and *p*-toluenesulfonates. II.EtCl (III) was synthesized as are similar salts of benzthiazole. Boiling III in alc. converted it into a methylene base. From III were obtained the following IIIs (R given): A ($n = 0$, $R' = Me$) (IV), B ($n = 1$, $R' = H$) (V), B ($n = 1$, $R' = Me$) (VI), A ($n = 1$, $R' = Et$) (VII), 2-[1-methyl-2(1*H*)-quinolylidene]ethylidene (VIII), B ($n = 2$, $R' = H$) (IX), and *p*-$Me_2NC_6H_4CH$: (X). Heptamethinecyanine could not be isolated. The basicity of V was 4.32 moles/l., while the basicity of diethylcarbocyanine was 2.64 moles/l. (The basicity is referred to as the concn. of HCl in a mixt. of 15 ml. alc. and 10 ml. $H_2O$ required to reduce by half the color of the dye dissolved in this mixt.) All the naphthoquinonothiazoles absorb at longer wavelengths than the derivs. of naphtho[2,3-*d*]thiazole, except VII, in which a hypsochrome shift of 5.5 mμ is caused by a difference in the basicity of the heterocycles. A still greater difference in the basicity of heterocycles and consequently a greater hypsochrome shift is found in VIII in which case it is 18 mμ. Nitration of dimethyl ether of hydroquinone in glacial AcOH yielded the mono-$H_2N$ deriv. (XI), m. 71°. XI was reduced by $SnCl_2$ and HCl to aminodimethylhydroquinone (XII), m. 81°.

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Its Ac deriv., m. 91°, was fused on a water bath with $P_2S_5$, leached with an 8% NaOH soln., $CO_2$ pptd. N-thioacetyl deriv. (XIII), m. 88°. XIII oxidized by $K_3[Fe(CN)_6]$ gave 2-methyl-4,7-dimethoxybenzothiazole (XIV), m. 101°. Boiling XIV in 65% $H_2SO_4$ removed the methoxy groups, giving 2-methyl-4,7-dihydroxybenzothiazole (XV), m. 215°. XV (5 g.) dissolved in 150 ml. of 82% $H_2SO_4$ and to it added dropwise 3.5 g. $K_2Cr_2O_7$ in 100 ml. $H_2O$ gave 80% I, m. 159°. Sulfonation at 50° converted α-naphthol into "α-naphtholsulfonic acid," from which by the action of HCl and $KClO_3$ was obtained 2,3-dichloro-1,4-naphthoquinone (XVI), m. 193°. To XVI dissolved in alc. was dropwise added concd. $NH_4OH$; boiling for 1 hr. produced 2-chloro-3-amino-1,4-naphthoquinone (XVII), m. 190°. XVII (1 g.) dissolved in 15 ml. of alc., to it added 1.15 g. $Na_2S$ in 3 ml. of $H_2O$, the mixt. boiled for 30 min., filtered, and the ppt. boiled in 6 ml. of $Ac_2O$ yielded 68% II, m. 199°. II was also produced from the Ac deriv. of XVII, m. 219°, by dissolving 1 g. of this substance in 60 ml. of alc., adding 0.86 g. of anhyd. $Na_2S$, heating 1 hr., distg. off 60 ml. of alc., dilg. the residue with $H_2O$, filtering, acidifying with dil. HCl, and removing [illegible]. Adding 5 ml. of a 33% alc. soln. of $EtNH_2$ to a boiling soln. of 5 g. XVI in 30 ml. alc., and cooling the mixt., produced 100% 2-chloro-3-ethylamino-1,4-naphthoquinone (XVIII), m. 115°. XVIII was transformed into III by 2 methods: (a) 1.1 g. of XVIII, 1.3 g. $Na_2S$, and 12 ml. of $H_2O$ was boiled for 35 min., 20 ml. $C_6H_6$ added, the mixt. acidified with AcOH, shaken, the $C_6H_6$ layer sepd., dried over $Na_2SO_4$, and treated with 1 g. of AcCl in 5 ml. $C_6H_6$ to yield III, m. 248° (decompn.), purified by 3 repptns. with ether from alc. (yield 13%); (b) 5 g.

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Cyanine dyes from 2-methylanthraquinone thiazole. A. I. Kiprianov and A. V. Stetsenko. *Ukrain. Khim.* 2[redacted](1963); *Referat. Zhur., Khim.* 1964, No. 19Zh37.—2-Methylanthraquinono[1,2-*d*]thiazole (I), I.MeCl (II), and I.MeI (IIa) were synthesized; II and IIa isomerized to methylene bases (III). I is a weak base, but stronger than 2-methylbenzoquinonothiazole and 2-methylnaphthoquinono[2,3-*d*]thiazole (cf. preceding abstr.). From II were obtained the following IIIa (R and X given): A, Cl (IV); 3-methyl-2-[1-methyl-2(1*H*)-quinolylidene]ethylidene, I (V); 3-methyl-2-benzothiazolinylidene, Cl (VI); *p*-$Me_2NC_6H_4CH$:, I (VII); *p*-$Me_2NC_6H_4N$:, I (VIII). These dyes absorb at

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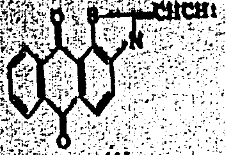
(IIIa)



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longer wave lengths than do the dyes derived from anthrathiazole. The greater basicity of I as compared with 2-methylnaphthoquinonothiazole is confirmed also by a comparison of the hypsochromic shift of V (2.5 mμ) with that characteristic of dyes having naphthoquinonothiazole and quinoline nuclei in the mol. (18 mμ). From 2-chloroanthraquinone and 25% $NH_3$ kept 6 hrs. in an autoclave at 210° was obtained 2-aminoanthraquinone (IX), m. 301° (cf. Vorozhtsov and Shkitin, *C.A.* 32, 5397). IX was acetylated by the action of $Ac_2O$ and chlorinated ([illegible], *C.A.* 7, 2743). The 1-chloro-2-acetamidoanthraquinone, m. [illegible], thus obtained, was saponif. with 5% KOH, thereby producing 1-chloro-2-aminoanthraquinone (X), m. [illegible]. X ([illegible] g.) dissolved in alc. and boiled for 1 hr. with [illegible] $Na_2S$ and 2 g. S in 4 ml. $H_2O$ produced 100% Na salt of 1-mercapto-2-aminoanthraquinone (XI). XI ([illegible] g.) and 12 ml. $Ac_2O$ boiled for 2 hrs. produced 85% I, m. [illegible]. I (0.70 g.) and 0.8 g. $Me_2SO_4$ heated 30 min. at 180-5°, the product washed with $C_6H_6$ and ether and dissolved in $H_2O$, the soln. treated with C and filtered, KCl added to the filtrate, produced 58% II, m. 232°. IIa m. 250° (decompn.). II (0.8 g.), 0.3 g. NaOH in 5 ml. $H_2O$, and 30 ml. $Me_2CO$, shaken 10 min., filtered, and the filtrate dild. with $H_2O$ gave 84% III, m. 173°. Heating III with dil. HCl produced II. II (0.32 g.), 0.33 g. orthoformic ester, and 2 ml. $Ac_2O$ boiled 45 min. gave 70% IV, m. 246-8° (decompn.), $\lambda_{max.}$ 640 mμ (in AcOH). II (0.33 g.), 0.43 g. 2-ω-acetanilidovinylquinoline-MeI and 0.2 g. anhyd. NaOAc, heated 15 min. with 2 ml. $Ac_2O$ at 100° gave 90% V, m. 253-4° (decompn.), $\lambda_{max.}$ 630 mμ (in alc.). II (0.66 g.), 0.62 g. 2-methylmercaptobenzothiazole-$Me_2SO_4$, 0.22 g. anhyd. Na acetate, and 6 ml. abs. alc. boiled 1 hr. gave 14% VI, m. 203°, $\lambda_{max.}$ 490 mμ (in alc.). II (0.33 g.) and 0.15 g. p-$Me_2NC_6H_4CHO$ in $Ac_2O$, and replacement of Cl by iodine with KI gave 28% VII, m. 209° (decompn.), $\lambda_{max.}$ 525 mμ (in alc.). II (0.33 g.), 0.15 g. p-$Me_2NC_6H_4NO$, and 2 ml. abs. alc. boiled 50 min. gave 43% VIII, m. 186° (decompn.), $\lambda_{max.}$ 690 mμ (in alc.).

M. Hoch

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Chemical Abst.
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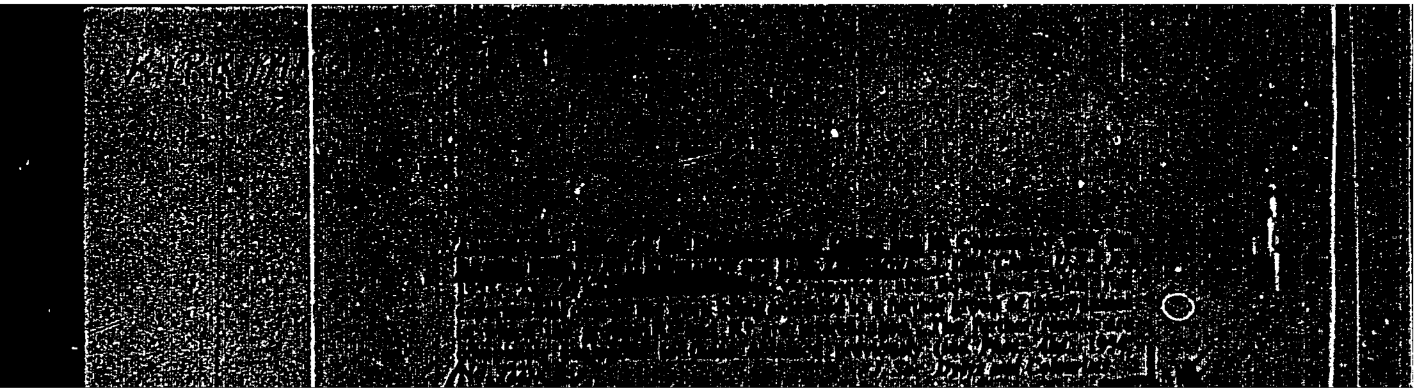
The effect of steric hindrance on properties of aromatic amines and nitro compounds. A. I. Kiprianov and I. N. Zhmurova. *Uspekhi Khim.* 22, 1240-77(1953).—Review with 133 references, covering numerous physical and chemical properties of aromatic compounds. G. M. K.



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KIPRIANOV, A. I.

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**Auxochromic Effect of the Dimethylamino Group and its Coplanarity with the Benzene Ring—II.** A. I. KIPRIANOV and I. N. ZHMUROVA. *J. Gen. Chem. U.S.S.R.*, 1953, 23, [illegible] The effect on the spectral characteristics of a dye of a disturbance, due to steric hindrance, in the coplanarity of a ring system of the dye molecule and an attached dimethylamino group—which has already been examined for cyanine dyes (*Phot. Abs.* 1954, No. 922) is now examined for seventeen azo dyes (eight of them new). Introduction of a substituent *ortho* to dimethylamino leads to a shift towards the short waves in the absorption maximum and to a reduction in the extinction coefficient. In an acid medium all the compounds undergo an indicator change, the absorption maximum moving towards the long waves; but, whereas in absence of an *ortho* substituent the extinction coefficient increases considerably in this change, all the *ortho*-substituted compounds (except *o*-methyl-substituted Methyl Red) show greatly reduced absorption, which is attributed to the occurrence of salt formation at the dimethylamino group (with complete loss of its auxochromic effect), instead of at the azo group. *J. Soc. Dyers and Col.*

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Chemical Abst.
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Organic Chemistry

