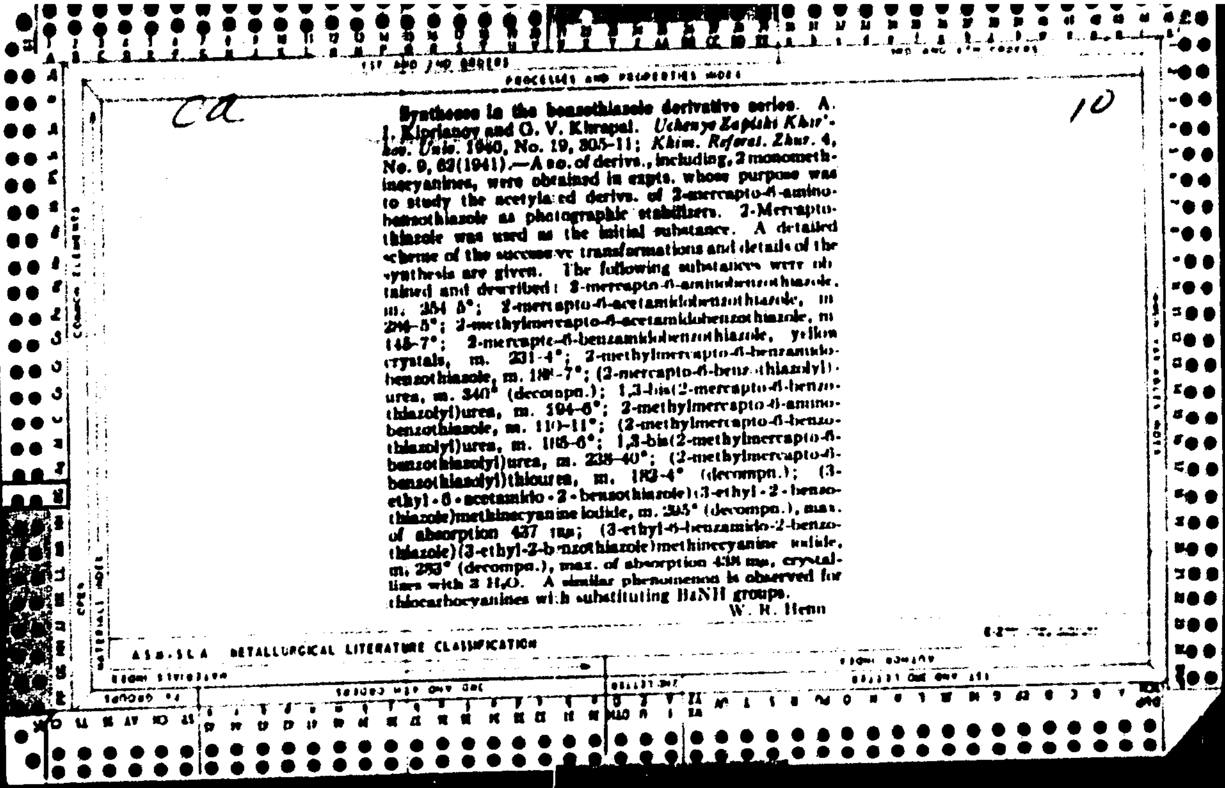
The color and symmetry in the structure of molecules of organic dyes. A. I. Kiprianov. *Doklady Akad. Nauk U. R. S. R.* 1940, No. 12, 317; *Khim. Referat. Zhur.* 4, No. 9, 49(1941); cf. *C. A.* 34, 40459.—According to the quantum resonance theory, any change in symmetry in the mol. of salt-like methine dyes must be connected with the displacement toward the short waves of the absorption band. This is confirmed on cyanine dyes with 3 and 5 methine groups if the dyes contain certain heterocyclic components (indolenine, thiazole), or if the symmetry of the polymethylene chain is considerably distorted. Substituents introduced into one of the benzene rings of cyanine dyes do not result in hypsochromic displacements of the absorption band. Aryl groups substituted on heterocyclic N atoms have no appreciable effect, because they do not distort the electronic symmetry in the mol. W. R. Henn

METALLURGICAL LITERATURE CLASSIFICATION



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Syntheses in the benzothiazole derivative series. A. I. Kiprianov and G. V. Khrapal. *Uchenye Zapiski Khar'kov. Univ.* 1940, No. 19, 305-11; *Khim. Referat. Zhur.* 4, No. 9, 62(1941).—A no. of derivs., including 2 monomethinecyanines, were obtained in expts. whose purpose was to study the acetylated derivs. of 2-mercapto-6-aminobenzothiazole as photographic stabilizers. 2-Mercaptothiazole was used as the initial substance. A detailed scheme of the successive transformations and details of the synthesis are given. The following substances were obtained and described: 2-mercapto-6-aminobenzothiazole, m. 254-5°; 2-mercapto-6-acetamidobenzothiazole, m. 294-5°; 2-methylmercapto-6-acetamidobenzothiazole, m. 145-7°; 2-mercapto-6-benzamidobenzothiazole, yellow crystals, m. 231-4°; 2-methylmercapto-6-benzamidobenzothiazole, m. 186-7°; (2-mercapto-6-benzothiazolyl)urea, m. 340° (decompn.); 1,3-bis(2-mercapto-6-benzothiazolyl)urea, m. 194-6°; 2-methylmercapto-6-aminobenzothiazole, m. 110-11°; (2-methylmercapto-6-benzothiazolyl)urea, m. 185-6°; 1,3-bis(2-methylmercapto-6-benzothiazolyl)urea, m. 238-40°; (2-methylmercapto-6-benzothiazolyl)thiourea, m. 183-4° (decompn.); (3-ethyl-6-acetamido-2-benzothiazole)(3-ethyl-2-benzothiazole)methinecyanine iodide, m. 305° (decompn.), max. of absorption 437 mμ; (3-ethyl-6-benzamido-2-benzothiazole)(3-ethyl-2-benzothiazole)methinecyanine iodide, m. 283° (decompn.), max. of absorption 438 mμ, crystallizes with 2 H_2O. A similar phenomenon is observed for thiocarbocyanines with substituting BzNH groups.

W. R. Henn

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

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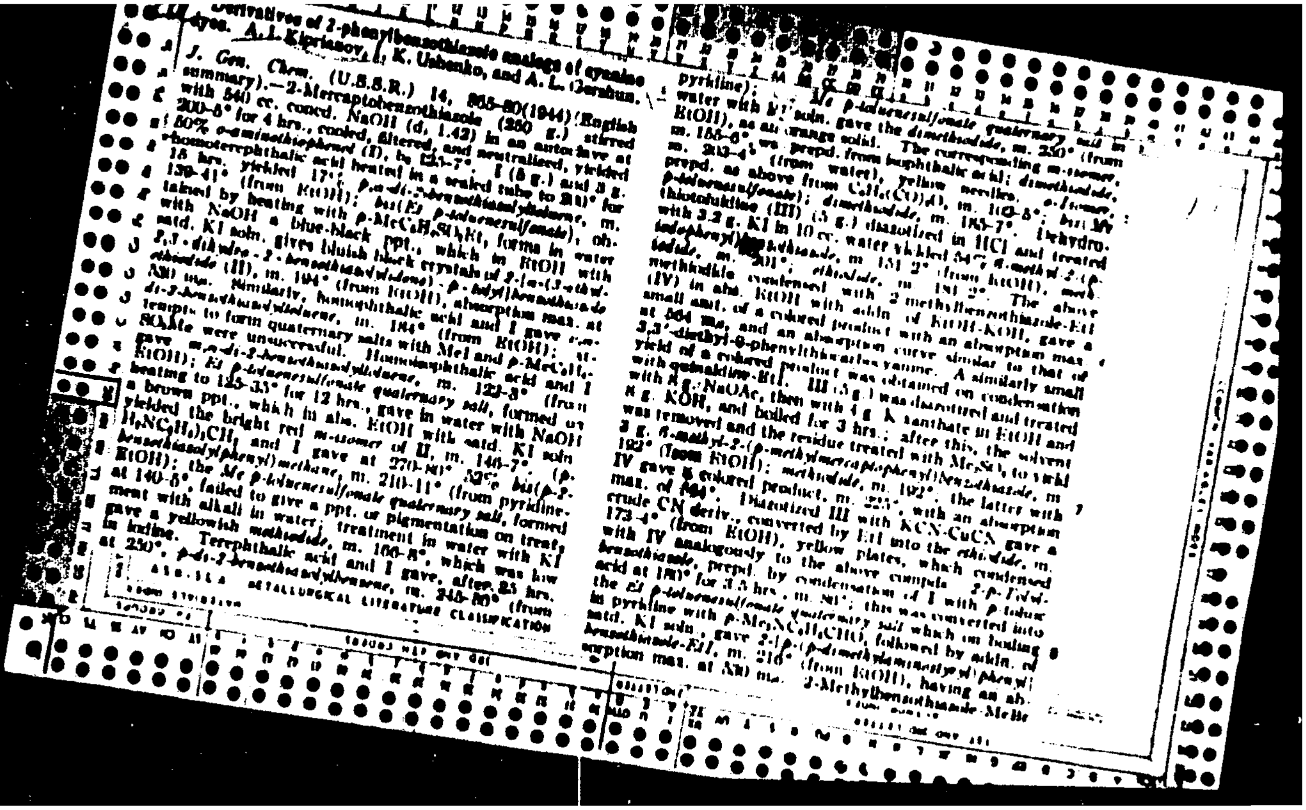
Making ether for narcosis. Ya. A. Fialkov, A. I. Kiprianov and L. M. Sol'ts. *Farmatsiya* 6, No. 1, 14-17 (1943).—Peroxide-free Et_2O is freed from AcH, H_2O and EtOH by washing with water, storing over 80% aq. NaOH or KOH about 5 days and distg. Dry alkali is equally effective, but its heat of hydration (with H_2O in the Et_2O) and its emulsifying effect are undesirable. App. is described and illustrated. On a lab. scale (6 kg.) the loss in this treatment (after recovering about 10% unchanged) is 12-15%. Julian F. Smith

ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION



Derivatives of 2-phenylbenzothiazole analogs of cyanine dyes. A. I. Kiprianov, I. K. Ushenko, and A. L. Gershun. J. Gen. Chem. (U.S.S.R.) 14, 865-80(1944)(English summary).—2-Mercaptobenzothiazole (250 g.) stirred with 540 cc. concd. NaOH (d. 1.42) in an autoclave at 200-5° for 4 hrs., cooled, filtered, and neutralized, yielded 80% o-aminothiophenol (I), b_{10} 123-7°. I (5 g.) and 5 g. o-homoterephthalic acid heated in a sealed tube to 200° for 18 hrs. yielded 17% p,α-di-2-benzothiazolyltoluene, m. 139-41° (from EtOH); bis(Et p-toluenesulfonate), obtained by heating with p-$MeC_6H_4SO_3Et$, forms in water with NaOH a blue-black ppt., which in EtOH with satd. KI soln. gives bluish black crystals of 2-[α-(3-ethyl-2,3-dihydro-2-benzothiazolylidene)-p-tolyl]benzothiazole ethiodide (II), m. 194° (from EtOH), absorption max. at 580 mμ. Similarly, homophthalic acid and I gave o,α-di-2-benzothiazolyltoluene, m. 184° (from EtOH); attempts to form quaternary salts with MeI and p-$MeC_6H_4SO_3Me$ were unsuccessful. Homoisophthalic acid and I gave m,α-di-2-benzothiazolyltoluene, m. 122-3° (from EtOH); Et p-toluenesulfonate quaternary salt, formed on heating to 125-35° for 12 hrs., gave in water with NaOH a brown ppt., which in abs. EtOH with satd. KI soln yielded the bright red m-isomer of II, m. 146-7°. $(p\text{-}H_2NC_6H_4)_2CH_2$ and I gave at 270-80° 32% bis(p-2-benzothiazolylphenyl)methane, m. 210-11° (from pyridine-EtOH); the Me p-toluenesulfonate quaternary salt, formed at 140-5°, failed to give a ppt. or pigmentation on treatment with alkali in water; treatment in water with KI gave a yellowish methiodide, m. 166-8°, which was low in iodine. Terephthalic acid and I gave, after 25 hrs. at 250°, p-di-2-benzothiazolylbenzene, m. 245-80° (from pyridine); Me p-toluenesulfonate quaternary salt in water with KI soln. gave the dimethiodide, m. 250° (from EtOH), as an orange solid. The corresponding m-isomer, m. 155-6°, was prepd. from isophthalic acid; dimethiodide, m. 203-4° (from water), yellow needles. o-Isomer, prepd. as above from $C_6H_4(CO_2H)_2$, m. 113-5°; bis(Me p-toluenesulfonate); dimethiodide, m. 185-7°. Dehydrothiotoluidine (III) (5 g.) diazotized in HCl and treated with 3.2 g. KI in 10 cc. water yielded 54% 6-methyl-2-(p-iodophenyl)benzothiazole, m. 151-2° (from EtOH), methiodide, m. 201°; ethiodide, m. 191-2°. The above methiodide condensed with 2-methylbenzothiazole-EtI (IV) in abs. EtOH with addn. of EtOH-KOH, gave a small amt. of a colored product with an absorption max. at 554 mμ, and an absorption curve similar to that of 3,3'-diethyl-9-phenylthiacarbocyanine. A similarly small yield of a colored product was obtained on condensation with quinaldine-EtI. III (5 g.) was diazotized and treated with 8 g. NaOAc, then with 4 g. K xanthate in EtOH and 8 g. KOH, and boiled for 3 hrs.; after this, the solvent was removed and the residue treated with Me_2SO_4 to yield 3 g. 6-methyl-2-(p-methylmercaptophenyl)benzothiazole, m. 192° (from EtOH); methiodide, m. 192°, the latter with IV gave a colored product, m. 225°, with an absorption max. of 584°. Diazotized III with KCN-CuCN gave a crude CN deriv., converted by EtI into the ethiodide, m. 173-4° (from EtOH), yellow plates, which condensed with IV analogously to the above compds. 2-p-Tolylbenzothiazole, prepd. by condensation of I with p-toluic acid at 180° for 3.5 hrs., m. 86°; this was converted into the Et p-toluenesulfonate quaternary salt which on boiling in pyridine with p-$Me_2NC_6H_4CHO$, followed by addn. of satd. KI soln., gave 2-[p-(p-dimethylaminostyryl)phenyl]benzothiazole-EtI, m. 210° (from EtOH), having an absorption max. at 530 mμ. 2-Methylbenzothiazole-MeHe

METALLURGICAL LITERATURE CLASSIFICATION

8 g.) and 2.5 g. p-tolualdehyde heated in pyridine for hrs. gave 2-(p-methylstyryl)benzothiazole·EtBr, m. 248° (from EtOH), lemon-yellow needles. This salt does not condense with $Me_2NC_6H_4CHO$ nor with $HC(OEt)_3$. The products formed from homoterephthalic and homoisophthalic acids may be considered to be analogs of cyanine dyes in which the polymethylene chromophore was partially substituted by the benzene ring. The intensity and the depth of color in these compds. is considerably less than in the corresponding thiacyanines, probably due to the disturbance of the equivalence of the polar structures existing in resonant condition. G. M. Kosolapoff

