Chemistry

1965

SovietRxiv

Abstract

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Chemistry

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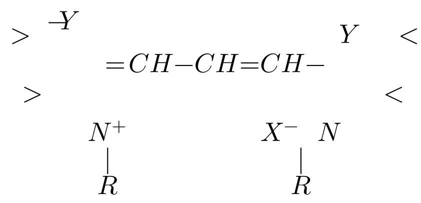
On the Action of Quaternary Salts of β-Chlorovinyl Derivatives of Heterocyclic Bases on Certain Carbo- and Dimethinemerocyanine Dyes

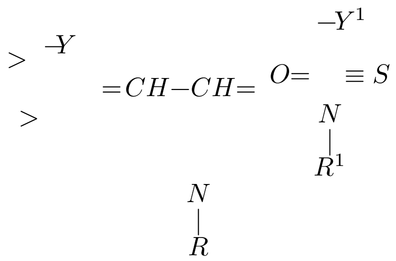
(Presented by Academician M. I. Kabachnik, 14 IX 1964)

In carbo- (I) and dimethinemerocyanines (II), electronic shifts take place from the cyclic nitrogen atom to the carbon atom connected with the hetero residue, as a result of which these dyes enter into certain electrophilic-substitution reactions.



$$> \overset{-Y}{} \; =CH-CH=CH- \; \overset{Y}{} < \quad \underset{\underset{R}{|}}{N^+} \quad X^- \; \underset{\underset{R}{|}}{N}$$

I



$$> \overset{-Y}{} \; =CH-CH= \; O= \overset{-Y^1}{} \equiv S \quad \underset{\underset{R^1}{|}}{N} \quad \underset{\underset{R}{|}}{N}$$

II

Thus, they react with aromatic diazonium salts, forming the corresponding α-arylazo derivatives (^{1}), and condense with ortho-thioformic-acid alkyl esters, giving α-alkylmercaptomethylene derivatives (^{2}, ^{3}), which, under the action of quaternary salts of heterocyclic bases containing an active methyl group (III), are converted into three-nuclear dyes, in particular the so-called neocyanines (^{4}, ^{5}). The formation of the latter upon condensation of salts (III) with ortho-formic-acid alkyl esters is evidently also associated with transformations of the carbocyanines initially obtained. These dyes subsequently either react with ortho-esters to form an α-alkoxymethylene derivative, which condenses with the unchanged salt (III) to give the corresponding neocyanine (^{6}), or form the latter as a result of interaction with the quaternary salt of a β-alkoxyvinyl derivative (^{7})—the condensation product of equimolecular amounts of (III) and the ortho-ester (^{8}).

The possibility of obtaining neocyanines by the latter scheme is confirmed by the data of Ogata (^{9}), who, under the action of methyl iodide of 2-β-acetanilinovinyl-4-methylthiazole on 4,4′-dimethylthiazolocarbocyanine, succeeded in synthesizing, in low yield (6%), the corresponding neocyanine. However, Kendall and Mayer ([10]), in attempting to condense the considerably more reactive methiodide of 2-β-ethylmercaptovinylbenzthiazole with 3,3′-diethylthiacarbocyanine tosylate (IV), isolated only the unchanged starting products.

In this connection it seemed of interest to attempt to bring into reaction with carbo- and dimethinemerocyanine dyes (I and II) the quaternary salts of 2-β-chlorovinyl derivatives of heterocyclic bases, which are very active electrophilic agents ([11]).

When 1 M chloroethylate of 2-β-chlorovinylbenzthiazole (V) in anhydrous chloroform was added to a solution of 1 M 3,3′-diethylthiacarbocyanine tosylate IV, the color rapidly changed from purple to blue. After 24 hours, following appropriate treatment, a dye was isolated from the reaction mixture which proved identical with 3,3′-diethyl-10-(3″-ethylbenzthiazolylidene-2″)-thiacarbocyanine diiodide (VI), obtained earlier by other methods ([10], [12]–[14]). The yield of VI was 55% of theory.

As it turned out, instead of the isolated chloroethylate of 2-β-chlorovinylbenzthiazole (11), salt V can be used, obtained directly in the reaction mixture by the interaction of 3-ethyl-2-formylmethylidenebenzthiazoline with phosgene (method b).

By the use of both methods, some other neocyanine dyes were analogously obtained.