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Coplanarity of the nitro group with the benzene ring and its effect on the color of dyes. A. I. Kiprianov and I. N. Zhmurova. *Zhur. Obshchei* ~~*Khim.* 23, 874-9~~ (1953); cf. following abstr.— Me and Et groups in the *o*-position to $NO_2$ have but a weak effect on the absorption. A *tert*-Bu group almost completely cancels the auxochromic action of the $NO_2$ group; the same effect is had by 2 Me groups in *o*-positions to $NO_2$. Refluxing 33 g. 4,3-$Br(O_2N)C_6H_3Et$ in 70 ml. EtOH 2 hrs. with 19 g. $Na_2S.9H_2O$, 2.8 g. S, and 20 ml. EtOH gave 21.5 g. $[4,2-Et(O_2N)C_6H_3S]_2$, which, treated in 120 ml. AcOH with 12 g. Zn dust and 90 ml. concd. HCl, stirred 1 hr., filtered, dild., and treated with NaOAc, gave a ppt. of the Zn mercaptide, and this heated 3 hrs. with excess $Ac_2O$, gave 60% *2-methyl-5-ethylbenzothiazole*, an oil (*picrate*, m. 165-7°; *methiodide*, m. 199-201°). This (6 g.) added to 4.8 ml. $HNO_3$ (d. 1.4) and 12 ml. concd. $H_2SO_4$, stirred 20 min. on a water bath, and the product crystd. from EtOH and pptd. from dil. HCl gave 1.5 g. *6-nitro deriv.* (I), m. 100-2°, and 0.6 g. *4-nitro deriv.*, m. 94-6°. Refluxing 0.3 g. 2-methyl-6-ethylbenzothiazole, 0.3 g. $HC(OEt)_3$, and 3 ml. pyridine 0.5 hr. gave 50% green *bis(3-methyl-5-ethyl-2-benzthiazole)trimethinecyanine iodide*, m. 280-2°, absorption max. 505 mμ. 2,5-Dimethyl-6-nitrobenzothiazole and *p*-$MeC_6H_4SO_3Et$ after 4 hrs. at 160-70° gave 42.5% quaternary salt, which, refluxed with $HC(OEt)_3$ in pyridine, gave 47% *bis(3-ethyl-5-methyl-6-nitro-2-benzothiazole)trimethinecyanine p-toluenesulfonate*, green, decomp. 267-8° (from EtOH), absorption max. 582 mμ. I heated with $Me_2SO_4$ 2 hrs. at 100°, and the resulting quaternary salt refluxed in pyridine with $HC(OEt)_3$ gave 30% violet *bis(3-methyl-5-ethyl-6-nitro-2-benzothiazole)trimethinecyanine methosulfate*, m. above 300°, absorption max. 580 mμ. Heating 0.2 g. 2-methyl-5-*tert*-butyl-6-nitrobenzothiazole with 0.2 g. *p*-$MeC_6H_4SO_3Et$ 1 hr. at 150-60° gave 75% quaternary salt, which, refluxed 20 min. with $HC(OEt)_3$ in pyridine, gave 60% *bis(3-ethyl-5-tert-butyl-6-nitro-2-benzothiazole)trimethinecyanine p-toluenesulfonate*, green, decomp. 277° (from EtOH), absorption max. 670 mμ. 3,4-$Me(O_2N)C_6H_3NH_2$ (0.4 g.), diazotized and treated with 0.4 g. $Me_2NPh$ in dil. HCl, yielded after several hrs. a ppt. which, dissolved in HCl and pptd. with $NH_4OH$, gave 40% crude product, purified by chromatography on $Al_2O_3$, yielding *4-dimethylamino-*

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**Kiprianov, A. I.** (2)

methyl-4'-nitroazobenzene, m. 160-2° (from $C_6H_6$), brown, absorption max. 460 mμ. 3,5,4-$Me_2(O_2N)C_6H_2NH_2$ (II) similarly gave 50% *4-dimethylamino-3',5'-dimethyl-4'-nitroazobenzene*, red, m. 176-8° (from EtOH), absorption max. [illegible] mμ. Diazotized II with o-$Me_2NC_6H_4Me$ in EtOH in the presence of NaOAc gave 40% *3,3',5'-trimethyl-4-dimethylamino-4'-nitroazobenzene*, orange, m. 112-14° (from EtOH), absorption max. 418 mμ. O. M. Kosolapoff

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KIPRIANOV, A. I.

USSR.

Reaction of methylene bases of nitrogen heterocycles with quinones. A. I. Kiprianov and A. V. [illegible] (State Univ., [illegible]). [illegible] Ukrain. Khim. Zhur. [illegible] Condensation products, which are [illegible] of the merocyanine type, were obtained by the reaction of quinones with methylene bases of N heterocycles. The absorption bands of all these dyes are not sharp and the maxima listed below are rather broad. The max. shift toward the shorter waves when the solvent is changed to one with lower dielectric constant. The products form salts, and addn. of HCl to such a soln. shifts the abs. max. to shorter wave region. The dyes are readily reduced to colorless substances, forming corresponding derivs. of hydroquinone, which have the properties of [illegible] since they develop color on exposure to air. Chlorination of 1,2-naphthoquinone in AcOH gave [illegible] (I), m. 173°, red needles. [illegible] treated with $KClO_3$ and HCl gave [illegible] quinone (II), yellow, m. 168°. 2-Methylbenzothiazole methyl methosulfate (0.27 g.) in 2 ml. $H_2O$ treated with 0.37 g. $K_2CO_3$, 2 ml. $H_2O$, and 10 ml. $C_6H_6$, shaken, and the $C_6H_6$ layer treated with 0.1 g. p-benzoquinone in $C_6H_6$ [illegible] gave 1.1% [illegible], violet, m. 227° (from $CHCl_3$); absorption max. [illegible] in $CHCl_3$, [illegible] in EtOH-HCl. Similarly [illegible] gave 38.5% 4-(3-methyl-2-benzothiazolinylidenemethyl)-1,2-naphthoquinone, violet, decomp. 247° (from $C_6H_6$), absorption max. 610 in EtOH, 615 in $CHCl_3$, 570 mμ in EtOH-HCl. This in dil. HCl treated with $NaClO_4$ gave a red perchlorate (65%), m. 230°, that is rapidly hydrolyzed by $H_2O$ or aq. EtOH. The quinone [illegible] forms a diacetate (83%), m. 72° (from dil. EtOH). The quinone deriv. heated in EtOH with $SnCl_2$ and HCl gave [illegible] colorless, m. 107° (from dil. EtOH), which with $Ac_2O$ gave the di-Ac deriv., m. 144° (from dil. EtOH). The reduction can be made also with $Na_2S_2O_4$. The hydroquinone deriv. with $Na_2S_2O_4$ in NaOH soln. gave the [illegible], yellow, m. 64° (from EtOH). Treatment as above of 2-methylbenzothiazole methyl methosulfate with [illegible]

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gave 41% 2-(3-methyl-2-benzothiazolinylidenemethyl)-3-chloro-1,4-naphthoquinone, blue, m. 194° (from $CHCl_3$), absorption max. 670 in EtOH, 640 mμ in $CHCl_3$; *perchlorate*, yellow, m. 232-4° (from abs. EtOH). Similarly the reaction with 1,2-naphthoquinone gave 20% 4-(3-methyl-2-benzothiazolinylidenemethyl)-1,2-naphthoquinone, blue, m. 22[illegible]°, absorption max. 640 in EtOH, 620 in $CHCl_3$, 430 mμ in EtOH-HCl. The reaction with I similarly gave 25% 4-(3-methyl-2-benzothiazolinylidenemethyl)-3-chloro-1,2-naphthoquinone, m. 181° (from $Cl_2CH_2$), absorption max. 660 in EtOH, 645 mμ in $CHCl_3$, 420 in EtOH-HCl. Similarly 2-methyl-4,7-benzthiazoloquinone gave 30% blue 2-(3-methyl-4,7-benzothiazolinylidenemethyl)-2-methyl-4,7-benzothiazoloquinone, m. 234-5° (from $C_6H_6$), absorption max. 680 mμ in $CHCl_3$. Similar reaction of 2-methyl-6-nitrobenzothiazole ethiodide and 1,4-naphthoquinone gave 32% 2-(3-ethyl-6-nitro-2-benzothiazolinylidenemethyl)-1,4-naphthoquinone, red, m. 300°, absorption max. 600 mμ in $CHCl_3$. 2-Methyl-6-dimethylaminobenzothiazole methiodide and 1,4-naphthoquinone similarly gave 20% brown 2-(3-methyl-6-dimethylamino-2-benzothiazolinylidenemethyl)-1,4-naphthoquinone, m. 210° (from $C_6H_6$), absorption max. 630 in EtOH, 600 in $CHCl_3$, 400 mμ in EtOH-HCl. 1,4-Naphthoquinone and 2-methylbenzoselenazole methyl methosulfate gave 30% blue 2-(3-methyl-2-benzoselenazolinylidenemethyl)-1,4-naphthoquinone, decomp. 172°, absorption max. 610 in EtOH, 600 in $CHCl_3$, 380 mμ in EtOH-HCl. 2-Methyl-6,7-benzobenzothiazole methyl methosulfate and 1,4-benzoquinone gave 25% violet 2-(3-methyl-6,7-benzo-2-benzothiazolinylidenemethyl)-1,4-benzoquinone, decomp. 270°, absorption max. 630 mμ in $CHCl_3$. The use of 1,4-naphthoquinone similarly gave 44% blue 2-(3-methyl-6,7-benzo-2-benzothiazolinylidenemethyl)-1,4-naphthoquinone, m. 240°, absorption max. 640 in EtOH, 650 in $CHCl_3$, 680 mμ in EtOH-HCl. Quinaldine methyl methosulfate and 1,4-benzoquinone gave 17% blue 2-(1-methyl-2-quinolylidenemethyl)-1,4-benzoquinone, decomp. 100°, absorption max. 600 mμ in $CHCl_3$. 1,4-Naphthoquinone in this case gave 20% violet 2-(1-methyl-2-quinolylidenemethyl)-1,4-naphthoquinone, m. 178°, absorption max. 670 in EtOH, 640 in $CHCl_3$, 600 mμ in EtOH-HCl; *perchlorate*, red, decomp. 20[illegible]° (from EtOH).

G. M. Kosolapoff

KIPRIANOV, A.I.; BABICHEV, F.S.; MUSHKALO, L.K.; POCHINOK, V.Ya.; PEL'KIS,P.S.

[Outline history of organic chemistry at Kiev University] Ocherki po istorii organicheskoi khimii v Kievskom universitete. Pod red. A.I. Kiprianova. [Kiev] Izd-vo Kievskogo gos. univ. im. T.G.Shevchenko, 1954. 130 p. (MLRA 9:8)

(Chemistry, Organic) (Kiev University)

KIPRIANOV, A.I.

Third Ukrainian State Conference on Organic Chemistry. Ukr.khim. zhur. 20 no.1:107-109 '54. (MLRA 7:3)
(Ukraine--Chemistry, Organic) (Chemistry, Organic--Ukraine)

Kiprianov, A.I.

USSR

**Azacyanines. II.** A. I. Kiprianov, V. Ya. Pochinok, and A. I. Tolmachev ([redacted] State Univ., Kiev). *Ukrain. Khim. Zhur.* 20, 204-10(1954)(in Russian).—Cyanine dyes in which one or several methine groups of a polymethine chain are replaced by N atom(s) are called azacyanines. Azacyanines with three N atoms substituted in the conjugated chain have been obtained by K., *et al.*, *ibid.* 15, 400(1940). Azacyanines with three N atoms and one or two para phenyl groups in the conjugated chain were synthesized from 2-aminobenzothiazole (I) and 2-(p-aminophenyl)benzothiazole(II) and their quaternary salts. It was demonstrated that the introduction of one phenyl group into the azacyanine displaces the absorption max. 45 mμ towards the short wave lengths, while introduction of 2 sym. phenyl radicals on the other hand leads to displacement toward the long wave lengths by 25-30 mμ. I, m. 120°, was prepd. according to Dyson (*C.A.* 32, 100) from phenylthiourea by its cyclization. *2-Imino-3-methylbenzothiazoline*, m. 125°, was prepd. by methylation of I with $CH_3I$ (Fischer,

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A. I. Kiprianov

Ann. 212, 330(1882); Hugershoff, Ber. 36, 3135(1903)). [illegible] benzamide(III), m. 231°, was prepd. by adding 16 g. p-nitrobenzoyl chloride in 80 ml. benzene to 10 g. o-aminothiophenol in 50 ml. dry benzene, the pptd. HCl salt of III being converted to free base with HCl, filtered, washed, and dried. The yield was 16 g. or 92% (Bogert and Chen, C.A. 18, 2006). The product was not recrystd. for reduction to the amine. II, m. 163, was prepd. in 75% yield from III by Sn + HCl reduction) (cf. B. and S., loc. cit.). 1,3-Di(2-benzothiazolyl)triazene, m. 247-50°, was obtained in up to 60% yield by adding 5 g. I, dissolved in 25 ml. glacial HOAc at 5°, slowly to nitrosylsulfuric acid (2.5 g. NaNO$_2$ in 8 ml. concd. H$_2$SO$_4$) cooled to 0°, keeping the temp. below 10° and then at room temp. for 30 min., filtering, and adding the filtrate to a cooled water-alc. soln. of 2 g. I and 50 g. cryst. NaOAc, whereupon the yellow ppt. which formed turned brownish upon standing. The mixt. was dild. with 300 ml. H$_2$O, the ppt. filtered off, washed with dil. HCl and H$_2$O, and dried; yield up to 60%. The crude triazene could not be completely purified from resinous impurities; recrystn. from glacial HOAc was possible only after a hot wash (80°) with nitrobenzene. 1,3-Di(2-benzothiazolyl)triazene is yellow; absorption max. at 440 mμ; poorly sol. in alc., ether, benzene, sol. when heated in glacial HOAc; sol. in concd. HCl changing from yellow to red; yellow color in strong H$_2$SO$_4$, turning red upon diln. with H$_2$O, and on further diln. turning yellow again. HCl salt was prepd. by passing dry HCl through an ether suspension, decompn. temp. 185-200°, insol. in benzene and ether, decompd. by H$_2$O, absorption max. in MeOH concg.