Mlu. Inst. Chem., AS, USSR

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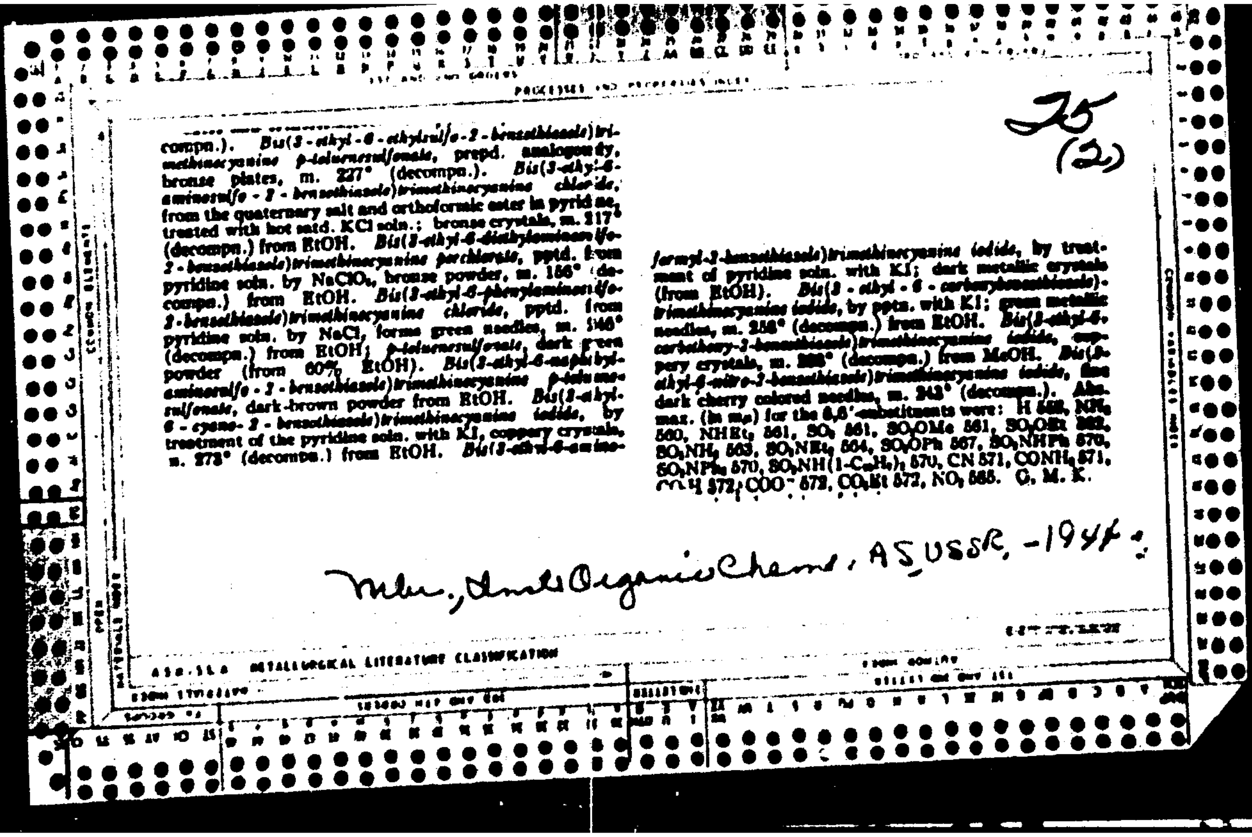
Color and structure of cyanine dyes. I. Thiocarbocyanines with electropositive substituents. A. I. Kiprianov, I. K. Ushenko, and E. D. Sych (Acad. Sci. U.S.S.R., Moscow). *J. Gen. Chem.* (U.S.S.R.) 15, 200-6(1945)(English summary); cf. *C.A.* 38, 1487.—Electropositive substituents introduced symmetrically into the 6,6'-positions of thiocarbocyanine form by their bathocromic activity a series which corresponds to the mobility of their electron pairs. Acylation of the phenol or the amino group displaces the absorption max. to a shorter-wave region. Action of alc. alkali on benzoylamino and *p*-toluenesulfamido derivs. of thiocarbocyanine deepens the color; the second example gives 6 times greater effect than the first. The bathochromic action of pos. substituents can be explained by the formation of resonant structures with a neg. charge on the C atoms of the polymethine chain. *p*-Acetanisidine (190 g.) was treated with 111 g. P_2S_5 in 800 cc. PhMe to yield 42% *thioacetanisidine*, m. 116-19°; 67 g. of this, in 1200 cc. *N* NaOH, was added dropwise with stirring to a cooled soln. of 321 g. $K_3Fe(CN)_6$ in 800 cc. water at 8-10°; after stirring for 1 hr. the mixt. was filtered and the ppt. washed with water; after soln. in benzene, the product was dried by azeotropic distn. of the solvent, and distd. in vacuo to yield 28% *2-methyl-6-methoxybenzothiazole*, b 154-65°. Heating 10 g. of the base with 11 g. Et *p*-toluenesulfonate for 6 hrs. at 130-40° gave 19.7 g. of the *quaternary compd.* as a red-brown, water-sol. solid mass. Heating with concd. HCl (18 hrs. at 150-60°) or concd. HBr (6 hrs. at 120-30°) gave *2-methyl-6-hydroxybenzothiazole hydrochloride*, m. 232-5° (decompn.) (isolated as dihydrate), *HBr salt*, m. 274-8°. 2-Methyl-6-nitrobenzothiazole (27 g.) in 150 cc. concd. HCl was heated on a steam bath, reduced with 34 g. Sn, and treated with an excess of 15% NaOH; extn. of the dried ppt. with hot MePh gave 79% of *2-methyl-6-aminobenzothiazole*, m. 123° (m. 125-6° from EtOH). Diazotization of 33.4 g. of this, treatment of the diazo soln. at 0° with 37.5 g. K xanthate with stirring, heating to 60-5° for 1 hr., taking up the sepd. oil in PhMe, evapn. of the solvent *in vacuo*, boiling the residue with 35 g. KOH in 150 cc. EtOH for 2.5 hrs., removal of EtOH, cooling, neutralization by HCl and extn. with Et_2O gave 30% of *2-methyl-6-mercaptobenzothiazole*, b_{14} 168-9°, m. 48°. The success of prepn. depends on uninterrupted operations; the product oxidizes readily in the air. The following quaternary salts were prepd.: *Et p-toluenesulfonate* (by heating with the ester for 2.5 hrs. at 120-30°) (no consts. given); *ethiodide* (by addn. of KI to aq. soln. of above salt) (no const. given); *methiodide* (by addn. of KI to aq. soln. of the dimethyl sulfate quaternary salt), m. 212° (from EtOH). *2-Methyl-6-iodobenzothiazole*, m. 141-2°, was prepd. by diazotizing 2.5 g. of the amino deriv., treating with 4 g. KI, letting stand overnight, heating on a steam bath, making the mixt. alk., distg. the product under 5 mm., and recrystg. from C_6H_6; heating with Et *p*-toluenesulfonate at 120-30° for 4 hrs., at 150° for 1 hr. gave the *quaternary salt*; the aq. soln. of this treated with KI gave the *ethiodide*, m. 227°. The following dyes were prepared: *Bis(3-ethyl-6-methoxy-2-benzothiazole)trimethinecyanine iodide*, $C_{23}H_{25}IN_2O_2S_2.2H_2O$, m. 276°, (I), 3 g. 3-ethyl-2-methyl-6-methoxybenzothiazole *p*-toluenesulfonate and 3 g. orthoformic ester in 10 cc. pyridine were heated to boiling for 25 min., evapd. to 1/3 vol. and treated with dil. EtOH, convert to the iodide by means of KI, and recrystallize from EtOH. I (2.7 g.) was heated in a sealed tube with 5 g. concd. HBr at 120-30° for 5 hrs., dild. with water, excess HBr neutralized by NH_4OH, and the cryst. dye transformed into the iodide by heating with aq. KI; after 4 crystns. from EtOH there was obtained 21% of *bis(3-ethyl-6-hydroxy-2-benzothiazole)trimethinecyanine iodide*, $C_{21}H_{21}IN_2O_2S_2.4H_2O$ (II), m. 204°. *Bis(3-ethyl-6-acetoxy-2-benzothiazole)trimethinecyanine iodide*, m. 256°, was prepd. by heating II with Ac_2O; action of alkali in EtOH even in the cold leads to hydrolysis of the Ac groups and the soln. changes from violet to blue. *Bis-(3-ethyl-6-mercapto-2-benzothiazole)trimethinecyanine p-toluenesulfonate*, by heating 1 g. 3-ethyl-2-methyl-6-mercaptobenzothiazole p-toluenesulfonate and 1 g. orthoformic ester in 10 cc. pyridine for 25 min., cooling, washing the ppt. with Et_2O, water, and EtOH gave 76% of a product whose analysis corresponded to $C_{20}H_{18}N_2O_2S_4$, which was apparently an oxidation product and did not have free SH groups; treatment with alkali in EtOH failed to change the position of absorption max. (560 mμ); however, on addn. to alk. alc. soln. of small amts. of hyposulfite the violet color changes to green-blue, max. 606 mμ; when the soln. stands in air, the max. slowly returns to 560 mμ. II. Thiocarbocyanines with electronegative substituents. A. I. Kiprianov and I. K. Ushenko (Acad. Sci. U.S.S.R., Moscow). *Ibid.* 207-14(English summary).—Thirteen new sym. thiocarbocyanines with electroneg. substituents in 6,6'-positions were prepd. All are colored more deeply than the unsubstituted thiocarbocyanine; the NO_2 group has the greatest effect; SO_3H and its derivs., less; and CO_2H and its derivs., least. The action of the neg. substituents is attributed to formation of resonant structures with pos. charge on the C atoms of the polymethine chain. This is confirmed by the rate of decolorization by alkali; the neg.-substituted dyes are decolorized more rapidly, those with pos. substituents more slowly than the unsubstituted thiocarbocyanine. *2-Methyl-6-benzothiazolesulfonyl chloride*, m.

66°, was prepd. by treating 20 g. 2-methylbenzothiazole with 60 g. chlorosulfonic acid with cooling and stirring, heating for 4 hrs., to 140-45°, pouring onto ice water and benzene, sepg. the benzene soln., and freeing of solvent; yield 84%; treatment with NH_3 gave the corresponding *amide*, m. 184-5°; boiling with water gave the corresponding *sulfonic acid*, m. 295°. The sulfonic acid was converted into the *quaternary salt* by heating with Et p-toluenesulfonate for 12 hrs. at 145-50°. The following *esters* were prepd. by heating the sulfonyl chloride with corresponding alc.: *Me*, m. 43° (from PhMe), *Et*, m. 59° (from EtOH), *Ph*, m. 124-5° (from EtOH); treatment of the chloride with Et_2NH gave the corresponding *diethylamide*, water-sol. brown mass which was not purified further; treatment of the chloride with $PhNH_2$ gave the *anilide*, m. 158° (from EtOH); 1-naphthylamine gave the *naphthylamide*, m. 184-8° (from EtOH). 2-Methyl-6-aminobenzothiazole was diazotized, and the soln. was added to soln. of 16.6 g. $CuSO_4$ and 13.2 g. KCN in 100 cc. water, heated on a steam bath for 1 hr., neutralized, and the ppt. washed with water, and dried to give *2-methyl-6-cyanobenzothiazole*, m. 135° (from PhMe). The cyano deriv. (1.5 g.) was heated in a sealed tube with 3.5 g. concd. HCl for 6 hrs. at 135-40°, the mixt. dissolved in dil. NaOH, filtered, and pptd. by HCl to yield 79% *2-methyl-6-carboxybenzothiazole*, m. 230-40° (from EtOH); *Et ester*, m. 73°, prepd. by satn. of EtOH soln. of the acid with dry HCl, was treated in EtOH soln. to satn. with dry NH_3 at 5° and let stand for 3 days to yield the *amide*, m. 181-2° (from EtOH). The following dyes were prepd.: *Bis(3-ethyl-6-sulfo-2-benzothiazole)trimethinecyanine*: from the quaternary salt of 2-methyl-6-sulfobenzothiazole and orthoformic ester in pyridine, forms a noncryst. mass, sol. in water, and appears to be a pyridinium salt; addn. of KI to the alc. soln. ppts. the amorphous K salt, sol. in water, insol. in EtOH, free of iodine, m. 182° (decompn.). *Bis(3-ethyl-6-methylsulfo-2-benzothiazole)trimethinecyanine p-toluenesulfonate*, from the quaternary salt of the Me ester of 2-methyl-6-sulfobenzothiazole and orthoformic ester in pyridine, m. 215° (de-



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compn.). *Bis(3-ethyl-6-ethylsulfo-2-benzothiazole)trimethinecyanine p-toluenesulfonate*, prepd. analogously, bronze plates, m. 227° (decompn.). *Bis(3-ethyl-6-aminosulfo-2-benzothiazole)trimethinecyanine chloride*, from the quaternary salt and orthoformic ester in pyridine, treated with hot satd. KCl soln.; bronze crystals, m. 217° (decompn.) from EtOH. *Bis(3-ethyl-6-diethylaminosulfo-2-benzothiazole)trimethinecyanine perchlorate*, pptd. from pyridine soln. by $NaClO_4$, bronze powder, m. 186° (decompn.) from EtOH. *Bis(3-ethyl-6-phenylaminosulfo-2-benzothiazole)trimethinecyanine chloride*, pptd. from pyridine soln. by NaCl, forms green needles, m. 246° (decompn.) from EtOH; *p-toluenesulfonate*, dark green powder (from 60% EtOH). *Bis(3-ethyl-6-naphthylaminosulfo-2-benzothiazole)trimethinecyanine p-toluenesulfonate*, dark-brown powder from EtOH. *Bis(3-ethyl-6-cyano-2-benzothiazole)trimethinecyanine iodide*, by treatment of the pyridine soln. with KI, coppery crystals, m. 273° (decompn.) from EtOH. *Bis(3-ethyl-6-aminoformyl-2-benzothiazole)trimethinecyanine iodide*, by treatment of pyridine soln. with KI; dark metallic crystals (from EtOH). *Bis(3-ethyl-6-carboxybenzothiazole)trimethinecyanine iodide*, by pptn. with KI; green metallic needles, m. 258° (decompn.) from EtOH. *Bis(3-ethyl-6-carbethoxy-2-benzothiazole)trimethinecyanine iodide*, coppery crystals, m. [illegible]° (decompn.) from MeOH. *Bis(3-ethyl-6-nitro-2-benzothiazole)trimethinecyanine iodide*, fine dark cherry colored needles, m. 243° (decompn.). Abs. max. (in mμ) for the 6,6'-substituents were: H 558, NH_2 560, $NHEt_2$ 561, SO_2 561, SO_2OMe 561, SO_2OEt 562, SO_2NH_2 563, SO_2NEt_2 564, SO_2OPh 567, SO_2NHPh 570, SO_2NPh_2 570, $SO_2NH(1-C_{10}H_7)$ 570, CN 571, $CONH_2$ 571, CO_2H 572, COO^- 573, CO_2Et 572, NO_2 585. G. M. K.