The interaction of quaternary salts of 2-β-chlorovinyl derivatives of heterocyclic bases with dimethinemerocyanines proceeded just as readily as with carbocyanines. Thus, upon addition of 1 M V to an orange solution of 1 M 3-ethyl-5(3′-ethylbenzthiazolinylidene-2′-ethylidene)thiazolidinethione(2)-one-(4) (VII) in anhydrous chloroform, a violet coloration appeared almost immediately. After 12 h a dye was isolated in the form of the iodide, which proved identical with 3,3′-diethyl-8-(3″-ethylthiazolidinethione-(2″)-one-(4″)ylidene-5″-methyl)thiacarbocyanine iodide (VIII) (yield 50% of theoretical), which had previously been obtained by another, more complicated route (15).

Starting from various dimethinemerocyanines, some analogous three-nuclear dyes were synthesized. These compounds are also readily formed in the preparation of salts of type V by the above-mentioned method in the reaction mixture.

The interaction of carbo- and dimethinemerocyanines with quaternary salts of β-chlorovinyl-substituted heterocyclic bases proceeds in all cases at ordinary temperature without the use of condensing agents. This clearly confirms the exceptionally high capacity of these compounds, noted earlier (11), to enter into electrophilic substitution reactions.

Experimental Part*

3,3′-Diethyl-10(3″-ethylbenzthiazolyl-2″)-thiadicarbocyanine diiodide (VI).

a) To a solution of 3,3′-diethylthiacarbocyanine tosylate IV (0.13 g) in anhydrous chloroform (25 ml) was added chloroethylate of 2-β-chlorovinylbenzthiazo — V (0.065 g), whereupon the color changed from purple to blue within 5–6 min, and golden-green crystals gradually began to separate. After 24 h the chloroform was distilled off in vacuo, the residue was dissolved in alcohol (3 ml), and a 10% solution of potassium iodide (3 ml) was added. The crystals that separated were filtered off and washed with water, alcohol, and ether. Yield 0.11 g (55%); mp 214–216°.

After two crystallizations from alcohol: green prisms, mp 239° (243° with decomposition [14]; 241° [10]). λ_{max} at 606 mμ* (601.5 mμ in methanol [14]).

b) To a solution of IV (0.13 g) and 3-ethyl-2-formylmethylenebenzthiazoline (IX) (0.08 g) in chloroform (15 ml) was added a solution of phosgene in the same solvent (0.3 ml; 0.1 g $COCl_2$), and the mixture was left for 12 h. After the above-described treatment, the yield was 0.2 g; mp 203–204°. The dye was washed with boiling alcohol and then crystallized from the same solvent. Mp 237–238°.

3,3′-Diethyl-10(3″-ethylbenzthiazolyl-2″)-selenatiadicarbocyanine diiodide.

To a solution of IV (0.09 g) in chloroform (10 ml) was added 2-β-chlorovinylbenzselenazole chloroethylate (0.05 g), which was accompanied by a change in color from purple to blue. The dye was isolated analogously to the preceding one. Yield 0.1 g (69%). After crystallization from alcohol: golden-green needles. Mp 236° (234° [16]); λ_{max} at 613 mμ (610 mμ in methanol [16]).

By method b), yield 84%; mp 232–233°.

3,3′-Diethyl-10(3″-ethylthiazoliniumyl-2″)-thiathiazolinodicarbocyanine diiodide.

a) To a solution of 3,3′-diethylthiazolinocarbocyanine iodide (X) (0.09 g) in chloroform (5 ml) was added V (0.065 g). The color of the solution rapidly changed from yellow to purple, and a resinous precipitate separated. After 24 h the chloroform was distilled off, the residue was dissolved in alcohol (2 ml), and a 10% solution of potassium iodide (6 ml) was added. Yield 0.13 g (80%); mp 223–224°. Shiny green prisms (from alcohol). Mp 224–225°.

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* With the participation of N. S. Stokovskaya.

Found, %: I 35.59
$C_{24}H_{31}N_3S_3J_2$. Calculated, %: I 35.72

The **diperchlorate** was obtained analogously from the ethyl perchlorate of 2-β-chlorovinylbenzthiazole. Yield 100%; mp 214-216°. After crystallization from methanol: golden-green prisms, mp 225-226° (235° with decomposition [16]), λ_{max} at 560 mμ (558 mμ in methanol [16]).

Found, %: Cl 11.02; 10.92
$C_{24}H_{31}O_8N_3S_3Cl_2$. Calculated, %: Cl 10.82

By method b), yield 86%; mp 224-225°.

3,3′-Diethyl-5′-methyl-10(3″-ethyl-5″-methylthiodiazol-(1″,3″,4″)-yl-2″)-thiathiodiazolo(1′,3′,4′)dicarbocyanine diperchlorate.