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HCl at 475 mμ. 3-(2-Benzothiazolyl)-1-(6-ethoxy-2-benzothiazolyl)triazene was prepd. in yields up to 50% by diazotizing 2-amino-6-ethoxybenzothiazole and coupling with I. After thorough washing with benzene and ether and 2 recrystns. from glacial HOAc, it decompd. at 237-40°. Absorption max. in alc. contg. HCl was 480 mμ. HCl salt m. 187-90°, sol. in alc. with orange-red color turning yellow slowly; red salt color disappeared immediately on contact with $H_2O$. II (3.5 g.) was diazotized, added to 2-methyl-3-iminobenzothiazoline HCl and then neutralized with NaOH. The pptd. base filtered off and washed with dil. HCl, $H_2O$, alc. and ether, resp., yielded 1.2 g. of crude product (IV) which did not crystallize and was used as such. IV was slightly sol. in alc., ether, acetone, and glacial HOAc and sol. in pyridine and dichloroethane. IV (0.5 g.) was heated 20 min. on water bath with 0.25 g. $Me_2SO_4$. The product of an azacyanine extd. with hot water and pptd. from soln. with sat. KI soln. yielded 0.42 g. (63%) of an azacyanine from HOAc, m. 170° with decompn., insol. in water, poorly sol. in alc. and acetone, sol. in $C_5H_5N$; 440 mμ absorption max. in alc. o-(Ethylamino)phenyl mercaptan was prepd. from 2-mercaptobenzothiazole according to K. and Pasenko (*C.A.* 44, 8487i). 2-(p-Nitrophenyl)benzothiazole-EtCl (V) was prepd. by adding 3.1 g. of p-nitrobenzoyl chloride in 10 ml. $C_6H_6$ to 2.5 g. of o-(ethylamino)phenyl mercaptan in 10 ml. dry $C_6H_6$, followed by heating 20 min.

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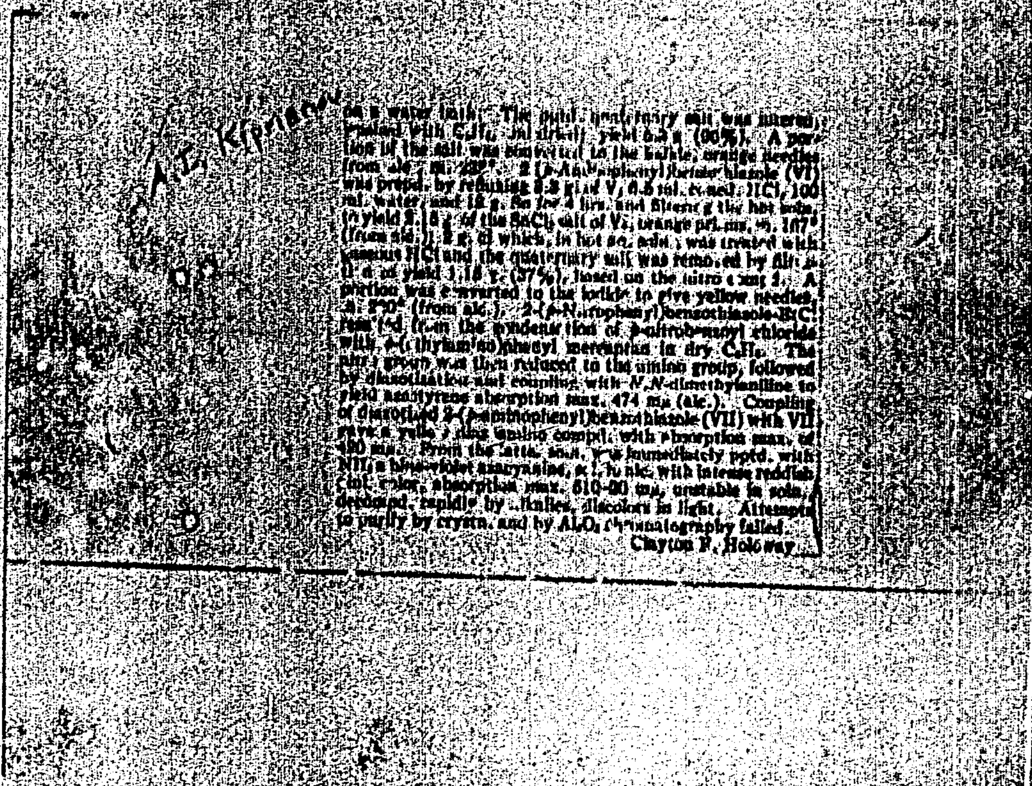


A. I. Kiprianov

on a water bath. The quat. quaternary salt was filtered, washed with $C_6H_6$, and dried; yield 6.3 g. (90%). A portion of the salt was converted to the iodide, orange needles (from alc.), m. 232°. 2-(p-Aminophenyl)benzothiazole (VI) was prepd. by refluxing 3.3 g. of V, 6.6 ml. concd. HCl, 100 ml. water, and 12 g. Sn for 4 hrs. and filtering the hot soln. to yield 3.15 g. of the $SnCl_4$ salt of VI, orange prisms, m. 167° (from alc.); 3 g. of which, in hot aq. soln., was treated with gaseous HCl and the quaternary salt was removed by filtration to yield 1.18 g. (37%), based on the nitro compd. A portion was converted to the iodide to give yellow needles, m. 270° (from alc.). 2-(p-Nitrophenyl)benzothiazole-[illegible] formed from the condensation of p-nitrobenzoyl chloride with o-(methylamino)phenyl mercaptan in dry $C_6H_6$. The nitro group was then reduced to the amino group, followed by diazotization and coupling with N,N-dimethylaniline to yield [illegible] absorption max. 474 mμ (alc.). Coupling of diazotized 2-(p-aminophenyl)benzothiazole (VII) with VII gave a yellow diazoamino compd. with absorption max. at 480 mμ. From the latter soln. was immediately pptd. with $NH_3$ a blue-violet azacyanine, [illegible] in alc. with intense reddish tint color, absorption max. 610-80 mμ, unstable in soln., decompd. rapidly by alkalies, discolors in light. Attempts to purify by crystn. and by $Al_2O_3$ chromatography failed.

Clayton F. Holoway

KIPRIANOV, A.I.

USSR

Thiacarbocyanines with aryloxy groups in 8,10-positions. A. I. Kiprianov, Zh. M. Ivanova, and S. O. Frikman. [illegible] 20, 641-6 (1954) (in Russian).—The following 2-aryloxymethylbenzothiazoles (I) [aryl = (a) Ph, (b) p-ClC6H4, (c) p-MeC6H4, (d) p-MeOC6H4, (e) 1-C10H7, and (f) 2-C10H7] are prepd. by condensing o-H2NC6H4SH with ArOCH2CO2H (aryl group, % yield, and m.p. given): a, 81, 86°; b, 71, 118°; c, 71, 122°; d, 79, 80°; e, 70, 111-12°; f, 80, 119°. Quaternary salts (II) of the following I are prepd. by heating I and p-MeC6H4SO3Et (1:1 molar ratio) 3 hrs. at 135-40°, washing the mass with Me2O, and crystg. from H2O (aryl group, % yield, and m.p. given): a, 27, 157-8°; b, 61, 168°; c, 56, 165-7°; d, 47, 166°; e, 60, 160-2°; f, 61, 151-2°. 8,10-Diaryloxythiacarbocyanine dyes (III) are obtained by heating 5 ml. dry C5H5N, 1 g. of the following II, and 0.6 g. o-formate 1 hr. at 115-20°, dilg. with EtOH, and adding hot aq. KI or NaClO4 to the boiling mixt. (aryl group, anion, % yield, m.p., and max. absorption spectra in mμ given): a, I−, 20, 182-4°, 580; b, ClO4−, 20, 230-1°, 585; c, I−, 16.5, 196-7°, 591; e, I−, 14, 161°, 590; d, ClO4−, 36, 236-8°, 588; f, I−, 11, 166-8°, 586. Styryl dyes (IV) are prepd. by heating equimolar amts. of the following II and p-Me2NC6H4CHO 30 min. at 135° in Ac2O, adding hot aq. KI or NaClO4, and crystg. from EtOH (aryl group, anion, % yield, m.p., and absorption spectra in mμ given): a, I−, 28, 240-1°, 520; b, ClO4−, 97, 223-5°, 520; c, ClO4−, 86, 196-7°, 520; d, ClO4−, 91, 212-15°, 520; e, I−, 95, 182-4°, 522; f, ClO4−, 93, 182-4°, 522. Introduction of 2 aryloxy radicals in the 8- or 8,10-positions shifts the absorption spectra (V) of the dyes, decreasing it by 8-10 mμ for III and increasing it by 27-32 mμ for IV; the V of the analogous unsubstituted dyes 560 and 558 mμ. Cf. Brooker and White, *C.A.* 44, 7684.

Elizabeth Barabash

**KIPRIANOV, A.I.**

Contributions of the Institute of Organic Chemistry of the Academy of Sciences of the Ukrainian S.S.R. to the synthesis of optical sensitizers. Usp.nauch.fot. 3:141-151 '55. (MLRA 9:1)
(Photographic emulsions)

KIPRIANOV, A.I.

USSR/Chemistry - Organic chemistry

Card 1/1 Pub. 116 - 13/25

Authors : Kiprianov, A. I., and Fedorova, I. P.

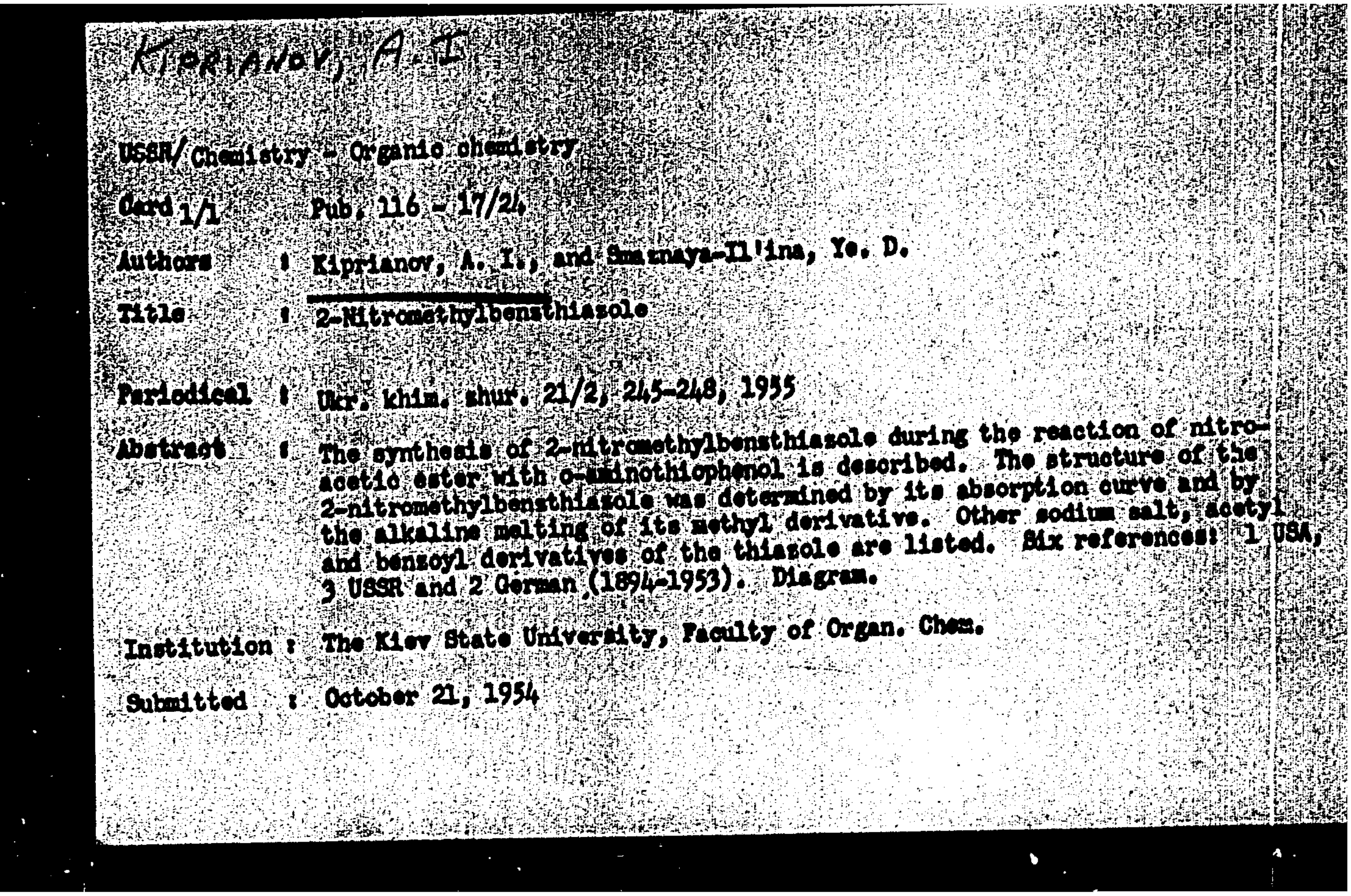
Title : Azo-derivatives of benzthiazole

Periodical : Ukr. khim. zhur. 21/1, 76-80, 1955

Abstract : The derivation of 2-symmetrical and 9-nonsymmetrical azo-compounds of the benzthiazole series during the synthesis of azothiacyanines is described. The absorption spectra were determined for 6 azo-compounds in an alcohol solution. The derivation of a hitherto unknown 2-methyl-6-nitrosobenzthiazole is announced. Seven references : 4 USSR and 3 USA (1923-1952). Graph.