Mbr., Inst. Organic Chem., AS USSR, -1944-

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

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Colour and Constitution of Cyanine Dyes II. Thiacarbocyanines with Electronegative Substituents. A. I. KIPRIANOV and I. K. USHENKO. *J. Gen. Chem. U.S.S.R.*, 15, 207-14, 1945. (English summary).—Describes thirteen new thiacarbocyanine dyes symmetrically substituted in the 6 : 6' positions by electronegative groups. A table lists the absorption maxima for these dyes and also for those derived by salt formation at the substituent group, *e.g.*, NH_3^+, COO-, SO_3-, etc. In each example a bathochromic shift is produced, this being least for NH_3^+ and greatest for COO-, $COOC_2H_5$ and NO_2. This effect is considered to be due to the development of resonance structures with a negative charge on the substituent and a positive charge on the trimethine chain ; this view is supported by the fact that these dyes are more rapidly decolorized by alkalies than the unsubstituted dye, whilst those with electropositive substituents are decolorized more slowly. D.J.F.

1ST AND 2ND ORDERS

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3RD AND 4TH ORDERS

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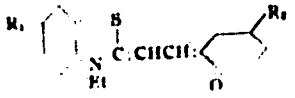
Color and structure of cyanine dyes. III. Substituted thiocarbocyanines of unsymmetrical structure. A.
I. Kiprianov and I. K. Ushenko. *J. Gen. Chem.* (U.S.
S.R.) 15, 684-9(1945)(English summary); cf. *C.A.* 40,
2300¹.—Destruction of symmetry of cyanine dyes leads to
displacement of the absorption band as it was first shown
by K. and Pilyugin (*Uch. Zap. Kharkov Gosudarst. Univ.*
10, 91(1937)). In the present paper the results of sym-
metry displacement by introduction of unequal substitu-
ents into 6,6-positions are given. In the presence of but
one substituent, the absorption shift does not occur, while
substitution of two unlike substituents produces a shift
which is the greater, the more different are the substitu-
ents. The unsym. thiocarbocyanines were prepd. con-
ventionally by heating one of the quaternary salts in Ac₂O
with diphenylformamidine, and the resulting intermedi-
ate was then condensed with the other quaternary compd.
in boiling pyridine; the dyes were purified by crystn.
from EtOH. For the following compds., the found and
calcd. values of the absorption max. are given: (*3-Ethyl-
6-hydroxy-2-benzothiazole*)(*3-ethyl-2-benzothiazole*)*tri-
methinecyanine iodide*, green, m. 245° (decompn.),
566 mμ, 567 mμ; (*3-ethyl-6-methoxy-2-benzothiazole*)(*3-
ethyl-2-benzothiazole*)*trimethinecyanine iodide*, black, m.
215° (decompn.), 563 mμ, 565.5 mμ; (*3-ethyl-6-nitro-2-
benzothiazole*)(*3-ethyl-2-benzothiazole*)*trimethinecyanine
iodide*, m. 263° (decompn.), 572 mμ, 571.5 mμ; (*3-
ethyl-6-dimethylamino-2-benzothiazole*)(*3-ethyl-2-benzo-
thiazole*)*trimethinecyanine iodide*, violet, m. 254° (de-
compn.), 585 mμ, 585 mμ; (*3-ethyl-6-nitro-2-benzothia-
zole*)(*3-ethyl-6-hydroxy-2-benzothiazole*)*trimethynecyanine
iodide*, dark powder, m. 270° (decompn.), 578 mμ, 580.5
mμ; (*3-ethyl-6-nitro-2-benzothiazole*)(*3-ethyl-6-acetoxy-2-
benzothiazole*)*trimethinecyanine iodide*, dark-violet, m.
279° (decompn.), 574 mμ, 573.5 mμ; (*3-ethyl-6-nitro-2-
benzothiazole*)(*3-ethyl-6-p-tolylsulfonamido-2-benzothia-
zole*)*trimethinecyanine iodide*, green, 582 mμ, 581.5 mμ;
(*3-ethyl-6-nitro-2-benzothiazole*)(*3-ethyl-6-amino-2-benzo-
thiazole*)*trimethinecyanine iodide* (by hydrolysis of above
by heating with H_2SO_4-AcOH on a steam bath for 2 hrs.),
dark crystals, m. 258° (decompn.), 580 mμ, 591 mμ; (*3-
ethyl-6-nitro-2-benzothiazole*)(*3-ethyl-6-dimethylamino-2-
benzothiazole*)*trimethinecyanine iodide*, bronze luster, m.
265° (decompn.), 588 mμ, 588.5 mμ. G. M. Kosolapoff

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

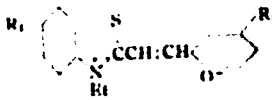
PROCESSES AND PROPERTIES INDEX

Effect of the solvent on the color of organic dyes. II. A. I. Kiprianov and E. S. Timoshenko (Kiev State Univ., Ukraine). *Zhur. Obshchei Khim.* (J. Gen. Chem.) 17, 1468-76(1947) (in Russian); cf. C.A. 34, 7783.—(1) Observed shifts of the max. of absorption, depending on the polarity of the solvent (H_2O and EtOH or $CHCl_3$ and C_6H_6), of substituted intramoid derivs. of the type

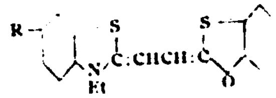


(I)

where R_1 and R_2 are OEt and NMe_2 (electron donor groups) or NO_2 (electron acceptor), confirm the assumption that such shifts are attributable to displacements of resonance between the above nonpolar form and the bipolar ion



With R_2 = H, and R_1 = H, EtO, Me_2N, NO_2, the max. lie, in H_2O, resp., at 495, 494, 501, 539 mμ, in EtOH at 532, 547, 542, --, in $CHCl_3$ at 500, 587, 586, --; with R_1 = H and R_2 = H, EtO, NO_2, in H_2O at 495, 532, 474, in EtOH at 532, 604, 513, in $CHCl_3$ at 500, 621, 520 mμ. An electropos. R_1 shifts the max. to shorter waves, an electroneg. R_1 to longer waves. On the other hand, an electropos. R_2 obviously favors the bipolar-ion form, an electroneg. R_2 the nonpolar form. In contrast thereto, a pos. R_1 should favor the nonpolar form, a neg. R_1 the ionic form, accordingly, a pos. R_2 shifts the max. to longer waves, a neg. R_2 to shorter waves. Substitution of a pos. R_1 and a neg. R_2 results in an accumulated strong hypsochromic effect, e.g., R_1 = EtO, R_2 = NO_2, max. in EtOH and in $CHCl_3$, 504 and 500, resp.; R_1 = Me_2N, R_2 = NO_2, 520 and 578. Substitution of NO_2 in both R_1 and R_2 has but little effect on the color (max. at 544 and 597 in EtOH and $CHCl_3$, resp.). EtO in both R_1 and R_2 gives, in H_2O, EtOH, and $CHCl_3$, max. at 525, 590, and 630 mμ, resp. The deriv. with R_1 = NO_2 and R_2 = EtO could not be isolated; under the action of NaOH on the corresponding hydrochloride, there appears a momentary deep color which, however, disappears rapidly. (2) In merocyanine derivs. of the type



(II)

an electropos. R_1 enhancing the bionic structure

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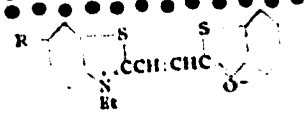
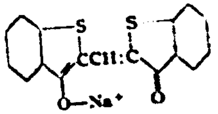


shifts the color towards the red side, an electroneg. R has the
contrary effect; e.g., R = H, EtO, Me_2N, Me_2NH, NO_2,
max. in EtOH at 556, 596, 598, 509, 548, in $CHCl_3$ at 548,
555, 575, 592, 548, in C_6H_6 at 533, 542, 559, 590, 541 mμ.
The hypsochromic shifts due to perturbation of equiva-
lence of resonance forms of an asymmetric dye can be
calcd. from the max. of absorption of 2 sym. "mother"
dyes; from absorption data for thiocarbocyanines and for
oxonin (II), the shifts, in EtOH, are, resp., 20, 18.5, 15, 68,



(II)

45.5 mμ, i.e., the inequality of the nonpolar and the in-
ionic forms is decreased by pos. R and is sharply increased
by neg. R. (3) The following are the syntheses of derivs.
of I: For $R_1 = H$, $R_2 = NO_2$: 2 g. of 2-methylben-
zothiazole ethiodide, 1.1 g. 2-hydroxy-5-nitrobenzalde-
hyde, and 7 ml. pyridine boiled 1 hr. ppt. 1.5 g.
dark red crystals, orange after recrystn. from EtOH,
$C_{22}H_{14}O_3N_2S.2EtOH$, m. 223° (decompn.). $R_1 = NO_2$,
$R_2 = H$: 1 g. 2-methyl-6-nitrobenzothiazole ethiodide,
0.33 g. salicylaldehyde, and 5 ml. pyridine boiled 30
min. ppt. dark red crystals contg. iodine; pptn. with
NH_4OH from a suspension in H_2O gave dark brown $C_{22}H_{16}$-
O_4N_2S, m. 238° (decompn.). $R_1 = R_2 = NO_2$: 2 g. 2-
methyl-6-nitrobenzothiazole ethiodide, 1 g. 2-hydroxy-
5-nitrobenzaldehyde, 5 ml. abs. alc., and 3 drops pyridine
boiled 30 min. gave 1.7 g. of a brown ppt. which, treated
with concd. HCl, gave a yellow salt, m. 235° (decompn.);
from its aq. suspension, alkali ppts. greenish black
$C_{22}H_{16}O_4N_2S$, m. 172° (decompn.). $R_1 = Me_2N$, $R_2 = H$:
0.33 g. 2-methyl-6-dimethylaminobenzothiazole
ethiodide, 0.2 g. salicylaldehyde, and 3 ml. pyridine
boiled 20 min. gave 0.28 g. of a dark brown cryst. ppt.
from the aq. suspension of which NaOH pptd. dark green
$C_{19}H_{20}ON_2S$, m. 252°. $R_1 = Me_2N$, $R_2 = NO_2$: 0.35 g.
2-methyl-6-dimethylaminobenzothiazole ethiodide, 0.17
g. 2-hydroxy-5-nitrobenzaldehyde, and 5 ml. pyridine
boiled 5 min. gave directly 0.4 g. (100%) of brown
$C_{19}H_{19}O_3N_3S$, m. 245° (decompn.). $R_1 = EtO$, $R_2 = H$:

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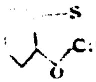
1 g. 2-methyl-6-ethoxybenzothiazole ethiodide, 0.35 g.
salicylaldehyde, and 3 ml. pyridine boiled 15 min. gave 1.02
g. of the iodide, from the aq. suspension of which NH_4OH
pptd. dark brown $C_{18}H_{19}O_2NS$, m. 219-31°. R_1 = EtO,
R_2 = NO_2: 0.5 g. 2-methyl-6-ethoxybenzothiazole
ethiodide, 0.3 g. 2-hydroxy-5-nitrobenzaldehyde, and 3 ml.
pyridine boiled 30 min. gave directly 0.2 g. (after re-
crysta. from EtOH) dark red $C_{18}H_{18}O_4N_2S$, m. 236°. R_1 =
H, R_2 = EtO: 0.5 g. 2-methylbenzothiazole ethiodide, 0.3
g. 2-hydroxy-5-ethoxybenzaldehyde, and 2.5 ml. pyridine
boiled 30 min. gave 0.62 g. of a red iodide, m. 238°, from the
aq. suspension of which NaOH pptd. $C_{18}H_{19}NO_2S$, m. 83°.
R_1 = NO_2, R_2 = EtO. 0.5 g. 2-methyl-6-nitrobenzothi-
azole ethiodide, 0.3 g. 2-hydroxy-5-ethoxybenzaldehyde,
5 ml. abs. alc., and a few drops of pyridine boiled
30 min. gave 0.6 g. (80%) orange $C_{18}H_{18}O_4N_2S$, m. 238°;
on treatment of the aq. soln. with alkali or NH_4OH the
color disappears instantaneously, giving a dark brown ppt.
which dissolves in H_2O, EtOH, and Et_2O with the same
yellow color. R_1 = R_2 = EtO. 0.5 g. 2-methyl-6-ethoxy-
benzothiazole ethiodide, 0.3 g. 2-hydroxy-5-ethoxy-
benzaldehyde, and 2 ml. pyridine boiled 30 min. pptd.
0.5 g. of an orange iodide; of this, 0.4 g. in suspension
in H_2O, treated with NaOH, pptd. 0.1 g. dark $C_{21}H_{23}O_3NS$,
m. 110°. (4) The following are the syntheses of the de-
rivs. of II: R = H: 0.8 g. diphenyl formamidine, 1 g.
3-hydroxythianaphthenecarboxylic acid, and 5 ml. abs.
alc. boiled 1 hr. pptd. 0.5 g. brown



C:CHNHPh,
m. 160°; 0.4 g. of this intermediate, 0.5 g. 2-methylbenzo-
thiazole ethiodide, and 0.14 g. anhyd. AcONa, boiled in
abs. alc. 1 hr., gave 0.45 g. $C_{20}H_{15}ONS_2$, m. 216-18°.
R = NO_2: 0.5 g. 2-methyl-6-nitrobenzothiazole ethiodide
0.36 g. of the above intermediate, 0.14 g. anhyd.
AcOH, and 10 ml. abs. alc., boiled 1 hr., gave 0.41 g.
(65%) of dark brown $C_{20}H_{14}O_3N_2S_2$, m. 341-2°, insol. in
H_2O and slightly sol. in EtOH. R = Me_2N: 0.5 g.
2-methyl-6-dimethylaminobenzothiazole ethiodide,
treated as above, gave 0.44 g. of a dark violet powder,
$C_{22}H_{20}ON_2S_2$, m. 292°. R = EtO: in the same way, 0.5
g. 2-methyl-6-ethoxybenzothiazole ethiodide, gave red
crystals. $C_{22}H_{19}O_2NS_2$, m. 237-8°.

N. Thon

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KIPRIANOW, A. I.