To a solution of 3,3′-diethyl-5,5′-dimethylthiodiazolo-(1,3,4)-carbocyanine iodide (0.1 g) in chloroform (2 ml) was added the ethyl perchlorate of 2-β-chlorovinylbenzthiazole (0.08 g). The orange color of the solution changed to violet. After 12 h the mixture was diluted with ether; the precipitate was filtered off, dissolved in alcohol (3 ml), and a 20% solution of $NaClO_4$ (14 ml) was added. Yield 0.11 g (76%); mp 188-190°. Golden-green prisms (from alcohol). Mp 190-192°; λ_{max} at 578 mμ.

Found, %: Cl 10.39; 10.27
$C_{24}H_{29}O_8N_5S_3Cl_2$. Calculated, %: Cl 10.41

3,3′-Diethyl-8(3″)-ethylthiazolidinthion(2″)-on-(4″)-ylidene-5′-methylthiacarbocyanine iodide (VIII).

a) 3-Ethyl-5-(3′-ethylbenzthiazolinylidene-2′-ethylidene)thiazolidthion(2)-one-(4) (VII) (0.17 g) was dissolved in chloroform (20 ml), and to it

* Here and below λ_{max} is in ethyl alcohol.

V (0.15 g) was introduced, whereupon the color rapidly changed from orange-red to violet.

The mixture was left for 12 h; the chloroform was then distilled off, the residue was dissolved in alcohol (2 ml), and 10% KI solution (4 ml) was added. The crystals that separated were filtered off, washed with water, alcohol, boiling benzene (3 portions of 10 ml each), and then ether. Yield 0.15 g (50%); m.p. 222-223°. Lustrous blue needles (from alcohol). M.p. 224-225° (227° (15)); λ_{max} at 581 mμ (575 mμ in methanol (15)).

b) To a solution of (VIII) (0.09 g) and (IX) (0.08 g) in chloroform (10 ml), a solution of phosgene was added (0.3 ml; see above). The dye was isolated as described above. Yield 0.16 g (96%); m.p. 215-216°.

After three crystallizations from alcohol, m.p. 224-225°.

3-Ethyl-3′-methyl-10(3″-ethyloxazolidinthion(2″)-on-(4″)ylidene-5″-methyl)thiathiazolinocarbocyanine iodide.

a) To a solution of 3-ethyl-5(3′-methylthiazolidinylidene-2′-ethylidene)-oxazolidinthion(2)-one-(4), (XI) (0.14 g), in chloroform (4 ml), V (0.15 g) was introduced, whereupon the color changed from yellow to dark red. After 12 h the solvent was removed, the residue was dissolved in alcohol (2 ml), and the liquid was diluted with 10% KI solution (4 ml). The precipitate that separated was washed with water and then ether.

Yield 0.21 g (70%). The dye was purified by washing with boiling benzene and subsequent crystallization from alcohol. Golden-green prisms with m.p. 216-217°; $\lambda_{\max}$ at 547 mμ.

Found, %:	J 21.61
$C_{22}H_{24}O_2N_3S_3J$. Calculated, %:	J 21.71

b) To a solution of XI (0.14 g) and IX (0.15 g) in chloroform (4 ml), a solution of phosgene was added (0.6 ml; see above). After 24 h the dye was isolated in the usual manner. Yield 0.23 g (79%); m.p. 175-176°. After washing with boiling benzene and crystallization from alcohol, m.p. 215-216°.

3-Ethyl-1′-methyl-10(1″,3″-dimethylimidazolidinthion-(2″)-on-(4″)-ylidene-5″-methyl)-thiadihydropyrroleninecarbocyanine perchlorate.

To a solution of 1,3-dimethyl-5(1′-methylpyrrolidinylidene-2′-ethylidene)imidazolidinthion(2)-one-(4) (0.12 g) in chloroform (5 ml), ethyl perchlorate of 2-β-chlorovinylbenzthiazole (0.16 g) was added, whereupon the yellow color changed to purple. After 12 h the chloroform was distilled off, the residue was dissolved in alcohol (3 ml), and 20% $NaClO_4$ solution (6 ml) was added.

Yield 0.22 g (81%); m.p. 158-160°. Lustrous dark-green prisms (from alcohol). M.p. 162-163°; $\lambda_{\max}$ at 546 mμ.

Found, %:	Cl 6.38; 6.42
$C_{23}H_{27}O_5N_4S_2Cl$. Calculated, %:	Cl 6.59

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Received
1 IX 1964

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