Institution : State University, Faculty of Organic Chemistry, Kiev

Submitted : October 2, 1954



KIPRIANOV, A. I.

USSR/Chemistry - Organic chemistry

Card 1/1 Pub. 116 - 17/24

Authors : Kiprianov, A. I., and Smaznaya-Il'ina, Ye. D.

Title : 2-Nitromethylbensthiazole

Periodical : Ukr. khim. zhur. 21/2, 245-248, 1955

Abstract : The synthesis of 2-nitromethylbensthiazole during the reaction of nitro-acetic ester with o-aminothiophenol is described. The structure of the 2-nitromethylbensthiazole was determined by its absorption curve and by the alkaline melting of its methyl derivative. Other sodium salt, acetyl and benzoyl derivatives of the thiazole are listed. Six references: 1 USA, 3 USSR and 2 German (1894-1953). Diagram.

Institution : The Kiev State University, Faculty of Organ. Chem.

Submitted : October 21, 1954

KIPRIANOV, A. I.

USSR/ Chemistry - Organic chemistry

Card 1/1 Pub. 116-16/30

Authors : Chernetskiy, V. P., and Kiprianov, A. I.

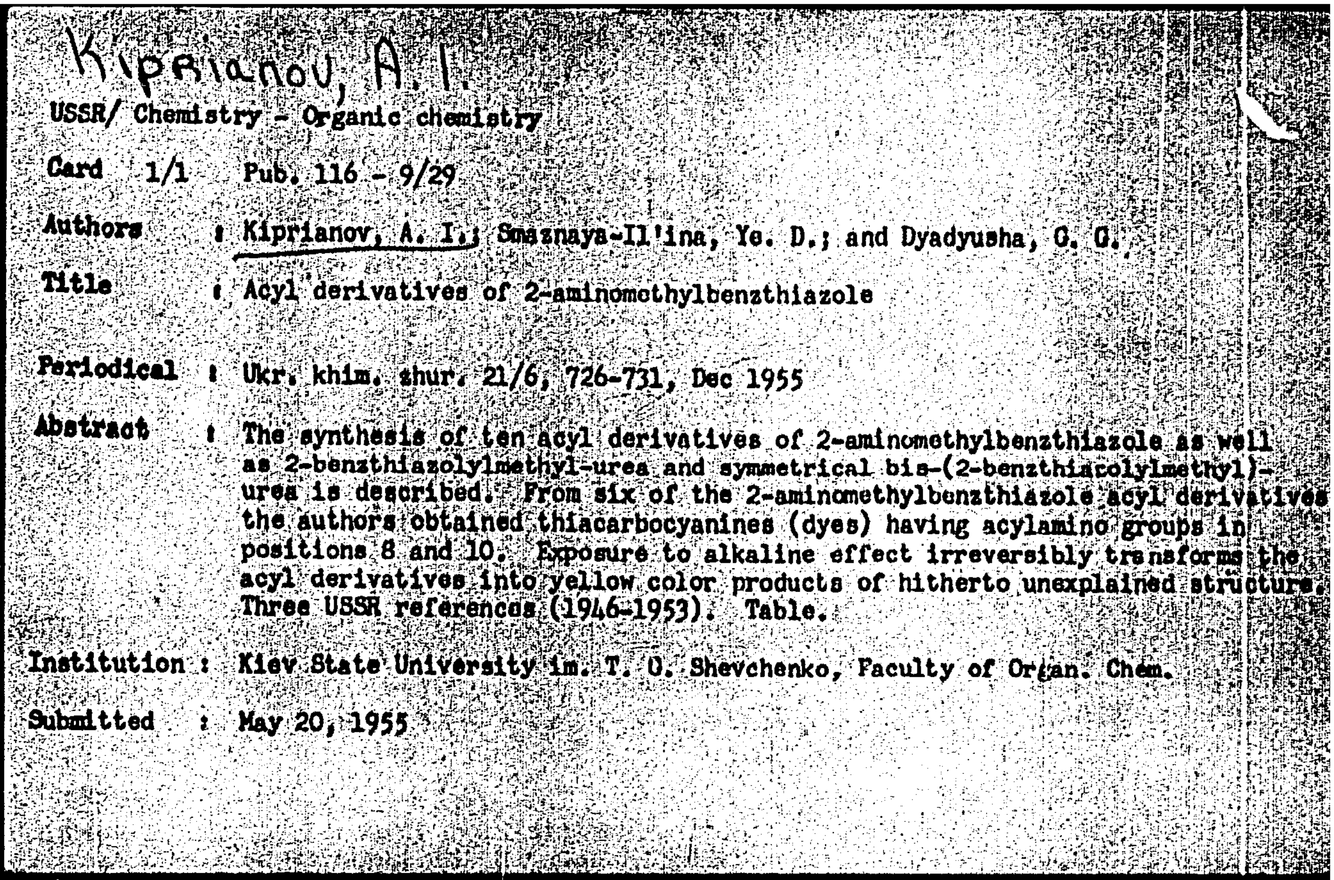
Title : Chlorination of phenazine

Periodical : Ukr. khim. zhur. 21/3, 367-369, June 1955

Abstract : It is proven experimentally that the chlorination of phenazine with gaseous Cl in carbon tetrachloride leads to the formation of 1-chlorophenazine and 1,4-dichlorophenazine. Chlorination of the phenazine under identical conditions but in the presence of anhydrous sodium acetate was found to be a more suitable method for the above mentioned chloro and dichlorophenazines. Five references: 2 USSR, 2 German and 1 Italian (1875-1954).

Institution : Acad. of Sc., Ukr. SSR, Inst. of Organ. Chem.

Submitted : December 24, 1954



Kiprianov, A. I.

USSR/ Chemistry - Organic chemistry

Card 1/1 Pub. 116 - 9/29

Authors : Kiprianov, A. I.; Smaznaya-Il'ina, Ye. D.; and Dyadyusha, G. G.

Title : Acyl derivatives of 2-aminomethylbenzthiazole

Periodical : Ukr. khim. zhur. 21/6, 726-731, Dec 1955

Abstract : The synthesis of ten acyl derivatives of 2-aminomethylbenzthiazole as well as 2-benzthiazolylmethyl-urea and symmetrical bis-(2-benzthiacolylmethyl)-urea is described. From six of the 2-aminomethylbenzthiazole acyl derivatives the authors obtained thiacarbocyanines (dyes) having acylamino groups in positions 8 and 10. Exposure to alkaline effect irreversibly transforms the acyl derivatives into yellow color products of hitherto unexplained structure. Three USSR references (1946-1953). Table.

Institution : Kiev State University im. T. G. Shevchenko, Faculty of Organ. Chem.

Submitted : May 20, 1955

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Chem

✓ **Condensation of o-aminophenylmercaptans with ketones.** A. I. Kiprianov and V. A. Portnyagina (State Univ., Kiev). *Zhur. Obshchei Khim.* 25, 2257-65(1955).—Heating 5 g. o-$H_2NC_6H_4SH$ and 2.8 g. $Me_2CO$ in a sealed tube 1 hr. at 100° gave 75% *2,2-dimethylbenzothiazoline*, m. 45°, $b_4$ 142-3°; *Ag deriv.*, m. 259-60°; *Bz deriv.*, m. 156-7°. Treatment with MeI 1 hr. at 100° gave *2,2,3-trimethylbenzothiazoline*, $b_4$ 140°. Similarly, $Pr_2CO$ gave 47% *2,2-dipropylbenzothiazoline*, $b_4$ 166-8° (*Ag deriv.*, decomp. 310°), and AcPh gave 65% *2-methyl-2-phenylbenzothiazoline*, $b_4$ 232-5° (*Ag deriv.*, decomp. 264°). Cyclopentanone gave 63% *2,2-tetramethylenebenzothiazoline*, m. 56°; *Ag deriv.*, decomp. 212°; *Bz deriv.*, m. 154-6°. Cyclohexanone gave 66% *2,2-pentamethylenebenzothiazoline*, m. 111-12°; *Ag deriv.*, decomp. 225°; *Bz deriv.*, m. 114°. 1,4-Cyclohexanedione gave *1,1,4,4-bis(benzothiazolinylidene)cyclohexane*, 63%, m. 233-4°; *di-Ag deriv.*, does not decomp. 300°; *di-Bz deriv.*, m. 200-7°. $Ac_2CH_2$ gave 54% *bis(2-methyl-2-benzothiazolinyl)methane*, $b_4$ 135-7°. Heating o-$MeNHC_6H_4SH$ with $Me_2CO$ 2 hrs. at 100° gave 81% *2,2,3-trimethylbenzothiazoline*, $b_4$

Chem

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CONDENSATION OF 6-AMINO-...

140°. Similarly the following ketones gave analogous products (% yield and phys. consts. given): Et$_2$CO, 68%, b$_8$ 140-8°; MePrCO, —, b$_8$ 148-7°; Pr$_2$CO, 80%, b$_8$ 140-2°; cyclopentanone, 59%, b$_8$ 178-80°; cyclohexanone, 78%, b$_8$ 160-8°; m. 85°; AcPh, 80%, m. 98°; o-tolylacetone, 30%, b$_8$ 85-7°; p-tolylacetone, 96%, b$_8$ 180-3°; 1,4-cyclohexanedione, 64%, m. 220°; AcCH$_3$, 86%, b$_8$ 180-8°. Me$_2$CO and 2,5-H$_2$N(O$_2$N)C$_6$H$_3$SH in 0.5 hr. on a steam bath (47) 83% 2,2-dimethyl-6-nitrobenzothiazoline, m. 120-1°; Ag deriv., decomp. over 200°; Ac deriv., m. 127-8°. Cyclopentanone gave 60% 2,2-tetramethylene-6-nitrobenzothiazoline, [illegible] b. 144-6°; Ag deriv., decomp. 230°; Ac deriv., m. 167-8°. o-H$_2$NC$_6$H$_4$SH and EtCH$_2$CO$_2$Et in 2 hrs. at 100° gave 71% 2-methyl-2-carbethoxymethylbenzothiazoline, b$_8$ 190-2°; Ag deriv., decomp. 227°; Bz deriv., m. 156-6°. The use of the N-Me deriv. in this case gave 61% 2,3-dimethyl-2-carbethoxymethylbenzothiazoline, b$_8$ 180-2°. 2,5-H$_2$N(O$_2$N)C$_6$H$_3$SH and AcCH$_2$CO$_2$Et in 0.5 hr. at 100° gave 60% 2-methyl-2-carbethoxymethyl-6-nitrobenzothiazoline, m. 95°; Ag deriv., decomp. 194-5°. The benzothiazolines are readily cleaved by acids and alkalies; heated above 200°, they give derivs. of benzothiazole. O. M. Kosolapoff

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KIPRIANOV, A.I.

Fourth Ukrainian National Conference on Organic Chemistry. Ukr.khim. zhur. 22 no.1:129-132 '56. (MIRA 9:6)
(Ukraine--Chemistry, Organic)

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

N-alkylphenazinones. Part 2. Ukr.khim.zhur.22 no.3:351-354 '56.
(MIRA 9:9)

1.Institut organicheskoy khimii AN USSR.
(Pyocyanine)

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

N -alkylphenazinones. Part 3. Ukr.khim.zhur.22 no.3:355-358 '56.
(MIRA 9:9)

1.Institut organicheskoy khimii AN USSR.
(Pyocyanine)

Киприанов А.И.