Kiprianow, A. I., and Ushenko, I. K.- "Oxidation of the Quarternary Salts of Dibenzthiasolyl and Dibenzoxasolylpropane into Carbocyanines" (p. 1542)

SO: Journal of General Chemistry, (Zhurnal Obshchei Khimii), 1947, Vol. 17, No. 8

[redacted]

CA

N-Phenylthiocyanines. A. I. Kiprianov and I. K. Ushenko. *J. Gen. Chem.* (U.S.S.R.) 17, 2001-7 (1947) (in Russian).—A very much simplified procedure for N-phenylbenzothiazoles consists of treatment of a benzene soln. of o-PhNHC$_6$H$_4$SH with an acyl chloride; the corresponding 2-alkyl-3-phenylbenzothiazolium chloride ppts. immediately and is readily converted to the corresponding iodide. In the case of the 2-Me deriv., obtainable by AcCl, the yield is 28%, 10 times that obtained by Brooker in a more complex synthesis (Brit. 551,330 (C.A. 38, 2281^9), 551,894 (C.A. 38, 2007^1), 552,300 (C.A. 38, 3016^6)). In addn., attempts to repeat the prepn. of 2-methyl-3-phenylbenzothiazolium halide under conditions

given in the patents (see above), using iodine in AcOH on MeCSNPh$_2$, failed to give the desired product. 3-Phenylbenzothiazolone (34 g.), 48 g. KOH, and 250 ml. EtOH, heated on a steam bath 3.5 hrs., then freed of EtOH and the residue neutralized with HCl and extd. with Et$_2$O, gave 77% *o-(phenylamino)thiophenol*, b$_6$ 174-6° (easily oxidizes to the disulfide, m. 162°). This (67%) was also made by heating 38 g. 3-phenyl-2-iminobenzothiazole with 60 g. KOH in 125 ml. EtOH on a steam bath 4.5 hrs. The product, with acyl chlorides (equimol. amts.) in benzene gave either the cryst. quaternary *3-phenyl-2-alkylbenzothiazolium chloride* or a rapidly freezing oil; evapn. of the mixt. and treatment of the residue in H$_2$O with KI gave the corresponding iodides as microcryst. solids. The following were prepd. (the *2-alkyl* is indicated): *2-methyl iodide*, from AcCl, m. 234°, 42% yield; *2-ethyl iodide*, from EtCOCl, m. 225°, 80%; *2-ethyl chloride*, m. 200°, 31%; *2-propyl iodide*, from PrCOCl, 13% (no m.p. given); *2-benzyl iodide*, from PhCH$_2$COCl, m. 162°, 28%. BrCH$_2$COBr gave the *2-(bromomethyl) bromide*, mixed with oily 4-phenyl-3-ketobenzothiazine; the mixt. is readily sepd. by the sol. in water of the former compd. (no phys. consts. of the products are given); the yield of the former is 18%. Condensation of the above iodides with Et orthoformate, orthoacetate, or orthopropionate by boiling for 0.25-1.5 hrs. in pyridine, followed by pptn. with Et$_2$O or water, gave the following *thiocarbocyanine halides*. *Iodides*: *3,3'-diphenyl*, m. 276° (from EtOH), 80%, green, abs. max. 565 mμ; *3,3'-diphenyl-9-methyl*, m. 243° (from EtOH), cherry-red, max. abs. 551 mμ, 50%; *3,3'-diphenyl-9-ethyl*, m. 221° (from EtOH), cherry red, max. abs. 550 mμ, 40%; *3,3'-diphenyl-8,10-dimethyl*, m. 210° (from EtOH), max. abs. 601 mμ, 72%; *3,3'-diphenyl-8,10-diethyl*, m.p. not given, abs. max. 602 mμ, 0%; *3,3',8,10-tetraphenyl*, m. 212° (from EtOH) (Ac$_2$O used for condensation as pyridine does not work), abs. max. 602 mμ, 25%. *Bromides*: *3,3'-diphenyl-8,10-dibromo*, m. 251° (from EtOH-Me$_2$CO), green, abs. max. 567 mμ, 17%; *3,3'-diphenyl-8,10-dibromo-9-methyl*, m. 230° (from EtOH), green, max. abs. 553 mμ, 23%. Condensation of the 2-alkyl-3-phenylbenzothiazole halides with p-Me$_2$NC$_6$H$_4$CHO in Ac$_2$O readily gave the following *benzothiazolium iodides*: *3-phenyl-2-(p-dimethylaminostyryl)*, m. 218° (from EtOH), blue-violet, abs. max. 547 mμ; *3-phenyl-2-(p-dimethylamino-β-methylstyryl)*, m. 194° (from EtOH), red, max. abs. 508 mμ, 51%; *3-phenyl-2-(p-dimethylamino-β-ethylstyryl)*, m. 175° (from EtOH), abs. max. 511 mμ, 60%; *3-phenyl-2-(p-dimethylamino-β-phenylstyryl)*, m. 185° (from EtOH), abs. max. 530 mμ, 35%; *3-phenyl-2-[(p-dimethylamino)bromostyryl]*, m.p. not given, violet crystals, too sol. for recrystn., 72% yield, abs. max. 540 mμ. A strong bathochromic effect is evident in 3-Ph derivs. and a very strong effect in 8,10-alkylated derivs. of the thiocarbocyanines listed above. O. M. K.

KIPRIANOV, A. I.

Kiprianov, A. I. and Rozum, Yu. S. "Synthesis of N-alkyl-akridones", Ukr. Khim. zhurnal, 1948, Issue 1, p. 17-26, - Bibliog: 7 items.

SO: U-3042, 11 March 53, (Letopis 'nykh Statey, No. 10, 1949).

KIPRIANOV, A. I.

Kiprianov, A. I. and Fridman, S. G. "Quaternary heterocyclic azomethine salt derivatives", Ukr. khim. zhurnal, 1948, Issue 1, p. 29-44, - Bibliog: 15 items.

SO: U-3042, 11 March 53, (letopis 'nykh Statey, No. 10, 1949).

USSR/Chemistry - Cyanine Dyes Feb 1948
Chemistry - Cyanines

"N-Arythiazolcyanines," A. I. Kiprianov, F. I. Asmina, I. K. Ushenko, Inst Org Chem, Acad Sci USSR, 5½ pp

"Zhur Obshch Khim" Vol XVIII (LXXX), No 2
p.165

Todd's, Bergel's, and Karimullah's methods were used in condensation of chloracetone with thioacetone produced aniline, alpha-naphthylamine, p-anisidine, and p-aminodimethyl-aniline. As a result authors obtained perchlorates of 3-phenyl-, 3-alpha-naphthyl, and 3-p-dimethylaminophenyl-2,4-dimethylazole. By synthesis these produced symmetrical and asymmetrical cyanide dyes. Established strong effect of radical in heteroatomic nitrogen on absorption of asymmetrical carbocyanide, which contains thiozole and benzthiozole nucleus. Submitted 23 Sep 1946.

[illegible] 68T49

KIPRIANOV, A. I.

KIPRIANOV, A. I.

Author: Kiprianov, A.I.

Title: Electronic Theory in Organic Chemistry. 2 Revision
diagrs.

Date: 1949. Kiev

Subject: 1. Atomic theory 2. Electronics 3. Chemistry

Available: Library of Congress, Call No: QD461.K5 1949

Source: Lib. of Cong. Subj. Cat., 1950

KIPRIANOV, A.I.; PAZENKO, Z.N.

Synthesis of benzo-1, 4-thiazine quaternary salts. Dop.AN URSR no.3: 9-14 '49. (MIRA 9:9)

1.Institut organichnoi khimii AN URSR. 2.Diysniy chlen AN URSR (for Kiprianov). (Benzothiazine)

KIPRIANOV, A.I.; PAŽENKO, Z.N.

Cyanine dyes and stryryls of the benzo-1, 4-thiazine series. Dop.AN URSR no.3:15-21 '49. (MLRA 9:9)

1.Institut organicheskei khimii AN URSR. 2.Diysniy chlen AN URSR (for Kipriyanov).
(Benzethiazine) (Cyanine dyes)

Ca

2

Cyanine dyes from isomeric 2-methylhydroxybenzothiazoles. A. I. Kiprianov and B. I. Dashevskaya. *Zhur. Obshchei Khim.* (J. Gen. Chem.) 19, 1158-66(1949). 2-Methyl-7-methoxybenzothiazole (1 g.) and 1 g. 48% HBr after 6 hrs. in a sealed tube at 145-50° gave 33% *2-methyl-7-hydroxybenzothiazole*, m. 192° (from PhMe). The *6-HO isomer*, obtained similarly at 120-30°, was isolated as the *HBr salt*, m. 274-8°, or the *HCl salt* (prepd. by using concd. HCl 18 hrs. at 150-60°), m. 235-8°; the *free base*, obtained from the salts, was crystd. from MePh (no m.p. given); hydrolysis of 2-methyl-6-methoxybenzothiazole ethiodide by concd. HBr at 130-5° gave the HBr salt cited above. Heating the 6-HO isomer with EtI to 110-15° 12 hrs. gave the *ethiodide*, m. 205° (from EtOH), while Ac_2O after 3 hrs. on a steam bath gave the *Ac deriv.* of the base, m. 99-100° (from EtOH), in 83% yield. Similar method gave *2-methyl-5-hydroxybenzothiazole*, 82%, m. 187° (from MePh), whose *Ac deriv.*, m. 93-4° (from EtOH), and the *4-HO isomer*, m. 145° (from MePh), whose *HBr salt*, m. 205°, and the *Ac deriv.*, m. 79° (from 50% EtOH), was obtained in 80% yield by Schotten-Baumann procedure with Ac_2O and 10% NaOH. 2-Methyl-7-hydroxybenzothiazolium Et *p*-toluenesulfonate (0.8 g.), 0.8 g. Et orthoformate, and 4 ml. pyridine boiled 1 hr., dild., and treated with KI gave 9% *bis(3-ethyl-7-hydroxy-2-benzothiazole)trimethinecyanine iodide*, decompg. 251-3° (from EtOH), also obtained in 34% yield by cleavage of the MeO groups in the di-MeO analog by 48% HBr at 140-50°; the product has absorption max. at 564 mμ in neutral soln. and 500 mμ in alk. soln. Similarly, 2-methyl-6-hydroxybenzothiazole ethiodide gave 20% *bis(3-ethyl-6-hydroxy-2-benzothiazole)trimethinecyanine iodide*, decompg. 204° (from EtOH)(contains H_2O on crystn.); its *di-Ac deriv.* was obtained by a similar condensation of the MeO deriv. in 40% yield, decompg. 290-91° (from EtOH); the product has absorption max. 576 mμ in neutral, 618 mμ in alk. solns., while di-Ac deriv. gives 562 mμ. The *5-HO analog* obtained by hydrolysis of the diAc deriv. by alk. KOH at room temp. was not isolated in solid form, but its maxima were 575 mμ in neutral and 612 mμ in alk. solns.; the *di-Ac deriv.*, prepd. by condensation of 2-methyl-5-acetoxybenzothiazole Et *p*-toluenesulfonate as above in 24% yield, decompg. 213-15° (from EtOH), had an absorption max. at 567 mμ. The *4-HO analog* prepd. from the corresponding Et *p*-toluenesulfonate in 13% yield, formed violet crystals (no m.p. given), having absorption max. at 563 mμ in neutral and 502 mμ in alk. soln.; the *di-Ac deriv.* (by similar condensation of the Ac deriv.) obtained in 13% yield, decomp. 206-7°, absorption max. 562 mμ. Boiling for 1 hr. 1 g. 2-methyl-6-hydroxybenzothiazole Et *p*-toluenesulfonate

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with 1.2 g. 2-(ω-acetanilidovinyl)benzothiazole and 4 ml pyridine gave 21% *(3-ethyl-2-benzothiazole)(3-ethyl-6-hydroxy-2-benzothiazole)trimethincyanine iodide*, decompg 215° (from EtOH), having absorption max. at 568 mμ in neutral and 588 mμ in alk. soln.; the product contd. H_2O of crystn. Similarly, the 2-methyl-5-acetoxybenzothiazole Et p-toluenesulfonate gave 17% *(3-ethyl-2-benzothiazole)(3-ethyl-5-hydroxy-2-benzothiazole)trimethincyanine iodide*, after treatment of the di-Ac deriv. by alc. KOH at room temp.; the *di-Ac deriv.* decomp. 275-6° (from EtOH), with an absorption max. at 564 mμ, the HO deriv. (not described), had 587 mμ in neutral and 577 in alk. soln. The *4-HO analog*, obtained similarly in 20% yield, gave max. 580 mμ in neutral and 562 mμ in alk. soln., while the *di-Ac* deriv., obtained in 10% yield, decompg 283-4°, gave 558 mμ max. Boiling 0.5 g. 2-methyl-4-acetoxybenzothiazole Et p-toluenesulfonate, 0.6 g. 2-(2-acetanilidovinyl)-3-ethyl-6-nitrobenzothiazole ethiodide and 5 ml. pyridine 45 min. gave 21% *(3-ethyl-4-hydroxy-2-benzothiazole)(3-ethyl-6-nitro-2-benzothiazole)trimethincyanine iodide*, decompg. 278-9° (purified by washing with hot EtOH), which on addn. of alkali gives the hydroxy nitro deriv. with change of color, with a shift to the shorter wavelengths by 12 mμ.

