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Abstract

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SYNTHESIS AND SOME REACTIONS OF β-ALKOXY-SUBSTITUTED POLYMETHINE HEMICYANINE DYES

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In quaternary salts of β-alkoxypropenyl derivatives of heterocyclic bases (I; $n = 1$), the hydrogen atoms of the methyl group possess considerable mobility, as a result of which these compounds readily enter into many condensation reactions characteristic of quaternary salts of 2- and 4-methyl-substituted bases (for example, I, $n = 0$) ([1]).

[structure of (I): heterocyclic quaternary salt bearing Y, R, $\bar{X}$, OAlk, and $(CH{=}C)_n - CH_3$ substituents]
(I)

In the present work, we investigated the possibility of converting propenyl salts I ($n = 1$) into the corresponding polymethine hemicyanine dyes.

From quaternary salts I ($n = 0$), hemicyanines, as is known, are obtained by reaction with N,N′-diarylformamidines ([2]) and their vinyl homologs ([3]), with alkylisoformanilides ([4]), and also with orthoformic acid alkyl esters and primary or secondary amines ([5]).

Already upon 5-minute heating on a boiling water bath of equimolecular amounts of ethyl methyl sulfate of 2-β-methoxypropenylbenzothiazole (I; $n = 1$; Y—S; R—C_2H_5; Alk—CH_3; X—SO_4CH_3), ethyl orthoformate, and aniline, a brown mass was formed, which, after washing with ether, was dissolved in alcohol and treated with an aqueous solution of potassium iodide. On cooling, violet prisms separated, m.p. 157–158° (from alcohol), which, as was established, were 2-β-methoxy-δ-anilinobutadienylbenzothiazole ethyl iodide (III; Alk—CH_3; R'—H). The yield was 46.5% of theory.

Found %: J 26.90;
$C_{20}H_{21}ON_2SJ$. Calculated %: J 27.13

It proved that quaternary salts of β-alkoxypropenyl derivatives of other heterocyclic bases and various primary and secondary amines also enter into an analogous reaction ([6]).

[structure of (II): benzothiazolium salt bearing R', OAlk, $SO_4CH_3^-$, CH=C−CH_3, N^+−C_2H_5]

$$+ \underline{(C_2H_5O)_2CH-OC_2H_5} + H_2NC_6H_5 \xrightarrow{\text{KI}}$$

[structure of (III): benzothiazolium iodide bearing R', OAlk, CH=C−CH=CH−NHC_6H_5, N^+−C_2H_5]

(II) (III)

Thus were obtained the ethyl iodides of 2-β-methoxy-δ-anilinobutadienylbenzselenazole (brown prisms, m.p. 146-147°; yield 48.9%)

Found, %: I 25.08

$C_{20}H_{21}ON_2SeJ$. Calculated, %: I 24.81.

2-β-Ethoxy-δ-N-tetrahydroquinolylbutadienylbenzthiazole (54%; lustrous green prisms, m.p. 147-148°; yield 54.0%).

Found, %: N 5.36

$C_{24}H_{27}ON_2SJ$. Calculated, %: N 5.40

and a number of other similar dyes.

Tetramethine hemicyanines III may also be synthesized by heating salts II with equimolecular amounts of ethyl isoformanilide (Alk $-C_2H_5$; R′ −H; yield 76%) or diphenylformamidine (Alk $-C_2H_5$; R′ −H; 57%). In the presence of ethyl *o*-formate the yield is 73%, cf. ([7]).

The reaction of II (Alk $-C_2H_5$; R′ −H) with diphenylformamidine in pyridine can be carried out even at ordinary temperature (yield 63%).

However, condensation of this salt with dianils of malonic and glutaconic aldehydes under the indicated conditions proceeded with the formation of difficultly separable mixtures of various dyes. At the same time, when the reaction was carried out in the presence of acetic anhydride, well-crystallizing products were readily isolated which, as it turned out, are the iodides of 2-β-ethoxy-ω-acetylphenylaminohexatrienylbenzthiazole (IV; $n = 2$; Alk $-C_2H_5$; A $-N(COCH_3)C_6H_5$; yield 54.5%; m.p. 214-215°)

Found, %: N 5.18; J 23.10

$C_{25}H_{27}O_2N_2SJ$. Calculated, %: N 5.13; J 23.25

and -octatetraenylbenzthiazole (IV; $n = 3$; Alk $-C_2H_5$; A $-N(COCH_3)C_6H_5$; 45.5%; m.p. 206-207° ([8]))

Found, %: J 22.10

$C_{27}H_{29}O_2N_2SJ$. Calculated, %: J 22.16

(IV) $$[\text{benzthiazole ring}] - CH_\alpha = C_\beta(OAlk) - (CH = CH)_n - A \\ N^+ - C_2H_5,\ J^-$$

(V) $$[\text{benzthiazole ring}] = CH - C(= O) - (CH = CH)_n - A \\ N - C_2H_5$$

Quaternary salts of β-alkoxy-δ-acetylphenylaminobutadienyl derivatives (for example, (IV; $n = 1$; Alk $-CH_3$; A $-N(COCH_3)C_6H_5$, light-yellow prisms with m.p. 247-249°; λ_{max} at 416 mμ*)

Found, %: N 5.58

$C_{22}H_{23}O_2N_2SJ$. Calculated, %: N 5.53

were obtained in quantitative yield by acetylation of the corresponding hemicyanines with acetic anhydride, in the presence of triethylamine, at ordinary temperature ([9]). When this reaction was carried out with heating on a water bath (5-10 min), instead of the ethyl iodide of 2-β-methoxy-δ-acetanilinobutadienylbenzthiazole there was obtained an almost colorless crystalline product (λ_{max} at 395 mμ; m.p. 260-262°), which, under the action of dimethyl sulfate, formed the hemicyanine (IV; Alk $-CH_3$; A $-N(COCH_3)C_6H_5$).