E-2

USSR/Organic Chemistry. Synthetic Organic Chemistry.

Abs Jour: Ref Zhur-Khimiya, No 6, 1957, 19223

Author : Kiprianov A. I., Prilutzkiy G. M.
Inst :
Title : N-alkylphenazinones. IV.

Orig Pub: Ukr. khim. zh. 1956, 22, No 3, 359-362.

Abstract: It is shown, that at the alkylation of 10-ethylphenazinone-1 (I) and 9-ethylphenazinone-2 (II) quarternary salts (QS) of alcozyphenazines are formed. From the latter by oxidation in an alkaline solution are obtained 9-ethylalcoxyphenazinones-1 [3.36 g. II and 6 cc $(CH_3)_2SO_4$ in 40 cc $C_6H_6$ are boiled 15. min.; on cooling are obtained methyl sulfate of 2-methoxy -9-ethylphenazine (III), yield 94%, m.p. 185-186°; iodide, m.p. 182° (from 50% alc.). From II and $CH_3I$ (tube 90°, 30 min.) the yield of iodide is 53%. From 2.24 g. II, 5 cc $(C_2H_5)_2SO_4$ in 30

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USSR/Organic Chemistry. Synthetic Organic Chemistry. E-2

Abs Jour: Ref Zhur-Khimiya, No 6, 1957, 19223

cc toluene (boiling 25 min.) is obtained ethylsulfate of 2-ethoxy-9-ethylphenazine (IV), yield 90%; iodide, m.p. 204.5° (from water) From II and $C_2H_5I$ (100°, 30 min.) yield of iodide is 37%. 2.24 g. I and 1.7g. $(CH_3)_2SO_4$ are heated 1 min. at 105° and washed with ether; yield of methylsulfate of 1-methoxy-10-ethylphenazine (V) is 55%; iodide, m.p. 189° (from 50% alc.). To a solution of 1.5 g. III in 500 cc water is added 1 g. $Na_2CO_3$ and is left standing in an open dish in direct sunlight for 8 hours, it is slightly alkalized, the products are extracted with $CHCl_3$ and chromatographed on $Al_2O_3$; II (crimson zone), m.p. 174°, and 3-methoxy-I (blue violet zone), yield 37%, m.p. 145-146° (from water) are isolated. From IV is obtained in an analogical way 3-ethoxy-I, yield 27%, m.p. 124-125° (from water). To a solution of 3.5g. III in 140

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Card : 4/4

6

[redacted]

[illegible]

**KIPRIANOV, A.I.; ISHCHENKO, A.M.**

Chemical and geological institutes of the Ukrainian Academy of Sciences during the last 3 years. Visnyk AN URSR 27 no.2: 44-52 F '56. (MLRA 9:6)
(Ukraine--Chemistry--Study and teaching)(Ukraine--Geology--Study and teaching)

KIPRIANOV, A., University of Kiev, USSR

"The Influence of Steric Hindrances upon the Absorption Spectra of Several 'Cyanine' Dyes," a paper submitted at the 16th International Congress of Pure and Applied Chemistry, Paris, 18-24 July 1957.

KIPRIANOV, A.I

AUTHOR: Kiprianov, A. I. and Fedorova, I. P. 73-1-9/26

TITLE: Nitroderivatives of Benzthiazole. II. (Azoproizvodnyye Benztiazola. II.)

PERIODICAL: Ukrainskiy Khimicheskiy Zhurnal, 1957, Vol.23, No.1 pp. 59 - 63 (USSR).

ABSTRACT: Azoderivatives of benzthiazole previously quoted in literature are listed. (Refs. 1 - 5). The authors' attention was attracted mainly by arylazobenzthiazoles which have an active methyl group in the second position capable of entering into condensation reactions under formation/cyano-dyes. A number of such azoderivatives of benzthiazole, obtained from 2-methyl-6- aminobenzthiazole or from 2-methyl-6-nitrosobenzthiazole were described in a previous article by the authors. They now give data on the synthesis and absorption curves of analogous arylazo-derivatives produced from 2-methyl-5-amino or 2-methyl-5-nitrosobenzthiazoles. The process was carried out by treating the compound with phenol, β-naphthol and dimethylaniline.3 azo-dyes were obtained. On comparing their absorption spectra in alcoholic solution with the absorption spectra of isomeric dyes (synthesised from 2-methyl-6-aminobenzthiazole) it was found that the

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Nitroderivatives of Benzthiazole. II. 73-1-9/26

transition of 2-methyl-6-arylazo- to 2-methyl-5-arylazo-derivatives is connected with a small displacement of the absorption lines in the short-wave part of the spectrum. Figure 1 gives the absorption curves of the 2 above named compounds in alcohol (curves 1 and 2) and also in alcohol to which sulphuric acid was added (curves 1' and 2'). Figure 2 gives the absorption curves of 2-methyl-5-phenyl-azobenzthiazole (curve1) and 2-methyl-5-nitrosobenzthiazole (curve 2) in an alcoholic solution. Figure 3 depicts the absorption curves of 2,2'-dimethyl-5,5'-azobenzthiazole (1) and of 2,2'-dimethyl-6,6' azobenzthiazole (2), the latter having been described in a previous communication. A comparison shows that the transition of 5,5'azo-derivatives to 6,6'azo-derivatives is coupled with a displacement of the maximum of the absorption (K) in the long wave part of the spectrum and with an appreciable increase in the intensity. There are 3 figures and 9 references, 3 of which are Slavic.

SUBMITTED: October, 12, 1956.

ASSOCIATION: Kiyev State University, Chair of Organic Chemistry.
(Kiyevskiy Gosudarstvennyy Universitet, Kafedra
Organicheskoy Khimii.)

Card 2/3

Nitroderivatives of Benzthiazole. II. 73-1-9/26

AVAILABLE: Library of Congress

Card 3/3

Kiprianov A. I.

KIPRIANOV, A.I.

Achievements in the field of organic chemistry in the Ukraine during the forty years of Soviet regime. Ukr.khim.zhur. 23 no.4:460-473 '57. (MIRA 10:10)
(Ukraine--Chemistry, Organic)

AUTHORS: Kiprianov, A. I., and Tolmachev, A. I.

TITLE: Derivation of Quaternary Salts of Weak Organic Bases (Polucheniye chetvertichnykh soley slabykh organicheskikh osnovaniy)

PERIODICAL: Zhurnal Obshchey Khimii, 1957, Vol. 27, No. 1, pp. 142-150 (U.S.S.R.)

ABSTRACT: Kinetic investigation was conducted with 2-methylbenzthiazole as a base to compare the rates of formation of quaternary salts of one and the same base with the application of well-known alkylating agents as well as esters of various nitrobenzosulfonic acids. The reaction was carried out at temperatures of 70, 80, 90 and 100° and the rate of reaction was determined by the weight of the quaternary salt separated from the solution. The rate constants calculated in accordance with the bimolecular reaction equation have shown perfect agreement. Results given in Table 1 show that methyl ether of m-nitrobenzenesulfonic acid by its methylating potential at 80° is equal to dimethylsulfate and is 70 times more active than methyl iodide. Methyl ether of o-nitrobenzenesulfonic acid was found to be approximately 6 times and methyl ethers of 2, 3- and 2,4-dinitrobenzenesulfonic acids 60 times more active than dimethyl sulfate which is considered the most potent of the alkylating

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agents used. The increase in the rate of formation of quaternary salts in the case of nitro-derivatives of benzene sulfo-acids is explained by the reduction in activation energy and sometimes also by the increase in the pre-exponential factor. It is evident therefrom that the nitro-group in ortho-position does not produce any steric hindrance in the methylation reaction. According to N. A. Menshutkin (8) the rate of formation of quaternary salts during the reaction of tertiary amines with methyl iodide increases very sharply during the conversion from less polar to more polar solvents. It appears however that the polarity of the solvent in the case of esters of benzenesulfonic acids has a comparatively slight effect on the rate of reaction.
Six tables and 3 graphs. There are 15 references, of which 5 are Slavic.

ASSOCIATION: Academy of Sciences Ukrainian SSR, Institute of Organic Chemistry (Institut Organicheskoy Khimii, Akademii Nauk Ukrainskoy SSR)

PRESENTED BY:

SUBMITTED: January 18, 1956

AVAILABLE:

KIPRIANOV, A. I.

AUTHORS: Kiprianov, A. I. and Tolmachev, A. I. 79-2-46/58

TITLE: Dinitrobenzenesulfonic Acids and Their Esters (Dinitrobenzolsul'fokisloty i Ikh Efiry)

PERIODICAL: Zhurnal Obshchey Khimii, 1957, vol 27, No 2, pp. 486-491 (U.S.S.R.)

ABSTRACT: This article describes the synthesis of 2,3-, 2,5- and 3,4-dinitrobenzenesulfonic acids, their esters and other derivatives as well as several new esters of already known nitro- and dinitrobenzenesulfonic acids. Table 1 lists a number of derivatives of three new dinitrobenzenesulfonic acids obtained for the purpose of identification, with their melting points and analyses. The authors, together with L. M. Yagupol'skiy (9), also obtained a hitherto unknown 2-nitro-4-trifluoromethylbenzenesulfonic acid. Under the effect of alkaline agents, the dinitrobenzenesulfonic acids may separate the sulfo-group (2,4-dinitrobenzenesulfonic acid) or the nitro group (2,3-, 2,5- and 3,4-dinitrobenzenesulfonic acid). It is recommended that the reaction with dinitrobenzenesulfochlorides be carried out at a temperature of about 5° and the amount of alcoholate added to the acid chloride solution must be exactly equivalent to the sulfochloride. It was

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Dinitrobenzenesulfonic Acids and Their Esters 79-2-46/58

determined that the most reliable method for the derivation of esters of dinitrobenzenesulfonic acids is the reaction of their silver salts with alkly iodide. The hitherto unknown esters of nitro- and dinitrobenzenesulfonic acids, their melting points and chemical analyses are listed in table 2. The o-nitrobenzenesulfonic acid esters obtained during the reaction of o-nitrobenzenesulfochlorides with n-propyl or n-octyl alcoholates in dry ether are described as oils which do not submit to crystallization or distillation without decomposition.

2 tables. There are 15 references, of which 2 are Slavic

ASSOCIATION: Academy of Sciences Ukr-SSR, Institute of Organic Chimistry

PRESENTED BY:

SUBMITTED: January 18, 1956

AVAILABLE: Library of Congress

Card 2/2

KIPRIANOV, A.I.

[redacted]

Decision of the May plenum of the Central Committee of the CPSU and the tasks for chemists in the Ukraine. Ukr. khim. zhur. 24 no.3:287-291 '58. (MIRA 11:9)

(Ukraine--Chemistry)

KIPRIANOV, A. I.

79-1-44/63

AUTHORS: Babichev, F. S., Kiprianov, A. I.

TITLE: On the Reaction Products of the Methylene Bases of Benzthiazole and Benzselenazole With Haloid Alkyls (O produktakh reaktsii metilenovykh osnovaniy benztiazola i benzselenazola s galoidnymi alkilami)

PERIODICAL: Zhurnal Obshchey Khimii, 1958, Vol.28, Nr 1, pp.209-212 (USSR)

ABSTRACT: The reaction of the methylene bases of the benzthiazole, benzselenazole and thiazole series with haloid alkyls was already quite thoroughly investigated by the authors in 1950. They state that the structure, ascribed to the reaction products by Larive and Collet (reference 1) according to scheme 1 (formulae (I) (III) (IV)) is incorrect, as actually in the reaction of methyl iodide with 3-methyl-2-methylene-benzthiazoline the compound (V), and with 3-methyl-2-methylene-benzselenazoline the compound (VI) is formed. These formulae (V) and (VI) are proved by the properties of these two compounds and by their hydrolysis products. Larive and Collet used for

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On the Reaction Products of the Methylene Bases of Benzthiazole and Benzselenazole With Haloid Alkyls

the synthesis the products of the linkage of methyl iodide to the methylene bases, a linkage which should be brought about with the aid of the new intermediate product suggested by them (N-methyl-2-benzthiazolsulphbetaine) of monomethyncyanines containing three nuclei. Consequently the dyes obtained from these compounds were also ascribed a wrong structure. According to Larive and Collet the reaction of the new dyes takes place according to scheme 2 (formulae (III) and (VII). In reality the conversion takes place according to scheme 3 (formulae (V) and (VIII)), where not monomethyncyanine, but the dye VIII substituted in the chain is obtained. The reaction of product (V) with 3-methyl-2-benzthiazolsulphobetaine was carefully investigated by the authors. The orange dye, as reaction product, easily hydrolyzes with caustic potash to a yellow product which decomposed at 339°C and proved to be the well-known ketone (IX) of scheme 4. The second hydrolysis compound was liberated as methyl ether of o-methylaminothiophenol. Consequently the hydrolysis of the dye obtained by Larive and Collet takes place according to scheme 5 (with the formulae(XIII) and (IX)) so that the dye (VII) naturally

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On the Reaction Products of the Methylene Bases of Benzthiazole and Benzselenazole With Haloid Alkyls 79-1-44/63

cannot form such products of hydrolysis. There are 7 references, 6 of which are Slavic.