G. M. K.

Synthesis of quaternary salts of benzothiazole. A. I. Kiprianov and Z. N. Pazenko. *Zhur. Obshchei Khim.* (J. Gen. Chem.) 19, 1515-22(1949). Quaternary salts of benzothiazole derivs. are readily obtained by the reaction of acyl halides with *N*-substituted *o*-aminothiophenols. Addn. of 0.8 g. AcCl in 2 ml. C_6H_6 to 1.39 g. *o*-MeNHC_6H_4SH (I) in 5 ml. C_6H_6 and cooling gave hygroscopic *2-methylbenzothiazole-MeCl*, which with aq. KI gave the corresponding *methiodide*, m. 221-2° (from H_2O), in 80% yield; 45% is obtained on heating 1.39 g. I, 0.6 g. AcOH, and 1 ml. concd. HCl 2 hrs. at reflux; 45% also results from 1.39 g. I, 0.65 g. $AcNH_2$, and 2.6 ml. concd. HCl after 2 hrs. at 120° in a sealed tube, while substitution of EtOAc for $AcNH_2$ gave 65%. Similarly, AcCl and *o*-EtNHC_6H_4SH (II) gave 72% *2-methylbenzothiazole-EtI*, m. 194°, while *o*-$PhCH_2$NHC_6H_4SH (III) gave 66% *3-benzyl-2-methylbenzothiazolium iodide*, m. 201°, and *o*-HO_2CCH_2NHC_6H_4SH gave 45% *3-carboxymethyl-2-methylbenzothiazolium iodide*, m. 267° (decompn.; from EtOH). I (1.4 g.) and 1.1 g. EtCOCl in C_6H_6 gave 78% *2-ethylbenzothiazole-MeI*, m. 175.5° (from H_2O), also obtained in 68% yield from I, $EtCO_2Et$, and concd. HCl in 4 hrs. at 120-40°; similarly, EtCOCl and II gave 70% *2,3-diethylbenzothiazolium iodide*, m. 161°, while PrCOCl and I gave 75% *2-propylbenzothiazole-MeI*, m. 215° (also obtained in 80% yield from I and $PrCO_2Et$ in 5 hrs. at 120-40°). PrCOCl and II in C_6H_6 similarly gave 62% *3-ethyl-2-propylbenzothiazolium iodide*, m. 181-2°, while AmCOCl and I gave 73% *2-amylbenzothiazole-MeI*, m. 180° (from EtOH); $C_7H_{15}COCl$ gave 54% *2-heptylbenzothiazole-MeI*, m. 168° (from EtOH-Et_2O), while $C_9H_{19}COCl$ gave 50% *2-nonylbenzothiazole-MeI*, m. 232°, and $C_{11}H_{23}COCl$ gave 14% *2-hendecylbenzothiazole-MeI*, m. 217°, while III in the latter reaction gave 71% *3-benzyl-2-hendecylbenzothiazolium iodide*, m. 205°; *chloride*, m. 192°. I with $C_{14}H_{29}COCl$ in C_6H_6 gave 60% *2-pentadecylbenzothiazole-MeI*, m. 320° (decompn.) (*chloride intermediate*, m. 280°), while II gave 50% of the corresponding *ethiodide*, decomp. 330° [the intermediate *chloride*, m. 205-7° (decompn.)], and III gave *3-benzyl-2-pentadecylbenzothiazolium chloride*, m. 251° (decompn.; from EtOH), which gave 50% of the *iodide*, decomp. 284°; similarly $C_{16}H_{33}COCl$ and I in Et_2O gave 58% *2-heptadecylbenzothiazole-MeI*, decomp. 321°, from the corresponding *chloride*, m. 29[illegible], while III gave 45% *3-benzyl-2-heptadecylbenzothiazolium iodide*, decomp. 307°, from the corresponding *chloride*, m. 298° (decompn.). BzCl and I in C_6H_6 gave 84% *2-phenylbenzothiazole-MeI*, yellow plates, m. 198°, while $PhCH_2COCl$ gave 58% *2-benzylbenzothiazole-MeI*, yellow needles, m. 196°. I and $(CH_2COCl)_2$ in cold PhMe gave 80% *1,2-bis(2-benzothiazolyl)ethane-2MeCl*, yellowish plates, m. 285-6°, which is poorly sol. in H_2O and with KI gave the *dimethiodide*, decomp. 310°, yielding with alkali *a yellow base*. Fumaryl chloride gave the *dimethochloride of the ethylene analog*, yellow needles, decomp. above 300°, which forms the *dimethiodide*, red brown, decomp. before melting; addn. of alkali to the chloride gave a yellow infusible solid which has 3 times the calcd. mol. wt. of $C_{18}H_{14}N_2S_2$. Addn. of 1.39 g. I in 3 ml. C_6H_6 to 1.04 g. $BrCH_2COBr$ in C_6H_6 and 0.5 hr.'s heating gave 80% *2-(bromomethyl)benzothiazole-MeBr*, decomp. 197° (from H_2O), which is readily hydrolyzed by water and must be crystd. in the presence of HBr. $Cl_2CHCOCl$ in the above gave 30% *2-[bis(o-methylaminophenylmercapto)methyl]benzothiazole-MeI* (after the usual treatment with KI), decomp. 262-3° (from EtOH). Refluxing 1.39 I, 0.6 g. 92% HCO_2H, and 1 ml. concd. HCl, followed by treatment of the ppt. with aq. KI, gave 60% *benzothiazole-MeI*, m. 211° (from EtOH).

G. M. Kosolapoff

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N-Alkyl and *N*-aryl *o*-aminophenyl mercaptans. A. I. Kiprianov and Z. N. Patenko. *J. Gen. Chem. U.S.S.R.* 19, 1529-35(1949)(Engl. translation).—See *C.A.* 44, 3487*e*.

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Structure of iodinine. A. I. Kiprianov, S. B. Serebryanyi, and V. P. Chernetskii. *Doklady Akad. Nauk S.S.S.R.* 69, 651-3(1949); cf. *C.A.* 45, 4249g. Clemo and Daglish (*C.A.* 43, 3057i) prepd. *1,6-* and *1,9-dimethoxyphenazines* (*C.A.* numbering), but failed to prove definitely the precise configuration of their 2 products; the product m. 245-6° was identical with the reduction product of iodinine. This substance is now shown to be the 1,5-isomer, indicating the correct structure of iodinine. Condensation of 3-methoxy-*o*-quinone with 3,1,2-MeOC$_6$H$_3$(NH$_2$)$_2$ and sepn. of the products via their picrates, gave a substance m. 290° (picrate, m. 258°), and an isomeric dimethoxyphenazine, m. 251°, obtained from the mother liquor of the 1st isomer (C. and D. give m. 245-6°). Condensation of *o*-O$_2$NC$_6$H$_4$OMe with *o*-anisidine in presence of powd. KOH gave the product m. 251°, identical with above described, proving it to be the *1,6-isomer*. Hence, the dimethoxyphenazine, m. 290°, must be the *1,9-isomer*. Further, condensation of *o*-O$_2$NC$_6$H$_4$OMe with *m*-anisidine gave the 1,9-dimethoxyphenazine, m. 289-90°, identical with the above, and a dimethoxyphenazine, m. 174° (from ligroine), which must be the *1,7-isomer*. G. M. Kosolapoff

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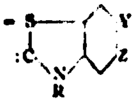
Color and planarity of molecules of organic dyes. A. I. Kiprianov and I. K. Ushenko. *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1950, 492-500; cf. *C.A.* 41, 5733g, 7837b.—In org. dyes with NMe_2 as the auxochromic group, substituents in an ortho position to the NMe_2 group which, through steric hindrance, enforce a rotation of that group relative to the plane of the ring, and thus disturb the planarity of the mol., give rise to a decrease of the absorption of light and to a shift of the absorption max. to shorter waves. Examples are $p\text{-}(p\text{-}Me_2NC_6H_4N{:}N)C_6H_4NO_2$, and $p\text{-}[(p\text{-}Me_2NC_6H_4)_2C]{:}C_6H_4{:}NMe_2$, both without and with Me in ortho-position to the NMe_2 groups. Similar changes, attributable to a perturbation of the planarity of the mol. as a result of substitution of 2H in the NH_2 group by 2Me, and the corresponding increase of the size of the group, were found in the recently synthesized cyanine dye, ACH:CH-CH:B

where A =  and B = 

(R = Me, Y = Me, Z = NH_2), which gives a blue soln. in alc. (absorption max. 504 $m\mu$) but which, after substitution of the 2H in the $2NH_2$ groups by 2Me, has a max at 578 $m\mu$ and appears red-purple in alc. soln. Here, contrary to the usual effect of a methylation of the NH_2, the absorption shifts to shorter instead of to longer waves, and that as a result of the perturbation of planarity due to steric hindrance, coplanarity of the NMe_2 group with the ring having become impossible. Substitution of H atoms for the Me groups in the rings has no effect on the absorption, whereas in the compd. with NMe_2 instead of NH_2, that same substitution shifts the absorption max. by 33 $m\mu$ to longer waves. Changes in the position of the absorption max. are also produced when the coplanarity of the chromophore system, i.e. of the conjugated aromatic or heterocyclic rings, is disturbed by the substitution, as in the substituted monomethinecyanines of the type AC(R'):B(Y and Z are always H). Following are, for the different substituents R and R', the positions of the absorption max. ($m\mu$) and the values 10^{-4} *E* of the absorption coeff.: H, H, 425, 8.0; Me, H, 425, 8.1; Et, H, 425, 7.5; Pr, H, 426, 7.3; Ph, H, 429, 7.5; H, Me, 425, —; H, Et, 425, —; H, Pr, 427, —; Me, Me, 465, 4.7; Et, Me, 480, 4.3; Me, Et, 465, 4.7,—; Me, Pr, 466, 4.5. Steric hindrance to coplanarity is present only in the last 4 derivs., and only these show a shift of absorption to longer waves and a lowering of *E*. The noncoplanarity of these 4 derivs. manifests itself also in the low yields, not over 15%, of their synthesis. The compd. $2,4,6\text{-}(NO_2)_3C_6H_2CH{:}B$(R = Me, Y = H, Z = H) in benzene soln. is red and has a max. of absorption

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at [illegible] mμ, E = 8 × 10⁴; substitution of the H in the CH group by Me gives a blue soln., max. at [illegible] mμ, E = 1.88 × 10⁴. Analogous effects of disturbance of coplanarity are observed also in dyes with longer chains, as the trimethine dyes of the type AC(R'):CHC(R'):B(Y and Z are always H). The positions of the absorption max. and values of 10^{-4} E for different R and R' are: Me, H, [illegible], 14.0; Me, Me, 570, 7.0; Me, Ph, 580, 4.1; Ph, H, [illegible], 15.5; Ph, Me, 602, 6.8; Ph, Et, 600, 6.6; Ph, Ph, 601, 4.0; shifts of the max. to longer waves and lowering of E are found with the substituents Me, Me; Me, Et; Ph, Me; Ph, Et; and Ph, Ph, i.e. in all cases where there is noncoplanarity on steric-hindrance grounds. Lowering of E and shift of the absorption max. are accompanied by increased diffuseness of the max. as compared with the sharp max. of the planar compds. In the series of cyanine dyes with a closed polymethylene bridge of the type $A\overbrace{C:CH.C}^{(CH_2)_n}:B$ (Y and Z are always H) the color varies in a peculiar way with n; the max. and 10^{-4} E are, for n = 1, [illegible], 14.5; n = 2, 601, 15.0; n = 3, 565, 13.0; n = 4, 578, 8.1. In the styryl-type polymethine dyes p-$Me_2NC_6H_4CH:CHA$ (R = Me, Y = H, Z = H), only substitution of the β-H atom by an alkyl gives rise to steric disturbance of the planarity, and to displacement of the max. to shorter waves, with a lowering of the intensity of absorption. The unsubstituted compd. in alc. soln. is red, max. [illegible] mμ, its β-Me deriv. is orange, max. 487 mμ, and its β-iso-Pr deriv. yellow, max. 437 mμ. In all cases of disturbance of planarity, except in one, the intensity of the absorption is lowered. The position of the max. is always shifted to shorter waves when the noncoplanarity is brought about by forcing the auxochrome group out of the common plane; where the coplanarity of the rings themselves is disturbed, the max. can suffer a shift either to shorter or to longer waves. Noncoplanarity is further assocd. with such properties as absence or near-absence of phosphorescence, lower melting temp., greater soly. in alc., lower resistance to decoloration by acids and particularly alkali, and lower resistance to decoloration by light. N. Thon

1967

KIPRIANOV, A. I.

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[illegible]

Synthesis of dyes from Michler's ketone and heterocycles containing an active methyl or methylene group. O. M. Okrenswindler and A. I. Kiprianov. *Ukrain. Khim. Zhur.* 16, [illegible](1950)(in Russian).—Heating 1 g. 2-methylbenzothiazole and 1.07 g. Michler's ketone (I) in 4 ml. Ac_2O 2 hrs. at 135-40°, followed by addn. of Et_2O, gave 11% *2-[2,2-bis(p-dimethylaminophenyl)vinyl]benzothiazole methiodide*, red, decompg. 232°, abs. max. 530 mμ (5.1×10^4); the same dye formed in 28% yield from auramine and 2-methylbenzothiazole methyl methosulfate. I and 2-methyl-5-methoxybenzothiazole methyl methosulfate gave similarly 6% *2-[2,2-bis(p-dimethylaminophenyl)vinyl]-5-methoxybenzothiazole methiodide*, m. 185°, abs. max. 535 mμ (4.7×10^4). I and 2-methyl-α-naphthothiazole methyl methosulfate gave 7% *2-[2,2-bis(p-dimethylaminophenyl)vinyl]-α-naphthothiazole methiodide*, violet, decompg. 215°, abs. max. 535 mμ (8.1×10^4). I and 2-methyl-6-nitrobenzothiazole gave 15% *2-[2,2-bis(p-dimethylaminophenyl)vinyl]-6-nitrobenzothiazole*, decompg. 212°, abs. max. 574 mμ (5×10^4). Heating 0.57 g. 2,6-dimethylbenzothiazole methyl methosulfate with 0.8 g. auramine 1 hr. at 140°, followed by 2 hrs. at 140° after addn. of 4 ml. Ac_2O and 1 drop pyridine, gave 21% *2-[2,2-bis(p-dimethylaminophenyl)vinyl]-6-methylbenzothiazole methiodide*, green, decompg. 195°, abs. max. 525 mμ (4.4×10^4). With auramine and 2-methylbenzothiazole ethyl ethosulfate treated as above there was formed 13% *2-[2,2-bis(p-dimethylaminophenyl)vinyl]benzothiazole ethiodide*, red, decompg. 272°, abs. max. 535 mμ (5.1×10^4). Auramine and 2-methyl-6-methoxybenzothiazole methyl methosulfate gave 43% *2-[2,2-bis(p-dimethylaminophenyl)vinyl]-6-methoxybenzothiazole methiodide*, m. [illegible]°, abs. max. 550 mμ (6×10^4). Auramine and [illegible] thiazole methyl methosulfate gave 22% 2-[2,2-bis(p-di-

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methylaminophenyl)vinyl]-4-phenylthiazole methiodide, m. 170°, abs. max. 492 mμ (4.9 × 10^4). Auramine and 2,4-dimethyl-5-carbethoxythiazole methyl methosulfate gave 32% green *2-[2,2-bis(p-dimethylaminophenyl)vinyl]-4-methyl-5-carbethoxythiazole methiodide*, decompg. 214°, abs. max. 620 mμ (5.7 × 10^4). Heating 0.57 g. Michler's thioketone (II) and 0.26 g. Me_2SO_4 in 4 ml. toluene 1 hr. at 115°, followed by distn. of toluene, soln. of the blue II methyl methosulfate in 5 ml. pyridine, and heating this with 0.6 g. 2-methyl-6-acetamidobenzothiazole methyl methosulfate 45 min. at 100-15° gave about 30% *2-[2,2-bis(p-dimethylaminophenyl)vinyl]-6-acetamidobenzothiazole methiodide*, decompg. 176°, abs. max. 585 mμ (5 × 10^4). The same dye was also formed either from auramine or I in Ac_2O, but contained less than the theoretical amt. of N. Similarly, II, Me_2SO_4, and 2-methylbenzoxazole methyl methosulfate gave 7% *2-[2,2-bis(p-dimethylaminophenyl)vinyl]benzoxazole methiodide*, m. 183°, abs. max. 505 mμ (5.9 × 10^4). Use of quinaldine methyl methosulfate in the above prepn. gave 22% *2-[2,2-bis(p-dimethylaminophenyl)vinyl]quinoline methiodide*, green, decompg. 207°, abs. max. 608 mμ (4.2 × 10^4). Use of trimethylindolenine methiodide in the above prepn. gave similarly 7% *2-[2,2-bis(p-dimethylaminophenyl)vinyl]-3,3-dimethylindolenine methyl perchlorate* ($NaClO_4$ used for final pptn. instead of the usual KI), black-blue, m. 207°, abs. max. 625 mμ (3 × 10^4). Heating 0.5 g. 2,4-dimethylthiazole with 0.6 g. Me_2SO_4 2 hrs. at 100° followed by heating as above with 2 g. II methyl methosulfate in pyridine gave 22% *2-[2,2-bis(p-dimethylaminophenyl)vinyl]-4-methylthiazole methiodide*, orange-brown, m. 261°, abs. max. 475 mμ (3.2 × 10^4). Melting together 0.2 g. 3-hydroxythianaphthene-2-carboxylic acid with 0.42 g. auramine at 125-30° until NH_3 evolution stopped, followed by 1.5 hrs. *in vacuo*, finally at 150° gave a mixt. which dild. with AcPh, followed by EtOH gave 58% *2-[bis(p-dimethylaminophenyl)methylene]-2,3-dihydro-3-oxothianaphthene*, red, m. 240°, abs. max. 530 and 465 mμ (1.76 × 10^4 and 1.9 × 10^4). Auramine (1.23 g.), 1 g. 1-phenyl-3-methyl-5-pyrazolone, and 1 ml. xylene after heating at 130-40° to expel NH_3, finally *in vacuo* 1 hr. gave 58% *4-[bis(p-dimethylaminophenyl)methylene]-1-phenyl-3-methyl-5-pyrazolone*, red-brown, m. 266°, abs. max. 485 mμ (5.2 × 10^4). Similarly 0.2 g. 3-ethylrhodanine and 0.33 g. auramine gave 41% *5-[bis(p-dimethylaminophenyl)methylene]-3-ethylrhodanine*, red-brown, m. 227°, abs. max. 480-500 mμ (3.4 × 10^4). Similarly 0.4 g. rhodanine and 0.8 g. auramine gave 28% *5-[bis(p-dimethylaminophenyl)methylene]rhodanine*, red, m. 224°, abs. max. 470-80 mμ (3.1 × 10^4). 3-Allylrhodanine and auramine gave 67% red *5-[bis(p-dimethylaminophenyl)methylene]-3-allylrhodanine*, m. 206°, abs. max. 480-500 mμ (3.3 × 10^4). Heating 2.7 g. auramine and 2 g. 2-imino-3-phenyl-4-thiazolidinone 10 min. at 170°, then 10 min. with 3 ml. xylene, gave 11% *5-[bis(p-dimethylaminophenyl)methylene]-2-imino-3-phenyl-4-thiazolidinone*, m. 276°, yellow-orange, abs. max. below 430 mμ. In the above-described condensations the order of reactivity of the quaternary salts declines in the order: II, auramine, I.

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Color of organic dyes and planarity of their molecules. I. A. I. Kiprianov and I. K. Ushenko (Acad. Sci. Ukrain. S.S.R., Kiev). *Zhur. Obshchei Khim.* (*J. Gen. Chem.*) **20**, 134-41(1950).—Cyanine dyes contg. proximal groups of large size display a shift of absorption max. toward the red end of the spectrum and a corresponding decrease of the intensity of absorption in comparison with unsubstituted derivs. The explanation probably lies in destruction of planarity of mols. with bulky groups, leading to closing-up the energy differences between ground and excited states (cf. Brooker, *et al.*, *C.A.* **42**, 1129a). Refluxing 2-methylbenzothiazole-MeI with 2-methylmercaptobenzothiazole-Me_2SO_4 and NaOAc in EtOH gave yellow *bis(3-methyl-2-benzothiazole)monomethinecyanine iodide*, decompg. 281° (from EtOH), λ_{max} 422 mμ, E_{max} 8.1 (× 10^{-4}). 2-Ethylbenzothiazole-MeI gave 35% *bis(3-methyl-2-benzothiazole)-8-methylmonomethinecyanine iodide*, orange, decompg. 217°, λ_{max} 405, E_{max} 6.0. Heating $CH_2(CO_2H)_2$ and 2-methylmercaptobenzothiazole-*p*-$MeC_6H_4SO_3Ph$ in pyridine gave *bis(3-phenyl-2-benzothiazole)monomethinecyanine iodide*, decompg. 318°, λ_{max} 420, E_{max} 7.5. Refluxing 1.2 g. 2-(methylmercaptobenzothiazole-*p*-$MeC_6H_4SO_3Ph$, 1 g. 2-ethylbenzothiazole-PhCl, and 1 g. NaOAc in EtOH gave 16% *bis(3-phenyl-2-benzothiazole)-8-methylmonomethinecyanine iodide*, decompg. 200°, bronze plates, λ_{max} 400, E_{max} 3.8. Similar use of 2-propylbenzothiazole-PhI gave 13% *bis(3-phenyl-2-benzothiazole)-8-ethylmonomethinecyanine iodide*, m. 214° (from EtOH), λ_{max} 401, E_{max} 2.1. Refluxing 0.78 g. 2-methylbenzothiazole-PhI and 1 g. 2-(2-acetanilidovinyl)benzothiazole-EtI 15 min. in pyridine gave 50% *(3-ethyl-2-benzothiazole)(3-phenyl-2-benzothiazole)trimethinecyanine iodide*, decompg. 243° (from EtOH), green, λ_{max} 560, E_{max} 11.8. Similarly, 2-ethylbenzothiazole-EtI and 2-(2-acetanilidovinyl)benzothiazole-PhI gave 60% *(3-ethyl-2-benzothiazole)(3-phenyl-2-benzothiazole)-9-methyltrimethinecyanine iodide*, m. 158° (from EtOH), λ_{max} 562, E_{max} 11.0, while 2-ethylbenzothiazole-PhCl gave *(3-ethyl-2-benzothiazole)(3-phenyl-2-benzothiazole)-9-methyltrimethinecyanine iodide*, blue green, m. 252°, λ_{max} 570, E_{max} 11.8, the corresponding PhI compd. gave *bis(3-phenyl-2-benzothiazole)-9-methyltrimethinecyanine iodide*, decompg. 275° (from EtOH), λ_{max} 572, E_{max} 15.0.

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while the mother liquor gave a *cyanine* without Me on the methine chain, C[illegible]H[illegible]N_2S_2I, m. 277°, λ_{max} 565. Refluxing 1 g. 2-(1-naphthylmethyl)benzothiazole-PhI, 1 g. $HC(OEt)_3$, and 4 ml. Ac_2O gave 32% *bis(3-phenyl-2-benzothiazole)-8,10-di-1-naphthyltrimethinecyanine perchlorate*, bronze crystals, decompg. 196-7° (from EtOH), λ_{max} 592, E_{max} 9.5. 2-(2-Tetrahydronaphthylmethyl)benzothiazole-PhI and $HC(OEt)_3$ gave crude *bis(3-phenyl-2-benzothiazole)-8,10-(tetrahydro-2-naphthyl)trimethinecyanine perchlorate*, λ_{max} 580. Heating 2-ethylbenzothiazole-MeI and $HC(OEt)_3$ in pyridine gave *bis(3-methyl-2-benzothiazole)-8,10-dimethyltrimethinecyanine iodide*, bronze needles, decompg. 221°, λ_{max} 570, E_{max} 7.0, while heating 2-benzylbenzothiazole-MeI with $HC(OEt)_3$ in Ac_2O gave 22% *bis(3-methyl-2-benzothiazole)-8,10-diphenyltrimethinecyanine perchlorate*, violet, decompg. 152°, λ_{max} 580, E_{max} 4.1; 2-(1-naphthylmethyl)benzothiazole-MeI gave 20% *bis(3-methyl-2-benzothiazole)-8,10-di-1-naphthyltrimethinecyanine perchlorate*, violet, decompg. 170° (from EtOH), λ_{max} 568, E_{max} 3.7, and the tetrahydro-2-naphthyl analog yielded *bis(3-methyl-2-benzothiazole)-8,10-bis(tetrahydro-2-naphthyl)trimethinecyanine perchlorate*, 25%, blue, decompg. 152° (from dil. EtOH), λ_{max} 578, E_{max} 2.1. Chloromethylation of *tetrahydronaphthalene* gave 52% *(2-chloromethyl) deriv.*, b_{11} 130-42°; this (71 g.) boiled 3 hrs. with 20 g. KCN in 400 ml. EtOH and 70 H_2O gave the *nitrile* (72%), b_{10} 178-82°, which boiled 10 hrs. with 20% NaOH gave 70% *tetrahydro-2-naphthaleneacetic acid*, m. 85° (from H_2O); *amide*, m. 142° (from H_2O), was a by-product. The free acid and $SOCl_2$ gave 78% of the *acyl chloride*, b_5 143-4°, which with o-$MeNHC_6H_4SH$ in C_6H_6 gave a yellow mass yielding on soln in H_2O and addn. of KI 72% *2-(tetrahydro-2-naphthylmethyl)benzothiazole-MeI*, m. 220° (from H_2O). The results of Ushenko (*Ukrain. Khem. Zhur.* 14, 30 (1948)) are interpreted similarly to the above. G. M. Kosolapoff

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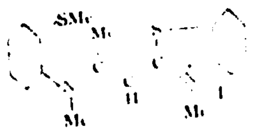
Reaction of methylene derivatives of the thiazole series with alkyl halides. A. I. Kiprianov and F. S. Babichev (State Univ., Kiev). *Zhur. Obshchei Khim.* (J. Gen. Chem.) 20, 148-57(1950). Methylene derivs. of thiazoles generally form with alkyl halides a 2:1 adduct, which is easily hydrolyzed. MeI (30 g.) and 22 g. *3-methyl-2-methylenebenzothiazoline* (m. 104-6°) in 50 ml. $CHCl_3$ gave 98% yellow adduct, needles, m. 229-30°, probably based on the dimer of the thiazoline and having the probable structure (I); other solvents give the same product,



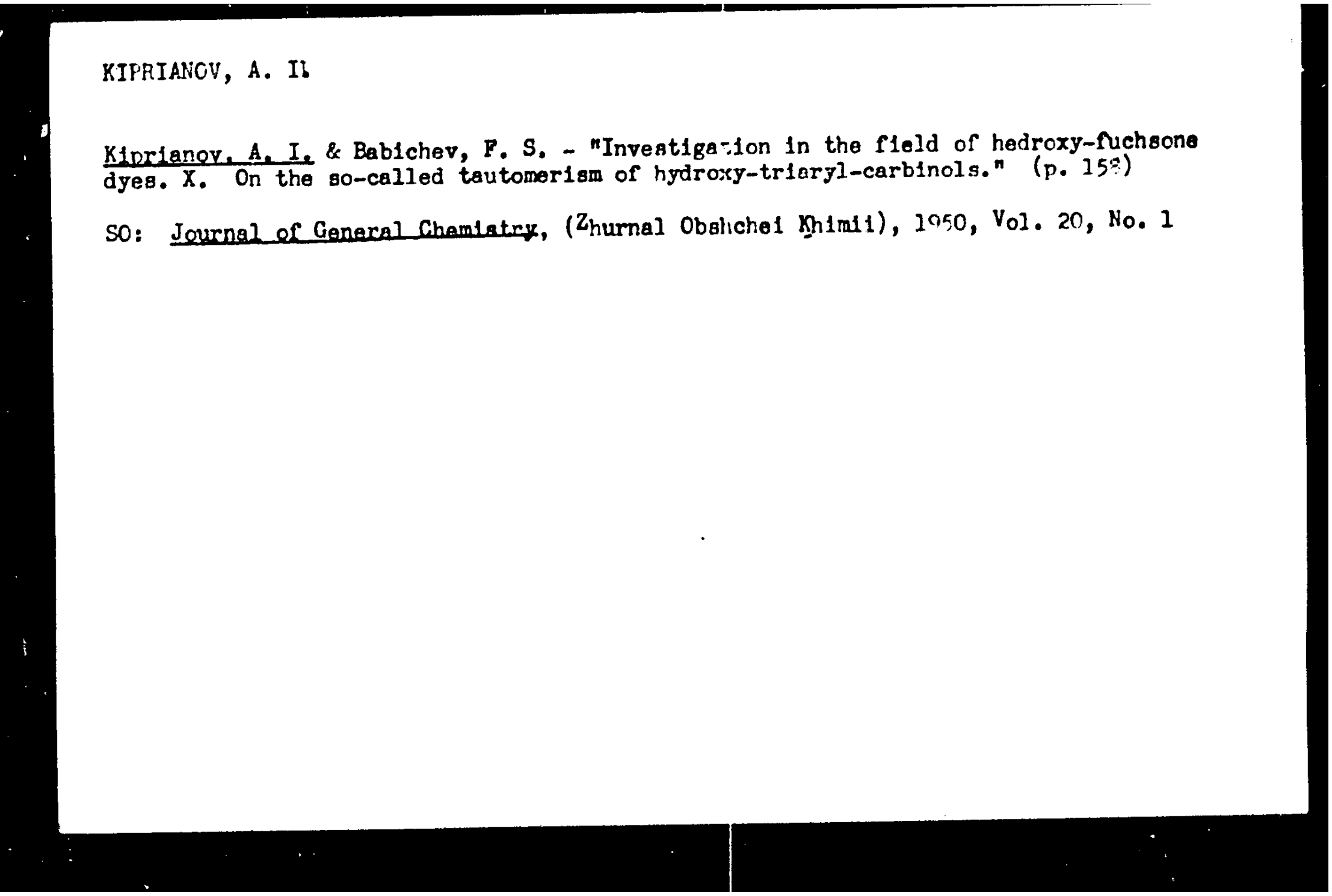
(I)

although in EtOH the product is obtained in impure

state; boiling I with 1:10 HCl gave *3-methyl-2-(acetyl-*
methylene)benzothiazoline-HCl (*free base*, m. 157-8° on
crystn. from EtOH, m. 160-1°), while the mother liquor
after addn. of NaOH gave 87% *o-methylmercapto-N-*
methylaniline, b_{10} 126-8°; *HI salt*, m. 161°; *Ac deriv.*,
by action of AcCl, m. 81-2°. Similar reaction with EtI
gave the *Et analog* of I, m. 190-1°, which boiled with
dil. HCl gave 91% of the same thiazoline-HCl deriv.
(above) and 73% *o-ethylmercapto-N-methylaniline*, b
112-14° [*Ac deriv.*, m. 55° (from petr. ether)]. Similar
reaction of MeI with 3-ethyl-2-methylenebenzothiazoline
gave 92% *3-Et analog* of I, m. 192-3° (from EtOH), which
on boiling with 1:6 HCl gave 81% *3-ethyl-2-(acetyl-*
methylene)benzothiazoline, m. 115-16°, and *o-methyl-*
mercapto-N-ethylaniline, b_{12} 99-101° (*Ac deriv.*, m. 66-
7°). Similar reaction of *3-methyl-2-methylene-α-naph-*
thothiazoline [from 2-methyl-α-naphthothiazole-Me_2SO_4
and KOH in dil. Me_2CO; m. 200-3° (decompn.); mol.
wt. close to dimeric] with MeI in warm $(CH_2Cl)_2$ gave
87% corresponding *analog* of I, m. 276-7° (from pyridine),
this boiled 5 min. with aq. alc. NaOH gave 79% *1-methyl-*
2-acetylmethylene-α-naphthothiazoline, m. 202-3°, and
165°; *1-methylmercapto-2-methylaminonaphthalene*, m.
55° (from EtOH), *Ac deriv.*, m. 127° (from EtOH);
EtI gave 92% corresponding *analog* of I, m. 246-7° (fr