ASSOCIATION: **Kiyev State University**
(Kiyevskiy gosudarstvennyy universitet)

SUBMITTED: January 2, 1957

AVAILABLE: Library of Congress

Card 3/3

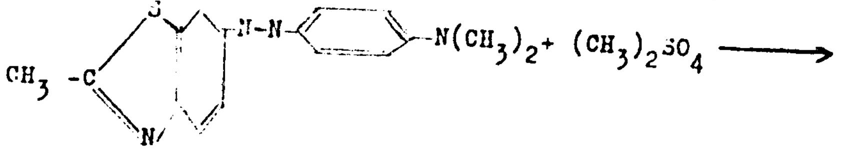
1. Chemistry 2. Cyclic compounds-Chemical reactions
3. Hydrolysis

**AUTHORS:** Kiprianov, A. I., Fedorova, I. P. 79-28-4-38/60

**TITLE:** Azo Derivatives of the Cyanine Dyes (Azoproizvodnyye tsianinovykh krasiteley)

**PERIODICAL:** Zhurnal Obshchey Khimii, 1958, Vol.28, Nr 4, pp. 1023-1031 (USSR)

**ABSTRACT:** It can be determined in colors, which simultaneously are polymethine- and azo-dyes, whether the azo groups form a common chromophor with the polymethine chain, or if they are separated to a certain degree. The authors also found, how the azo groups act upon the sensitizing power of the thiacyanines. A series of such dyes, predominantly thiacarbocyanines and styryles, were synthesized. On that occasion the authors started with the lately described (Ref 2) 2-methyl-5- and 2-methyl-6-arylazo derivatives.



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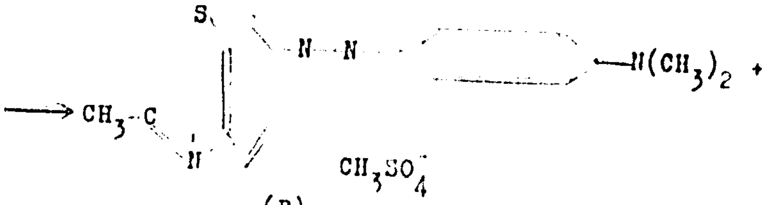
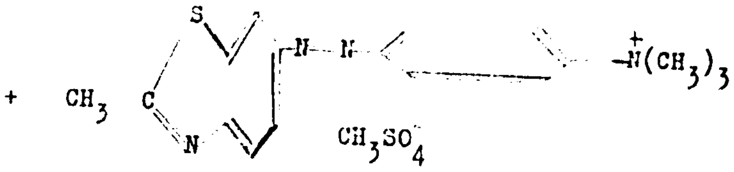


(B)



(C)

The obtained quaternary salt could be condensed and formed a series of symmetrical and asymmetrical styryls and thiacyanines, which contained arylazo groups as substituents in the benzene rings. It was found that the adsorption spectra of these dyes show a separate intensive adsorption band.

Card 2/3

Azo Derivatives of the Cyanine Dyes 79-28-4-38/60

Therefore the azo groups and the polymethine chain form a common chromophor. In the case of 6-arylazo derivatives of the thiacyanines the adsorption band is shifted considerably nearer to the red end of the spectrum, than in case of 5-arylazo derivatives. There are 3 figures, 7 tables, and 3 references, 2 of which are Soviet.

ASSOCIATION: Kiyevskiy gosudarstvenny universitet
(Kiyev State University)

SUBMITTED: January 8, 1957

Card 3/3

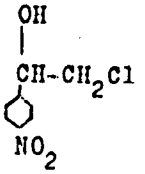
SOV/79-28-6-38/63

AUTHORS: Yagupol'skiy, L. M., Gruz, B. Ye., Kiprianov, A. I.

TITLE: The Synthesis of p-Nitrophenylhalogenmethylcarbinols (Sintez p-nitrofenilgaloidmetilkarbinolov)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol. 28, Nr 6, pp. 1608-1610 (USSR)

ABSTRACT: p-nitrophenylhalogenmethylcarbinols are intermediate products in the synthesis of the synthetic antibiotics of synthomycin (sintomitsin). The synthesis of p-nitrophenylchloromethylcarbinol (I) was first carried out from styrene by V. A. Mikhalev and co-workers. The chlorohydrin of styrene was acetylated, the acetyl derivative was nitrated, the p-isomer was separated from the obtained mixture of nitro products and was saponified to the compound (I). It was of interest to the authors to carry out directly the nitrification of chlorohydrin styrene. They found that on the addition of this compound to the nitrification mixture at a temperature not above 0° nitrogen ether of the m- and p-nitrophenylchloro-



(I)

Card 1/3

The Synthesis of p-Nitrophenylhalogenmethylcarbinols SOV/79-28-6-38/63

od of the synthesis of p-nitrophenylchloromethylcarbinol and p-nitrophenylbromomethylcarbinol by nitrification of the corresponding halogenhydrin styrene, with subsequent saponification of the formed nitrogen ether was carried out. There are 7 references, 2 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii Akademii nauk Ukrainskoy SSR (Institute of Organic Chemistry, AS Ukr SSR)

SUBMITTED: May 31, 1957

1. Methanol--Synthesis

Card 3/3

YAGUPOL'SKIY, L.M.; VISHNEVSKAYA, G.O.; YAVORSKIY, D.F.; GRUZ, B.Ye.; MAKSIMENKO, A.S.; KHASKIN, I.G.; GONSETSKAYA, Ya.V.; KIPRIANOV, A.I.

Improvement in the method for producing p-nitrophenylchloromethylcarbinole. Med.prom. 13 no.3:20-21 Mr '59.

(MIRA 12:5)

1. Institut organicheskoy khimii AN USSR i Kiyevskiy khimikofarmatsevticheskiy zavod imeni M.V.Lomonosova.

(METHANOL)

5(0)

SOV/30-59-3-23/61

AUTHORS: Arbuzov, B. A., Academician, Kiprianov, A. I., Academician of the AS UkrSSR

TITLE: Congress on Chemical Engineering (Kongress po promyshlennoy khimii)

PERIODICAL: Vestnik Akademii nauk SSSR, 1959, 29 Nr 3, pp 82-85 (USSR)

ABSTRACT: The XXXI International Congress took place in Liège, Belgium from September 7 to 12, 1958. It was attended by more than 1000 chemists and engineers of various countries. The Soviet delegation was represented by B. A. Arbuzov, G. A. Razuvayev, K. A. Kocheshkov, A. I. Kiprianov, S. I. Zav'yalov, and a number of scientists and engineers of scientific branch research institutes and enterprises of the chemical industry. The discussions covered the whole range of chemical engineering, from atomic metallurgy to pharmaceutical products. The Soviet chemists delivered the following reports: V. A. Kargin and M. N. Shteding reported on the inhibiting properties of stabilizers; K. A. Kocheshkov spoke of the effect of $\gamma$-radiation on the synthesis of organo-metallic stabilizers and catalysts for plastics; B. A. Arbuzov reported on the regeneration of carene and pinene oxides; A. I. Kiprianov and

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I 15/14

5 (3)

AUTHORS: Kiprianov, A. I., Prilutskiy, G. M. SOV/79-29-3-57/61

TITLE: Reaction of Phenazine and N-Phenazine Oxide With Organomagnesium Halide Compounds (Vzaimodeystviye fenazina i N-okisi fenazina s galoidmagniyorganicheskimi soyedineniyami)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 3, pp 1020-1026 (USSR)

ABSTRACT: Besides the reactions of the organomagnesium halide compounds with phenazine derivatives, their quaternary salts, "Flavinduline", et al, the reaction of the phenazine itself with the above mentioned magnesium compounds has hitherto not been investigated (Refs 1-4). Mikhaylov and Blokhin (Ref 4) affiliated lithium phenylate to phenazine and transformed the reaction product without precipitation by methyl iodide into the 9-methyl-10-phenyl-hydrophenazine (Scheme 1). The authors found that the alkyl magnesium bromides react with phenazine analogously to $C_6H_5Li$. In the case of action of water upon the affiliation product the 9-alkyl-9,10-dihydrophenazines were obtained.

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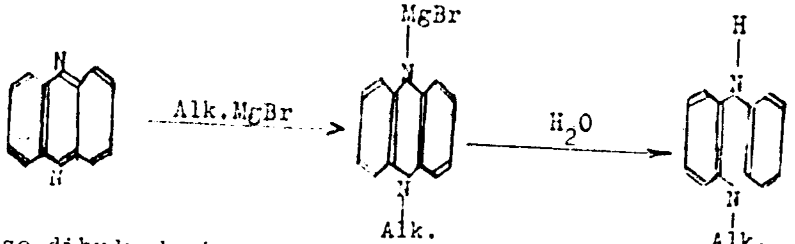
Reaction of Phenazine and N-Phenazine Oxide With Organomagnesium Halide Compounds

SOV/79-29-3-57/61



These dihydroderivatives which are unstable in air were not precipitated and transformed by the oxidation with diluted nitric acid into the corresponding quaternary phenazine salts (yield 39%). The dihydroderivatives are in alkaline solution transformed into the 9-alkyl-phenazinone-2 by potassium ferricyanide (50%) (Scheme 3). In order to obtain the above mentioned reaction the ratio Grignard reagent - phenazine has to be 2,5 mole: 1 mole. The reaction of phenazine with phenyl magnesium bromides differs from that with alkyl magnesium bromides (Scheme 4). The quaternary phenazine salts were synthesized as well by the reaction of the organomagnesium halide compounds with phenazine oxide, with subsequent decomposition of the reaction products

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SOV/79-29-3-57/61

Reaction of Phenazine and N-Phenazine Oxide With Organomagnesium Halide Compounds

by mineral acid. Thus the perchlorate of N-phenyl phenazinium was obtained and in the case of its photochemical oxidation the 9-phenyl-phenazinone-2 (Scheme 6). Thus 9-alkyl-9,10-dihydrophenazines and the corresponding quaternary salts of phenazine were newly synthesized. There are 6 references, 2 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii Akademii nauk USSR (Institute of Organic Chemistry of the Academy of Sciences, Ukrainskaya SSR)

SUBMITTED: January 17, 1958

Card 3/3

5 (3)

AUTHORS: Kiprianov, A. I., Shrubovich, V. A. SOV/79-29-4-55/77

TITLE: **Steric Hindrance** in Quaternary Salts of 2-Arylbenzothiazoles, 2-Arylbenzimidazoles, and 2-Arylpyridines (O prostranstvennykh prepyatstviyakh v chetvertichnykh solyakh 2-arilbenztiazolov, 2-arilbenzimidazolov i 2-arilpiridinov)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 4, pp 1290 - 1299 (USSR)

ABSTRACT: The authors are now in a position to supplement the observations reported on in a previous article (Ref 1) by data concerning the light absorption of 2-p-dimethylaminophenylbenzimidazole salts. In the article under review the three salts (III), (IV), and (V) are compared in regard of their absorptions. The observations made with these salts were the same as in the case of the salts (I) and (II), where there occurred, in the transition from the simple to the quaternary salt, a shift of the absorption band not toward the long-wave, but toward the short-wave range of the spectrum (Ref 1). The approach of alkyls to the nitrogen atoms in the heterocycle causes a shift of the absorption band toward the short-wave range of the spectrum - to

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Steric Hindrance in
Quaternary Salts of 2-Arylbenzothiazoles, 2-Aryl-
benzimidazoles, and 2-Arylpyridines

SOV/79-29-4-55/77

a lesser degree in the case of salt (IV), but to a particularly high degree with salt (V). This fact suggests a disturbance of the co-planarity of the nuclei due to steric hindrance. . This disturbance is known to cause, in the case of aromatic compounds, not only a shift of the absorption band toward the short-wave range of the spectrum, but also a reduction of the absorption intensity (Ref 2). A comparison of the intensities of simple and quaternary salts of 2-dimethylaminophenyl derivatives of nitrogen heterocycles is difficult, and for this reason the spectrum determinations were extended to the salts of the 2-aryl derivatives of nitrogen heterocycles without amino groups. In the case of a sufficient sulphuric acid excess the alcoholysis of such salts in alcohol solutions may be suppressed, and it is possible to determine not only the absorption maximum of the salt but also its molecular extinction. The absorption spectra in the alcoholic solution of some 2-arylbenzothiazoles, 2-arylbenzimidazoles, 2- and 4-phenylpyridines as well as 2-phenylbenzoxazole, their sulphates and quaternary salts were determined. A comparison

Card 2/3

**Steric Hindrance in** Quaternary Salts of 2-Arylbenzothiazoles, 2-Arylbenzimidazoles, and 2-Arylpyridines

SOV/79-29-4-55/77

of the absorption curves of the sulphates and quaternary salts showed that in all cases (except 4-phenylpyridine) the absorption maxima of the quaternary salts shifted toward the short-wave range of the spectrum, and the intensities declined (Figs 1-7). There are 7 figures and 19 references, 3 of which are Soviet.

ASSOCIATION: Kiyevskiy gosudarstvennyy universitet (Kiyev State University)

SUBMITTED: February 28, 1958

Card 3/3

5 (3)

AUTHORS: Rozum, Yu. S., Kiprianov, A. I. SOV/79-29-4-57/77

TITLE: On the Guiding Effect of the Substituents in the Formation of N-Phenazine Oxides (O napravlyayushchem deystvii zamestiteley pri obrazovanii N-okisey fenazina)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 4, pp 1306 - 1311 (USSR)

ABSTRACT: In the reaction of oxidizing agents with mono-substituted phenazine derivatives two formations of isomeric monoxides are possible (Scheme 1). In this oxidation process the oxygen atom acts as electron acceptor so that the attack of the oxidizing agent has to be directed against that nitrogen atom of the asymmetrically substituted molecule which possesses the higher electron density. In the course of the investigations discussed in the article under review the authors studied the guiding effect of the following substituents: the 2-methoxy group, the chlorine atom in position 2, and the chlorine atom in position 1. The correlation of the resulting monoxide was determined according to the ultraviolet absorption spectra. The following method was used: In advance two monoxides to be expected were prepared separately for each case under investigation. This was done by alkaline

Card 1/3

On the Guiding Effect of the Substituents in the Formation of N-Phenazine Oxides SOV/79-29-4-57/77

condensation of the corresponding aromatic amines with nitro compounds. The oxygen atom is known to appear in such condensations at the expense of the nitro group (Ref 1). For this reason the two isomeric oxides, e.g. those of 2-chlorophenazine, were obtained as a result of the condensations according to scheme 2. The absorption curves of the two isomers of the N-oxides were photographed by means of the spectrophotometer SF-4 in benzene- and alcohol solutions. Subsequently, the mixture of the same monoxides was prepared by oxidation of the corresponding weighed phenazine derivative in glacial acetic acid with $H_2O_2$. The reaction product was chromatophotographed until the mixture of the two N-oxides was completely separated from the incompletely reacted base and the N,N-dioxide. The weighed mixture of isomeric monoxides was dissolved in benzene or alcohol and the absorption curve of the mixture was determined. It is not difficult to calculate the percentages of the individual components of the mixture by means of the absorption curve of the binary mixture and that of the two individual components. The afore-mentioned curves are explained in detail in the figures. There are 5 figures

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On the Guiding Effect of the Substituents in the Formation of N-Phenazine Oxides SOV/79-29-4-57/77

and 5 references, 4 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii Akademii nauk Ukrainskoy SSR (Institute of Organic Chemistry of the Academy of Sciences Ukrainskaya SSR)

SUBMITTED: February 7, 1958

Card 3/3

5(3)
SOV/79-29-5-64/75

AUTHORS: Kiprianov, A. I., Dyadyusha, G. G.

TITLE: Reactions of the Addition to Salts of 2-Phenyl Acetylenyl Quinoline (Reaktsii prisoyedineniya k solyam 2-fenilatsetilenilkhinolina)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 5, pp 1708-1715 (USSR)

ABSTRACT: The quaternary salts of 2-phenyl acetylenyl quinoline readily affiliate sodium sulfohydrate, amines and compounds with active methyl- and methylene groups. The following products were obtained: 2-thiobenzoyl methylene-1,2-dihydroquinoline, 2-α-methylmercapto styryl quinoline, p-methyl-2-thiobenzoyl methylene-1,2-dihydroquinoline, N-methyl-2-(α-ethylamino styryl)-quinolinium perchlorate, N-methyl-2-(α-piperidylstyryl)-quinolinium iodide, N-methyl-2-(α-anilinostyryl)-quinolinium methosulphate, 2-[α-phenyl-β-(1'-methyldihydro quinolinylidene)-ethylidene]-aceto-acetic ester, 2-[α-phenyl-β-(1'-methyl dihydroquinolinylidene)-ethylidene]-benzoyl acetone, 1,1'-dimethyl-10-phenyl-2,2'-quinocarbocyanine iodide, 1,3'-dimethyl-10-phenyl-2-quinothiacarbocyanine perchlorate, 1,1'-diethyl-5'-methoxy-10-phenyl-2-quinoselenocarbocyanine perchlorate, 1,1',3',3'-tetramethyl-10-phenyl-2-quinoindocarbocyanine per-

Card 1/2

SOV/79-29-5-64/75

Reactions of the Addition to Salts of 2-Phenyl Acetylenyl Quinoline

chlorate, 3-methyl-5-[α-phenyl-β-(1'-methyl dihydroquinolinylidene-2'-ethylidene]-rhodanine, 1-phenyl-3-methyl-4-[α-phenyl-β-(1'-methyl dihydroquinolinylidene-2')-ethylidene]-pyrazolone-5. The heterocyclic acetylene derivatives of the type 2-phenyl acetylenyl quinoline may serve as intermediate products in the synthesis of chain-substituted cyanine dyes. There are 1 table and 11 references, 3 of which are Soviet.

ASSOCIATION: Kiyevskiy gosudarstvennyy universitet (Kiyev State University)

SUBMITTED: February 16, 1957

Card 2/2

3(5) SOV/79-29-9-14/76

AUTHORS: Kiprianov, A. I., Tolmachev, A. I.

TITLE: Tertiary Oxonium Salts of Chromones and Thiochromones

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 9, pp 2868-2874 (USSR)

ABSTRACT: It may be observed from the investigation made by various foreign chemists, as cited by references 1-4, that tertiary oxonium salts of γ-pyrone and its derivatives are difficult to produce; this is the reason why they have been so little investigated. The properties of these salts reveal, however, that they are highly reactive, and may serve as initial products for a number of different transformations (Refs 2, 3, 5). Thus, for instance, methyl perchlorate of dimethyl pyrone may enter autocondensation in the presence of bases, and under formation of an orange dye (IV) (Scheme 2), what is indicative of the activity of methoxy groups with respect to nucleophilic-, and of the activity of methyl groups with respect to electrophilic compounds. A more comprehensive investigation of properties and reactions of tertiary oxonium salts of pyrones, and especially chromones, however, calls for a more expedient method of synthesizing these products. A synthesis, recently made by the authors (Ref 6), of quaternary salts of

Card 1/3

SOV/79-29-9-14/76

Tertiary Oxonium Salts of Chromones and Thiochromones

weak organic bases, was successfully applied to chromone and its derivatives. On heating an equimolecular mixture of chromone and methyl ester of 2,4-dinitrobenzosulfonic acid at 50°, tertiary oxonium salt (V) is already quantitatively formed after 20 min. Isomeric benzochromones with methyl ester of o-nitrobenzosulfonic acid more readily form tertiary oxonium salts (VI) and (VII) than does chromone (90% and 95% yield). The tertiary oxonium salts of flavone (VIII), 1-thiochromone (IX), 4-thiochromone (X), and 2-methylchromone (XI) were obtained in the same manner. The synthesis of the tertiary salt of 2-methyl chromone (XI) proceeded with more difficulty. It was obtained only with methyl ester of 2,4-dinitrobenzene sulfonic acid in a yield of 81%. Xanthone, thioxanthone, xanthione, thioxanthione and isoflavone do not react with the methyl ester of this acid. All the new synthesized tertiary salts are colorless, crystalline compounds with high melting points. Their purification was rather difficult, as they are unstable to water and alcohol. There are 31 references, 5 of which are Soviet.

Card 2/3

SOV/79-29-9-14/76

Tertiary Oxonium Salts of Chromones and Thiochromones

ASSOCIATION: Institut organicheskoy khimii Akademii nauk Ukrainskoy SSR (Institute of Organic Chemistry of the Academy of Sciences of the Ukrainskaya SSR)

SUBMITTED: September 1, 1958

Card 3/3

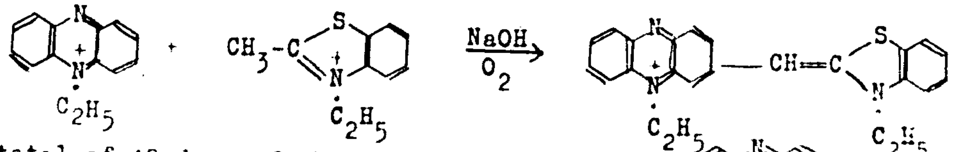
S/073/60/026/001/012/021
B004/B054

AUTHORS: [redacted] and Ponomareva, E. A.

TITLE: Cyanine Dyes From Phenazine Derivatives

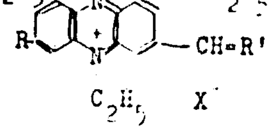
PERIODICAL: Ukrainskiy khimicheskiy zhurnal, 1960, Vol. 26, No 1, pp. 78-85

TEXT: Quaternary salts of nitrogenous heterocyclic compounds having a $CH_3$ group in α- or γ-position easily react in alkaline solution with quaternary phenazine salts. Example:



(IV)

A total of 18 dyes of the general structure



Card 1/2

Cyanine Dyes From Phenazine Derivatives

S/073/60/026/001/012/021
B004/B054

were synthesized by this reaction. Components used were quaternary salts of phenazine or 2-methoxy phenazine on the one hand, and quaternary salts of 2-methyl-substituted benzthiazole, 6,7-benzobenzthiazole, benzoselenazole, 4-methyl thiazole, benzoxazole, 4,5-benzobenzoxazole, 3,3-dimethyl indolenine, N-methyl benziminazole, and quinoline, on the other. Synthesis was conducted by three methods: 1) Equimolar amounts of the components (0.001-0.002 mole) were precipitated in aqueous solution by crystallized sodium acetate; 2) mixing of the components and dropwise addition of 20% NaOH; 3) an equimolar mixture of the components was dissolved in pyridine, and heated to boiling. The precipitates filtered off were recrystallized from methanol. Absorption maxima of these substances lie between 700 and 800 mμ. There are 1 figure, 2 tables, and 6 references: 3 Soviet, 2 US, 3 British, and 3 German.

ASSOCIATION: Kiyevskiy gosudarstvennyy universitet im. T. G. Shevchenko, kafedra organicheskoy khimii (Kiyev State University imeni T. G. Shevchenko, Department of Organic Chemistry)

SUBMITTED: August 11, 1958

Card 2/2

S/073/60/026/002/011/015
B023/B067

AUTHORS: Kiprianov, A. I., Ponomareva, E. A., and Skavinskiy, Ya. P.

TITLE: Cyanine Dyes From Phenazine Derivatives

PERIODICAL: Ukrainskiy khimicheskiy zhurnal, 1960, Vol. 26, No. 2, pp. 237-242

TEXT: In continuation of Ref. 1 the authors subjected quaternary salts of phenazine, methoxy phenazine, phenanthrazine, and methoxy phenanthrazine to oxidizing condensation with thiocyanate and pyrazolone derivatives. They obtained a number of dyes called merocyanines, from which they synthetized three-cyclic dyes - rhodacyanines. Also quaternary salts of phenanthrazine, methoxy phenanthrazine, acenaphthylene quinoxaline, and methoxy acenaphthylene quinoxaline were condensed with quaternary salts of 2-methyl-benzo thiazole. Thus, monomethine cyanines were obtained as dyes. The absorption maxima of the new dyes lie at the boundary between the visible and infrared regions of the spectrum. Table 1 illustrates the formation of rhodacyanine, and gives its yield and absorption maxima (in mμ). Table 2 shows the formation of monomethine cyanine, its yield,

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Cyanine Dyes From Phenazine Derivatives

S/073/60/026/002/011/015
B023/B067

and its absorption maxima in alcohol (in mμ). The attached scheme illustrates the formation of monomethine cyanine. Data published by A. I. Kiprianov (first author) and G. M. Prilutskiy are mentioned. Legend to Table 2: a) structure; b) yield; c) absorption maximum There are 2 tables and 6 references: 5 Soviet, 2 US, 1 French, 1 Belgian, and 1 German.