compd.), which on hydrolysis with dil. alc. NaOH gave the same 3-methyl-2-(acetylmethylene)-α-naphthothiazoline and 52% *1-ethylmercapto-2-(methylamino)naphthalene*, b. 190-1 (*Ac deriv.*, m. 112-13° (from petr. ether)]. *3-Methyl-4,5-diphenyl-2-methylenethiazoline* (prepd. in 91% yield analogously from the corresponding methosulfate), m. 152-4° (decompn.), is nearly dimeric (in C_6H_6); its reaction with MeI gave the corresponding *analog* of I, decompg. 183-4° (from EtOH), which boiled with dil. alc. HCl gave *PhCH(SMe)Bz*, m. 75-6° (from EtOH) (with $PhNHNH_2$ yields $[PhC(:NNHPh)]_2$), $MeNH_2$ (identified as the HCl salt, m. 225-6°), and 80% *3-methyl-4,5-diphenyl-2-(acetylmethylene)thiazoline*, m. 229-30° (from EtOH), which yields cyanine dyes on warming with quaternary salts of N heterocycles. EtI in the above reaction gave 93% of the corresponding *analog* of I, decompg. 214-15°, which on hydrolysis in dil. alc. HCl gave 75% thiazoline deriv. (above) and 83% *PhCH(SEt)Bz*, m. 78° (also yielding a benzil deriv. with $PhNHNH_2$). *3-Methyl-6-nitro-2-methylenebenzothiazoline* (by similar reaction of the corresponding methosulfate, in 73% yield, decompg. 230-2°, dimeric mol. wt.) on heating 15 hrs. in a sealed tube with MeI gave only *2-methyl-6-nitrobenzothiazole-MeI*, similar reaction at 130° with Me_2SO_4 gave only the corresponding *Me methosulfate*, m. 203-4°.

G. M. Kosolapoff



KIPRIANOV, A. I.

Kiprianov, A. I. & Babichev, F. S. - "Investigation in the field of hedroxy-fuchsone dyes. X. On the so-called tautomerism of hydroxy-triaryl-carbinols." (p. 158)

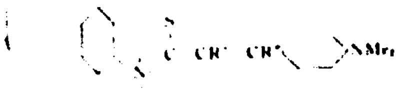
SO: Journal of General Chemistry, (Zhurnal Obshchei Khimii), 1950, Vol. 20, No. 1

CA

10

Color of organic dyes and the planarity of their molecules. II. A. I. Kiprianov and I. K. Ushenko (Acad. Sci. Ukr. S.S.S.R.). *Zhur. Obshchei Khim.* (J. Gen. Chem.) **20**, 514-17(1950); cf. C.A. **44**, 5733g.—The absorption spectra of the several styryl derivs. studied show a displacement of the max. to the shorter waves with concurrent decrease of intensity when alkyl or aryl groups are substituted in the α- or β-positions of the fundamental unit (I). The results are explained by destruction of coplanar structure of the benzene and the thiazole rings. The following max. (in mμ) and ε were observed (R, R', R'' given): *Ph, H, H* (I), 540, 6.2 × 10⁴; *Ph, Me, H* (II), 508, 2.4 × 10⁴, *Ph, Et, H* (III), 500, 2.6 × 10⁴, *Ph, [illegible] H* (IV), 500, 3.3 × 10⁴, *Et, H, H* (V), 530, 11 × 10⁴, *Et, Me, H* (VI), 481, 6.2 × 10⁴, *Et, Et, H* (VII), 482, [illegible], *Et, Ph, H* (VIII), 508, 2.5 × 10⁴, *Ph, H, Me* (IX), 552, 2.2 × 10⁴, *Ph, H, Ph* (X), 550, 1.5 × 10⁴, *Et, H, Me* (XI), 518, 2.1 × 10⁴, resp. New syntheses were as follows. VI was prepd. in 50% yield by refluxing 1 hr. 0.5 g. 2-ethylbenzothiazole-EtI, 0.4 g. *p*-$Me_2NC_6H_4CHO$, and 2 ml. Ac_2O, followed by addn. of $NaClO_4$ in EtOH, yielding the *etho-perchlorate*, m. 240° (decompn.) (from EtOH). VII, prepd. similarly, could not be obtained completely pure. VIII was prepd. similarly from 2-benzylbenzothiazole-EtI and isolated as the *etho-perchlorate*, decomp. 172°, cherry-red, in 18% yield. IX prepd. similarly from 2-methylbenzothiazole-PhBr and *p*-$Me_2NC_6H_4Ac$ in 20% yield, isolated as the *phenyl perchlorate*, decomp. 215° (from EtOH). X (in 16% yield), similarly prepd. from *p*-$Me_2NC_6H_4Bz$, decomp. 265° (from EtOH). XI, isolated as the *etho-perchlorate*, decomp. 240°, red, obtained in 31% yield from 2-methylbenzothiazole, *p*-$MeC_6H_4SO_3Et$, and $Me_2NC_6H_4Ac$ in Ac_2O.

G. M. K.



(I)

CA

10

The color of organic dyes and the planarity of their molecules. II. A. I. Kiprianov and I. K. Ushenko. J. Gen. Chem. U.S.S.R. 20, 543 (1950) (Engl. translation). R. M. S.
See C. A. 44, 7817b.

1951

KIPRIANOV, A.I.

"Iodine Synthesis," Dkk. AN., 70, Nol 4, 1950. Inst. of Org. Chem., Ukrainian SSR Acad. Sci., -c1950-.

KIIRIANCV A. I.

USSR/Chemistry - Photographic Sensitizers

Nov 50

"Cyanin Dyes Containing Fluorine. I. Cyanin Dyes From Derivatives of 6-Fluorobenzothiazol," A. I. Kiprianov, L. M. Yagupol'skiy, Chair of Org Chem, Kiev State U

"Zhur Obshch Khim" Vol XX, No 11, pp 2111-2117

Synthesized 2-methyl-6-fluoro- and 2-methylmercapto-6-fluorobenzothiazols and their quaternary salts. Obtained 11 thiocyanin dyes containing F as substitute in position 6,

170T28

USSR/Chemistry - Photographic Sensitizers (Contd)

Nov 50

in place of H. Showed this substitution has practically no effect on position of maximum absorption, as distinguished from Cl, Br, and I.

170T28

OKSENGENDLER, G.M.; KIPRIANOV, A.I.

Condensation of auramine with 2-aminothiazole derivatives. Ukr.khim.zhur. 17 no.5:736-743 '51. (MLRA 9:9)

1. Institut organicheskoy khimii AN USSR.
(Auramine) (Thiazole)

OKSENGENDLER, G.M.; KIPRIANOV, A.I.

Condensation of β,β-bis(p-dimethylaminophenyl)-acrolein with heterocyclic compounds containing an active methyl or methylene group. Ukr.khim.zhur.17 no.5:744-750 '51. (MIRA 9:9)

1. Institut organicheskoy khimii AN USSR.
(Acrolein) (Dyes and dyeing--Chemistry)

KIPRIANOV, A. I.

Pa. 173T36

USSR/Chemistry - Photographic Sensitizers Jan 51

"Investigation Into Series of Derivatives of Benzo-1, 4-Thiazine. I. Quaternary Salts of Benzo-1, 4-Thiazine and Its Derivatives," A. I. Kiprianov, Z. N. Pazenko, Inst Org Chem, Acad Sci Ukrainian SSR

"Zhur Obshch Khim" Vol XXI, No 1, pp 156-163

Synthesized heretofore unknown quaternary salts of benzo-1, 4-thiazine deriv by condensing α-halogenoketones with N-alkyl- or N-aryl-o-aminothiophenols. Obtained 6 methyl- and phenylperchlorates of benzo-1, 4-thiazine. Synthesized methylperchlorate of benzo-1, 4-thiazine by condensing

173T36

USSR/Chemistry - Photographic Sensitizers Jan 51
(Contd)

N-methyl-o-aminothiophenol with sym dibromethylene. Showed that above salts are easily isomerized into corr quaternary salts of 2-alkylbenzothiazols.

173T36

Pa. 173T37

USSR/Chemistry - Photographic Sensitizers Jan 51

"Investigation Into Series of Derivatives of Benzo-1, 4-Thiazine. II. Cyanine Dyes of Benzo-1, 4-Thiazine Series," A. I. Kiprianov and Z. N. Pazenko, Inst Org Chem, Acad Sci Ukrainain SSR

"Zhur Obshch Khim" Vol XXI, No 1, pp 163-170

Describes 9 new cyanine dyestuffs (benzo-1, 4-thiazinocyanines). Synthesized them (2 monomethine-, 6 trimethine-, and 1 pentamethinecyanine) by heating quaternary salts of benzo-1, 4-thiazine and its

[redacted] 173T37

USSR/Chemistry - Photographic Sensitizers Jan 51
(Contd)

deriv with orthoformic ester in pyridine or in mixt of acetic anhydride and pyridine. Due to isomerization thiacarbocyanines formed simultaneously with thiazinocarbocyanines.

KIPRIANOV, A., I.,

[redacted] 173T37

KIPRIANOV, A. I.

Pa. 173T38

USSR/Chemistry - Photographic Sensitizers Jan 51

"Investigation Into Series of Derivatives of Benzo-1, 4-Thiazine. III. Condensation of Quaternary Salts of Benzo-1, 4-Thiazine and Its Derivatives With Aldehydes," A. I. Kiprianov, A. N. Pazenko, Inst Org Chem, Acad Sci Ukrainian SSR

"Zhur Obshch Khim" Vol XXI, No 1, pp 170-174

Condensed quaternary salts of 3-methylbenzo-1, 4-thiazine and certain deriv with p-dimethylaminobenzaldehyde in acetic anhydride to form corr styryls, which are unstable to action of

[redacted] 173T38

USSR/Chemistry - Photographic Sensitizers Jan 51
(Contd)

alkalis. Quaternary salts of benzo-1, 4-thiazine and deriv not contg methyl group in 3 position condensed with aromatic aldehydes at methylene group in 2 position of thiazine ring.

[redacted] 173T38

KIPRIANOV A. I.

PA 194T51

USSR/Chemistry - Thiacyanine Dyestuffs Benzothiazole Derivatives **Nov 51**

"Ultraviolet Absorption Spectra of Benzothiazole Derivatives," A. I. Kiprianov, Yu. S. Rozum, Inst of Org Chem, Acad Sci USSR

"Zhur Obshch Khim" Vol XXI, No 11, pp 2038-2045

Studied ultraviolet absorption spectra in alc solns of 2-methylbenzothiazole (I), its derivs contg amino groups on benzene rings, 2-ethyl-α-naphthothiazole, and a number of quaternary salts of benzothiazole derivs. Detd absorption curves of 2 methylene bases formed under action

194T51

USSR/Chemistry - Thiacyanine Dyestuffs (Contd) **Nov 51**

of Na alcoholate on alk soln of iodomethylates of I and 2-methyl-6-dimethylaminobenzothiazole (II) and of II with different concns of H_2SO_4 in soln. Absorption curves of II in alc soln at increasing concns of H_2SO_4 showed that salt of this base forms much more easily on amino group than on benzothiazole ring.

194T51

KRAVCHENKO, V.M.; PASTUKHOVA, I.S.; KIPRIANOV, A.I., diysnyy chlen.

Indol in binary systems binuclear compounds. Dop.AN URSR no.3:193-200 '52.
(MLRA 6:9)

1. Akademiya nauk Ukrayins'koyi RSR (for Kiprianov). 2. Donets'kyy industrial'nyy instytut im. M.S.Khrushchova (for Kravchenko and Pastukhova).
(Indol)

HORBAN', A.K.; KIPRIANOV, A.I., diysnyy chlen.

Acetaldehyde alkyl-β-chlorethyl acetals. Dop.AN URSR no.3:201-204 '52.
(MLRA 6:9)

1. Akademiya nauk Ukrayins'koyi RSR (for Kiprianov). (Acetals)

HORBAN', A.K.; KIPRIANOV, A.I., diysnyy chlen.

Action of an alcoholic solution of alkali on β-chlorethyl acetals of acetaldehydes. Dop.AN URSR no.3:205-207 '52. (MLRA 6:9)

1. Akademiya nauk Ukrayins'koyi RSR (for Kiprianov). (Acetals)

1. KIPRYANOV, A.I.

2. USSR (600)

4. Chemistry, Organic

7. The second conference of the Ukrainian republic on organic chemistry, Ukr.khim.zhur. 18 no. 1, 1952.

9. Monthly List of Russian Accessions, Library of Congress, APRIL 1953, Uncl.

KIPRIANOV, A. I.; PAZENKO, Z. I.

"Scientific Records of the A.M. Gor'kii State University in Kharkov. Vol. 38. Transactions of the Scientific Research Chemical Institute. Vol. 9" Reviewed by A. I. Kiprianov, Z. N. Pazenko, Ukr. khim. zhur. 18 no. 3:335-336 '52.
(MIRA 6:9)

Institut organicheskoy khimii Akademii nauk Ukrainskoy SSR.
(Chemistry--Periodicals)

KiPRIANOV, A.I.

1 Color of organic compounds and the so-called resonance theory. A. I. Kiprianov. *Ukrain. Khim. Zhur.* 18, 330-40 (1952).—The "resonance" point of view in explanation of color phenomena is criticized on grounds of idealism and the author's previous work on color is presented. It is suggested that the formulation of substances in which "resonance" exists in conjugated systems, be written with an outline of dots around the formula to indicate equalization between single and double bonds; in cases of incomplete equalization a light broken arrow outline around the affected parts of the mol. is suggested. G. M. Kosolapoff

KIPRIANOV, A. I.