ASSOCIATION: Kiyevskiy gosudarstvennyy universitet im. T. G. Shevchenko, kafedra organicheskoy khimii (Kiyev State University imeni T. G. Shevchenko, Chair of Organic Chemistry)

SUBMITTED: August 11, 1958

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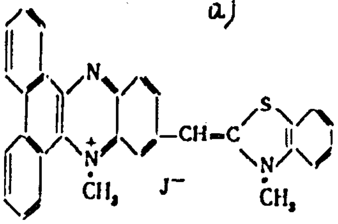
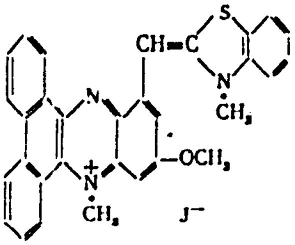
S/073/60/026/002/011/015
B023/B067

| № | Строение монометинцианина<br>a) | Выход, %<br>b) | Максимум поглощения в спирте, mμ<br>c) |
|---|---|---|---|
| XI |  | 65 | 755 |
| XII |  | 46 | 718 |

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S/073/60/026/002/011/015
B023/B067

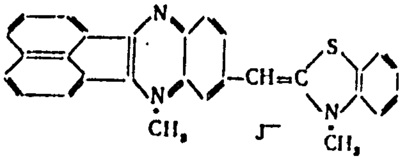
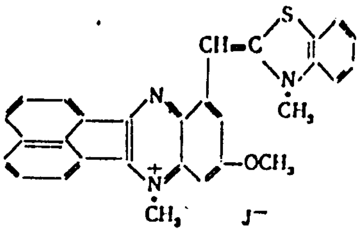
| | | | |
|---|---|---|---|
| XIII |  | 31 | 665 |
| XIV |  | 26 | 665 |

*Table 2*

Card 4/4

KIPRIANOV, A.I.

S.N. Reformatskii and his reaction; on the 100th anniversary of his birth. Ukr. khim. zhur. 26 no.4:471-475 '60. (MIRA 13:9)

1. Institut organicheskoy khimii AN USSR.
(Reformatskii, Sergei Nikolaevich, 1860-1934)
(Chemical reactions)

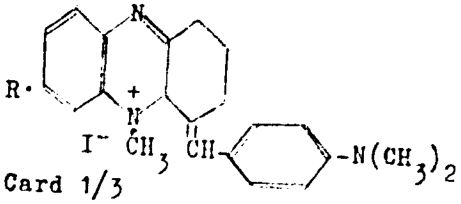
S/073/60/026/005/011/019
B004/B063

**AUTHORS:** Kiprianov, A. I. and Ponomareva, E. A.

**TITLE:** Cyanine Dyes From Phenazine Derivatives. III. Dyes From Tetrahydrophenazine

**PERIODICAL:** Ukrainskiy khimicheskiy zhurnal, 1960, Vol. 26, No. 5, pp. 633-636

**TEXT:** Proceeding from a paper by J. S. Morley (Ref. 1) the authors have synthesized the dye "Styril" (I) (condensation of tetrahydrophenazine iodomethylate with p-dimethyl aminobenzaldehyde according to Morley) and the methoxy derivative II (oxymethylation of tetrahydrophenazine with dimethyl sulfate, followed by condensation with the above aldehyde):



I: R = H·; $\lambda_{max}$ = 559 mμ, log ε = 3.83

II: R = $CH_3O$·; $\lambda_{max}$ = 586 mμ, log ε = 4.50

(The spectroscopic data refer to an alcoholic solution)

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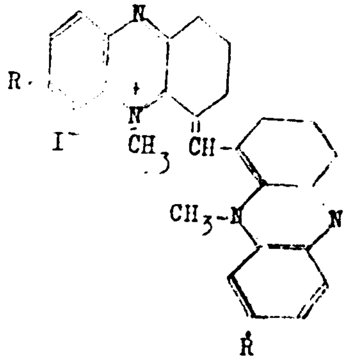
Cyanine Dyes From Phenazine Derivatives.
III. Dyes From Tetrahydrophenazine

S/073/60/026/005/011/019
B004/B063

A reaction of tetrahydrophenazine or of its methoxy derivative with dimethyl sulfate, sodium formate, and acetanhydride led to dyes III and IV, respectively:



III: R = H'; $\lambda_{1_{max}}$ = 690 mμ, log $\varepsilon_1$=3.91, $\lambda_{2_{max}}$ = 743 mμ, log $\varepsilon_2$ - 3.90

IV: R = $CH_3O$'; $\lambda_{1_{max}}$ = 703 mμ, log $\varepsilon_1$ = 407, $\lambda_{2_{max}}$ = 760 mμ, log $\varepsilon_2$ = 4.06

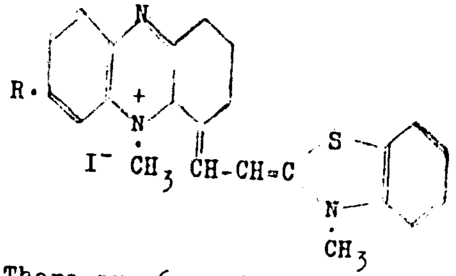
A reaction of methyl methoxysulfate of tetrahydrophenazine or of its

Card 2/3

Cyanine Dyes From Phenazine Derivatives.
III. Dyes From Tetrahydrophenazine

S/073/60/026/005/011/019
B004/B063

methoxy derivative with 2-acetanilidovinyl benzothiazole led to dyes V and VI, respectively:



V: R = H'; $\lambda_{1_{max}}$ = 618 mμ, log $\varepsilon_1$ = 3.76,

$\lambda_{2_{max}}$ = 646 mμ, log $\varepsilon_2$ = 3.69

VI: R = $CH_3O$'; $\lambda_{1_{max}}$ = 628 mμ, log $\varepsilon_1$ = 4.3;

$\lambda_{2_{max}}$ = 668 mμ, log $\varepsilon_2$ = 4.35

There are 6 non-Soviet references: 6 British.

ASSOCIATION: Kiyevskiy gosudarstvennyy universitet im. T. G. Shevchenko (Kiyev State University imeni T. G. Shevchenko)

SUBMITTED: April 14, 1959

Card 3/3

KIPRIANOV, A.I.

Influence of the solvent on the color of dyes (solvatochromism).
Usp. khim. 29 no.11:1336-1352 N '60.
(MIRA 13:11)

1. Institut organicheskoy khimii AN USSR.
(Color) (Dyes and dyeing)

5.3610

77909
SOV/79-30-2-60/78

AUTHORS: Kipryanov, A. I., Tolmachev, A. I.

TITLE: Condensation of Tertiary Oxonium Salts of Chromones and Thiochromones With Compounds Containing Active Methyl or Methylene Groups

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol 30, Nr 2, pp 638-646 (USSR)

ABSTRACT: In their previous study (this J., 1959, our abstract 75199) the authors reported the synthesis of tertiary oxonium salts of chromones and thiochromones in the reaction of these weak bases with esters of nitrobenzenesulfonic acid. The present study deals with the condensation of these salts with quaternary salts of 2-methylbenzothiazole and its derivatives, or with 2-methylenebenzothiazole, which yielded a series of asymmetric dyes (momomethinylcyanines) containing benzothiazole- and benzopyrylium-groups. Equimolecular amounts of o-nitrobenzenesulfonate of 4-methoxybenzothiopyrylium and methylbenzenesulfonate of

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Condensation of Tertiary Oxonium Salts of Chromones and Thiochromones With Compounds Containing Active Methyl or Methylene Groups

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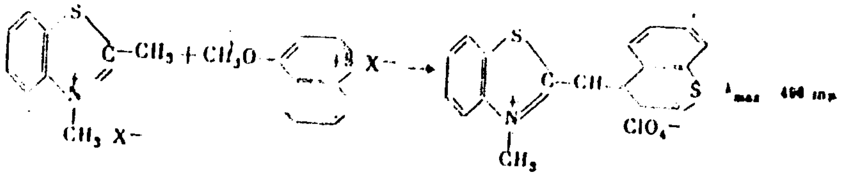
2-methylbenzothiazole heated for 30 min at 100 ° C in a mixture of acetic acid, acetic anhydride, and pyridine gave readily (I) dark-red needles; yield 20%, decomp. 264 ° C.



I

Dye I was obtained in 61% yield when 3-methyl-2-methyleneberzothiazoline was substituted for the quaternary salt of 2-methylbenzothiazole. Dyes (II) (orange needles; yield 60%; decomp. 278 ° C) and (III) (orange needles; yield 37%; decomp. 277 ° C) were obtained similarly from o-nitrobenzenesulfonate of

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Condensation of Tertiary Oxonium Salts of Chromones and Thiochromones With Compounds Containing Active Methyl or Methylene Groups

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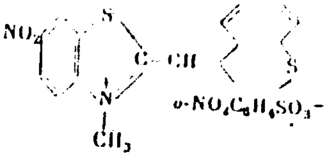
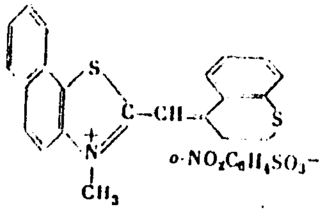
4-methoxybenzothiopyrylium with, respectively, methyl-o-nitrobenzenesulfonate of 2-methyl-6-nitrobenzothiazole, and o-nitrobenzenesulfonate of 2-methyl- α-naphthothiazole.



(II)

$\lambda_{max}$ 530, 510 mμ.



(III)

$\lambda_{max}$ 512 mμ

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Condensation of Tertiary Oxonium Salts of Chromones and Thiochromones With Compounds Containing Active Methyl or Methylene Groups

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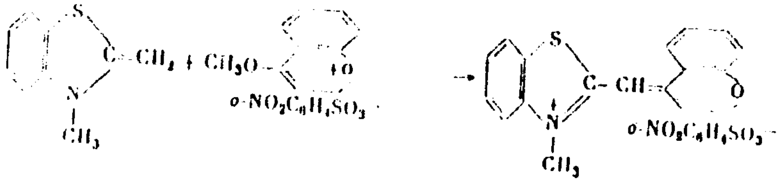
Tertiary oxonium salts of chromones do not yield monomethinecyanines under the above conditions, but can be condensed easily with quaternary salts of 2-methylbenzothiazole when the latter were converted with alkali into methylene bases. Accordingly, o-nitrobenzenesulfonate of 4-methoxybenzopyrylium in acetic anhydride, and 3-methyl-2-methylenebenzothiazoline in glacial acetic acid on heating for 1 hr at 100 °C gave (IV) (red-orange needles; yield 50%; decomp. 256 °C).



(IV)

$\lambda_{max}$ [illegible] mμ

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Condensation of Tertiary Oxonium Salts of Chromones and Thiochromones With Compounds Containing Active Methyl or Methylene Groups

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In this manner, the condensation of the salts of chromone, flavone, and 5,6-benzochromone with 2-methylene-3-methyl-(or 3-ethyl)-benzothiazoline, 2-methylene-3-methyl-6-nitrobenzothiazoline, and 2-methylene-3-methyl-(or 3-ethyl)- $\alpha$ -naphthothiazoline gave the yellow and orange monomethinecyanines (V) - (X), in quantitative yield. Monomethinecyanine (XI) (orange flakes; decomp. 295 ° C) of a similar structure was obtained by condensing 2-methylchromone with Larivé reagent (3-methylbenzothiazole-2-sulfobetaine) for 3 hr at 150 ° C and heating the base, thus obtained, for 1 hr at 150 ° C with dimethyl sulfate. Heating 2-methyl chromone with methyl ester of o-nitrobenzenesulfonic acid in toluene gave (XII) (dark purple needles; decomp. 264 ° C). Heating 2-methylchromone with $P_2S_5$ in xylene, and treating the base thus obtained with dimethyl sulfate gave (XIII) (dark purple needles; decomp. 249 ° C). Flavone in reaction with Grignard's reagent in ethyl ether gave easily salts of 4-methylflavylium containing an active methyl group.

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KIPRIANOV, A.I.; DYADYUSHA, G.G.

Reactions of addition to salts of phenylacetylenylpyridines.
Zhur. ob. khim. 30 no.11:3647-3654 N'60. (MIRA 13:11)

1. Institut organicheskoy khimii Akademii nauk Ukrainskoy SSR.
(Pyridine)

KIPRIANOV, A.I.; DYADYUSHA, G.G.

Organomagnesium synthesis of 2-acetylenylquinolinium salts.
Zhur. ob. khim. 30 no.11:3654-3658 N '60. (MIRA 13:11)

1. Institut organicheskoy khimii Akademii nauk Ukrainskoy SSR.
(Quinolinium compounds)