1/2

Effect of the solvent on color of organic coloring substances. III. A. I. Kiprianov and E. S. Timoshenko (Kiev State Univ.). Zhur. Obshchei Khim. 22, 347-57 (1952); cf. C.A. 47, 8475h; preceding abstr.—A series of dyes was prepd. by condensation of quaternary salts of N-heterocycles with active Me groups, with various aromatic aldehydes; the resulting products alter their color in various neutral solvents. The color changes with change in polarity of solvents is discussed on the basis of changes in polarization of the dye molecules. Refluxing 1.2 g. 2,4-dimethylthiazole methyl methosulfate with 0.86 g. 2-hydroxy-1-naphthaldehyde in EtOH in the presence of a little piperidine 20 min. gave on cooling 21% red-brown *(3,4-dimethyl-2,3-dihydro-2-thiazolidene)(1',2'-naphthoquinono)ethane*, decomp. 225-7° (from EtOH), giving pink soln. in H_2O, red-violet in EtOH and violet in $CHCl_3$; abs. max. in EtOH 579 mμ, in $CHCl_3$ or C_6H_6 590. Similarly 2,4-dimethylthiazole methiodide and 1,4-hydroxynaphthaldehyde gave 81% *(3,4-dimethyl-2,3-dihydro-2-thiazolidene)(1',4'-naphthoquinono)ethane*, decomp. 213-19° (from EtOH in presence of NH_4OH), abs. max. in H_2O 500, in EtOH 604, in $CHCl_3$ 592, in C_6H_6 574. 2-Methylbenzothiazole ethiodide and 2-hydroxynaphthaldehyde similarly gave *(3-ethyl-2,3-dihydro-2-benzothiazolidene)(1',2'-naphthoquinono)ethane*, green, decomp. 210-12° (from EtOH), abs. max. in EtOH 578, in $CHCl_3$ 590, in C_6H_6 583. 2-Methylbenzothiazole methiodide and 4-hydroxynaphthaldehyde gave 18% *(3-methyl-2,3-dihydro-2-benzothiazolidene)(1',4'-naphthoquinono)ethane*, decomp. 248-9° (from EtOH), abs. max. in EtOH 607, in $CHCl_3$ 645, in C_6H_6 632. Refluxing 1 g. 2-methyl-α-naphthothiazole methiodide with 0.36 g. salicylaldehyde in 5 ml. pyridine 30 min. gave a yellow ppt. (67%) of *(3-methyl-2,3-dihydro-α-naphtho-2-thiazolidene)(o-quinono)ethane-HI*, decomp. 203°; this treated with aq. NH_4OH gave the *base* (anhydro form of the dye, $C_{20}H_{15}ONS$), violet, decomp. 178° (from EtOH in presence of NH_4OH), abs. max. in EtOH 562, in $CHCl_3$ 605. Similarly p-HOC_6H_4CHO gave 65% *(3-methyl-2,3-dihydro-α-naphtho-2-thiazolidene)(p-quinono)ethane-HI*, orange, decomp. 270°, which with aq. NH_4OH gave the *base*, violet, decomp. 180° (from EtOH).

OVER

A. I. Kiprianov

2/2

[illegible] max. in EtOH 585, in $CHCl_3$ 580, in C_6H_6 570. Similarly 2-hydroxy-1-naphthaldehyde gave 56% *(3-methyl-2,3-dihydro-α-naphtho-2-thiazolidene)(1',2'-naphthoquino)ethane*, blue, m. 220-2° (from EtOH), abs. max. in EtOH 591, in $CHCl_3$ 603, in C_6H_6 600. Similar reaction of 2-methyl-α-naphthothiazole methyl methosulfate with 1-hydroxy-4-naphthaldehyde in EtOH (piperidine) gave 86% *(3-methyl-2,3-dihydro-α-naphtho-2-thiazolidene)(1',4'-naphthoquino)ethane*, green, decomp. 258-60° (from pyridine), abs. max. in EtOH 614, in $CHCl_3$ 606, in C_6H_6 606. Refluxing 2-methyl-β-naphthothiazole methiodide and salicylaldehyde in EtOH in presence of pyridine 1 hr. gave 58% orange *(3-methyl-2,3-dihydro-β-naphtho-2-thiazolidene)(o-quino)ethane-HI*, decomp. 222-3° (from EtOH); with aq. NH_4OH this gave the *free base*, violet-blue, decomp. 144-7° (from EtOH), abs. max. in EtOH 565, in $CHCl_3$ 605, in C_6H_6 insol. Refluxing β-naphthothiazole methiodide and p-hydroxybenzaldehyde in pyridine 1 hr. gave 46% orange *(3-methyl-2,3-dihydro-β-naphtho-2-thiazolidene)(p-quino)ethane-HI*, decomp. 224° (from EtOH); abs. max. in EtOH 567, in $CHCl_3$ 585, in C_6H_6 570, was found in the *free base*, brown, decomp. 209-10°, obtained by treatment of the above with NH_4OH. Similar reaction of 2-hydroxy-1-naphthaldehyde run in EtOH in presence of piperidine gave 60% *(3-methyl-2,3-dihydro-β-naphtho-2-thiazolidene)(1',2'-naphthoquino)ethane*, blue, decomp. 198-200° (from EtOH), abs. max. in EtOH 594, in $CHCl_3$ 606, in C_6H_6 600. Reaction of 2-methyl-β-naphthothiazole methyl methosulfate with 1-hydroxy-4-naphthaldehyde gave 100% *(3-methyl-2,3-dihydro-β-naphtho-2-thiazolidene)(1',4'-naphthoquino)ethane*, [illegible] decomp. 245° (from EtOH), abs. max. in EtOH 610, in $CHCl_3$ 638, in C_6H_6 602. 2-Methylpyridine methiodide and 1-hydroxy-4-naphthaldehyde in EtOH (piperidine) gave 42% brown ppt., which treated with concd. NaOH gave 35% *(1-methyl-1,2-dihydro-2-pyridylidene)(1',4'-naphthoquino)ethane*, red-violet (from H_2O), blue-violet after vacuum drying, and green after drying at 100°, abs. max. in EtOH 430, in $CHCl_3$ 575, in C_6H_6 584. Quinaldine methiodide similarly gave 25% *(1-methyl-1,2-dihydro-2-quinolylidene)(1',4'-naphthoquino)ethane*, green, decomp. [illegible] (from EtOH-NH_3), abs. max. in H_2O 648, in EtOH 600, in $CHCl_3$ 603, C_6H_6 590. Similarly 2-methyl-4-phenylthiazole methiodide gave *(3-methyl-4-phenyl-2,3-dihydro-2-thiazolidene)(1',4'-naphthoquino)ethane*, violet, decomp. 190° (from EtOH), abs. max. in EtOH 508, in $CHCl_3$ 601, in C_6H_6 572; the ppt. formed directly from the reaction mixture gives red color in EtOH, turning yellow on addn. of acids or blue with alkali; it appears to be a complex of quinhydrone type between the base and the HI salt. Similarly 2-methyl-4,5-diphenylthiazole methiodide gave 81% *(3-methyl-4,5-diphenyl-2,3-dihydro-2-thiazolidene)(1',4'-naphthoquino)ethane*, green, decomp. 197-8° (from EtOH), abs. max. in EtOH 615, in $CHCl_3$ 610, in C_6H_6 598. 2,3,3-Trimethylindolenine methiodide gave 66% *(1,3,3-trimethyl-1,3-dihydro-2-indolenine)(1',4'-naphthoquino)ethane-HI*, red; this with NH_4OH gave 50% *free base*, decomp. 220° (from EtOH), violet, abs. max. in EtOH 507, in $CHCl_3$ 530, in C_6H_6 504.

G. M. Kosolapoff

KIIRIANOV, A. I.

USSR/Chemistry - Benzothiazole Derivatives Feb 52

"Derivatives of Dibenzothiazolylmethane," A. I. Kiprianov, L. P, Yakovlev, Yu. S. Rozum, Inst of Org Chem, Acad Sci Ukrainian SSR

"Zhur Obshch Khim" Vol XXII, No 2, pp 302-309

Condensation of o-aminothiophenol with esters of methyl-, ethyl-, n-propyl-, iso-propyl-, phenyl-, and dimethylmalonic acids yielded 6 new bases: dibenzothiazolylmethanes substituted in methane residue. Detd ultraviolet absorption curves of dibenzoyhiazolylmethane (I) and its 6 derivs, compared them with absorption curves of 2-(N-methylbenzothiazolydene-(2))-methylbenzothiazole. Showed

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USSR/Chemistry - Benzothiazole Derivatives Feb 52
(Contd)

that I and its mono derivs develop tautomerism in solns. Prepd 3 new monomethinethiazyanines contg alkyl as substituent at central C atom. Detd their absorption curves in alc solns and showed that mols of these dyestuffs exhibit spatial hindrances preventing coplanarity of thiazole rings.

209T28

1. CHERNETSKIY, V. P., KIPRYANOV, A. I.
2. USSR (600)
4. Phenazines
7. Synthesis of N-oxides of phenazine derivatives. Part 1. Nono-N-oxides of alkoxyphenazines. Zhur. ob. khim., 22, no. 10, 1952

9. Monthly List of Russian Accessions, Library of Congress, February 1953. Unclassified.

[illegible]

[illegible]

PA 227T10

KIPRIANOV, A. I.

USSR/Chemistry - Dyestuffs 1 Aug 52

"Coplanarity of Dimethylamine Group With the Benzene Ring and It$ Auxochromic Action," A.I. Kiprianov, Acting Mem Acad Sci Ukrainian SSP I.N. Zhmurova, Inst of Org Chem, Acad Sci Ukrainian SSR

"Dok Ak Nauk SSSR" Vol 85, No 4, pp 789-791

Cyanine dyestuffs contg radicals in the ortho position to the amino group were studied. The amino group itself strongly shifts the absorption max to the long-wave region. Introduction of a methyl or ter-butyl group in the ortho position has little effect, but a dimethylamino group

227T10

shifts absorption max by 33 mμ into the short-wave region. The dimethylamino group alone lowers the extinction max sharply, but introduction of a methyl or ter-butyl group into the ortho position results in a growth in extinction with a shift of the absorption max to the short-wave region. Thus the voluminous hydrocarbon radicals cancel the effect of dimethylamino groups on the color of dyestuffs.

(CA 47 no.19:9979 '53)

227T10

KIPRIANOV, A.I.; STOLYAROV, N.Z.

2-benzothiazolylacrylic acid and its derivatives. Ukr.khim.zhur. 19 no.1:57-60 '53. (MLRA 7:4)

1. Kiyevskiy gosudarstvennyy universitet im. T.G.Shevchenko, kafedra organicheskoy khimii. (Acrylic acid)

KIPRIANOV, A.I.; KROSHCHENKO, M.M.

Synthesis of 1,2-benzophenazine derivatives. Ukr.khim.zhur. 19 no.1:73-80 '53. (MLRA 7:4)

1. Institut organicheskoy khimii Akademii nauk USSR. (Phenazine)

KIPRIANOV, A.I.; POCHINOK, V.Ya.

2-aminomethylbenzothiazole. Ukr.khim.zhur. 19 no.2:165-168 '53.
(MLRA 7:4)

1. Kiyevskiy gosudarstvennyy universitet, kafedra organicheskoy khimii.
(Thiazole)

KIPRIANOV, A.I.

USSR.

✓Achievements of organic chemistry in fighting tuberculosis. A. I. Kiprianov. *Ukrain. Khim. Zhur.* 10, 230-40(1953); *Referat. Zhur. Khim.* 1954, No. 32634.—A review. B. Wierbicki

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✓Synthesis of derivatives of 1,2,3,4-dibenzophenazine and acenaphthylene(1',2',2,3)quinoxaline. A. I. Kiprianov and M. M. Kroshchenko. *Ukrain. Khim. Zhur.* [illegible] (1953); *Referat. Zhur., Khim.* 1954, No. [illegible].—The derivs. of 1,2-benzophenazine, 1,2,3,4-dibenzo-[illegible]phenazine (*C.A.* [illegible]10-methoxydibenzo[*a,c*]phenazine) (I), and 1,2,3,4-dibenzo-7-methoxyphenazine (II), were synthesized. Heating them with HBr produced the corresponding HO compds. (III and IV, resp.) from which the MeI salts were prepd. By the action of Na_2CO_3 on the methyl toluenesulfonates of III and IV were obtained 1,2,3,4-dibenzo-10-methyl-8-phenazinone (V) and 1,2,3,4-dibenzo-10-methyl-6-phenazinone (VI). Similarly were obtained acenaphthylene-2-methylquinoxaline (*C.A.*: 9-methylacenaphtho[1,2-*b*]quinoxaline) (VII) and acenaphthylene-8-methoxyquinoxaline (VIII) and its 7-MeO analog (IX), the HO analogs (X and XI, resp.) of VIII and IX, and acenaphthylene-4-methyl-8-quinoxalone (XII) and its 7-quinoxalone isomer (XIII). I, m. 270-1°, was obtained (53%) by condensation of 0.5 g. of phenanthrenequinone (XIV) with 0.51 g. 2,3-diaminoanisole-HCl (XV) in 30 ml. of AcOH and 15 ml. of alc. by boiling for 20 min. II, m. 201-2°, was similarly obtained (59%) from 0.5 g. XIV and 0.51 g. 3,4-diaminoanisole (XVI). Heating 1 g. I with 5 ml. 65% HBr in a sealed tube for 4 hrs. at 150-60° gave III, m. 255-6° (from toluene); III.MeI, m. above 300° (from H_2O); addn. of a Na_2CO_3 soln. to aq. p-$MeC_6H_4SO_3Me$.III ppts. V, m. 182-3°. IV m. 305-6°; IV.MeI, m. above 300°. VI m. 215-16°. Acenaphthenequinone (XVII) was obtained from acenaphthene [Gräbe and Gfeller, *Liebig's Annalen* 276, 4 (1893)]. VII, m. 228-9°, was obtained (81%) from 0.5 g. XVII and .33 g. of 3,4-diaminotoluene. VIII m. 269-70° (83% rom 0.36 g. XVII and 0.4 g. XV). IX m. 197-8° (85% from .5 g. XVII and 0.54 g. XVI). XI (45%) m. 255-7°; 23% I.MeI was obtained. X (65%) m. 283-5°; 15% X.MeI as obtained. XII (60%) m. 183-4°. XIII ([illegible]%) m. 77-9°.

M. Hosch

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"Organic chemistry." E.C.Khotyns'kyi. Reviewed by A.I, Kypryanov.
Ukr.khim.zhur. 19 no.4:461-462 '53. (MIRA 8:2)
(Chemistry, Organic) (Khotyns'kyi, E.S.)

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[illegible] 2-methylnaphthoquinonothiazole. A. I. Kiprianov and A. V. Stetsenko. Ukrain. Khim. Zhur. [illegible]; Referat. Zhur., Khim. 1954, No. 19830.— 2-Methylnaphthoquinonothiazole (I) and 2-methylnaphthoquinono[2,3-d]thiazole (II) were synthesized in order to obtain a dye contg. a quinone residue in its mol. I and II are weak bases forming no quaternary salts with dialkyl sulfates

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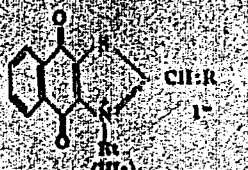
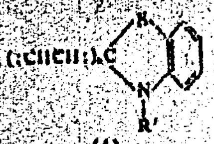


(IIIa)



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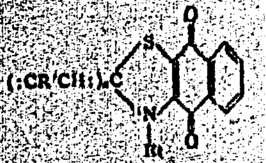

(B)