This property of the substance obtained, as well as its elemental composition, made it possible to assign to it the structure 1-(3′-ethylbenzthiazolinylidene-2)-

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* Here and below, the values of λ_{max} are in ethyl alcohol.

4-(phenylacetylamino)-buten-(3)-one-(2) (V; $n = 1$; A $-N(COCH_3)C_6H_5$; yield 100%)

Found, %: N 7.77

$C_{21}H_{20}O_2N_2S$. Calculated N %: 7.69

The same compound and its higher vinylene homologs, for example 1-(3′-ethylbenzthiazolinylidene-2′)-6-(phenylacetylamino)-hexadien-(3,5)-one-(2) (V; $n = 2$; A $-N(COCH_3)C_6H_5$; light-yellow prisms with m.p. 221–222°; yield 90%; λ_{max} at 420 mμ)

Found, %: N 7.14; S 8.26

$C_{23}H_{22}O_2N_2S$. Calculated, %: N 7.18; S 8.22

and 1-(3′-ethylbenzthiazolinylidene-2′)-8-(phenylacetylamino)-octatrien-(3,5,7)-one-(2) (V; $n = 3$; A $-N(COCH_3)C_6H_5$; light-yellow prisms with m.p. 218–219°; yield 95%; λ_{max} at 436 mμ.

Found, %: N 6.70; S 7.34

$C_{25}H_{24}O_2N_2S$. Calculated, %: N 6.73; S 7.07

were also obtained by brief (5–15 min) heating of the hemicyanines (IV; $n = 1, 2, 3$; Alk $-CH_3$ or C_2H_5; A $-N(COCH_3)C_6H_5$) in pyridine at 115°.

As it turned out, the nonacetylated β-alkoxypolymethinehemicyanines undergo dealkylation markedly less readily. Thus, from the ethyl iodide of 2-β-ethoxy-δ-N-tetrahydroquinolylbutadienylbenzthiazole (IV; $n = 1$; Alk $-C_2H_5$; A $-NC_9H_{10}$; λ_{max} at 485 mμ), only upon 30-min heating in pyridine at 115°, a light-yellow substance (V; $n = 1$; A $-NC_9H_{10}$; λ_{max} at 415 mμ; m.p. 195–196°) is formed in a yield of 75% of theory,

Found, %: N 7.61; 7.83

$C_{22}H_{22}ON_2S$. Calculated, %: N 7.73

which, upon heating with diethyl sulfate, is converted into the initial hemicyanine.

The unusually high tendency toward dealkylation of the β-alkoxy-substituted ω-phenylacetylaminohemicyanines (IV; A $-N(COCH_3)C_6H_5$) is evidently connected with the fact that in these compounds the positive charge is to a considerable extent concentrated on the oxygen atom of the alkoxy group, as a result of which the bond of the latter to the alkyl residue is weakened.

As was to be expected, the phenylacetylamino group in the polymethinehemicyanines (IV; Alk $-CH_3$ or C_2H_5; $n = 1, 2, 3$; A $-N(COCH_3)C_6H_5$) is very labile, as a result of which these compounds readily enter into reaction with nucleophilic agents. Thus, upon 5–20-min heating in ethyl alcohol solution with primary or secondary aromatic and heterocyclic amines, the corresponding ω-amino derivatives are obtained (cf. (10)). In this way there were synthesized, for example, the ethyl iodides of 2-β-ethoxy-δ-*p*-toluidino- (yield 85%; golden-green prisms with m.p. 172–173° (cf. (6))), -β-N-tetrahydroquinolyl (see above) butadienylbenzthiazole, 2-β-ethoxy-ω-anilinohexatrienylbenzthiazole (83%, dark-blue prisms with m.p. 160–161°).

Found, %: N 5.65

$C_{23}H_{25}ON_2SJ$. Calculated, %: N 5.55

2-β-ethoxy-ω-anilinooctatetraenylbenzthiazole (86%, dark-green prisms with m.p. 150–151)

Found, %: N 5.37

$C_{25}H_{27}ON_2SJ$. Calculated, %: N 5.28

and a number of other polymethinehemicyanines.

It was further found that hemicyanines (IV; A $-N(COCH_3)C_6H_5$; $n = 1$); extremely readily, already at ordinary temperature, condense in alcoholic solution in the presence of triethylamine with quaternary salts of various heterocyclic bases containing an active methyl group (I; $n = 0$), ketomethylene compounds, and also with quaternary salts of β-alkoxypropenyl derivatives (I; $n = 1$), with formation, respectively, of symmetrical and unsymmetrical β-al-

cocyaninecarbo-, γ-alkoxytetramethinemero- (9) (cf. 11), and previously unknown β,β'-dialkoxytricarbocyanines (12).

[reaction scheme]

Thus, for example, 3,3′-diethyl-β-ethoxythiadicarbocyanine iodide was obtained (87.6%, m.p. 159–160°; cf. (13)), 3-ethyl-5-(3′-ethylbenzthiazolinylidene-2′-γ-ethoxybutenylidene)-thiazolidinethione-(2)-one-(4) (95.5%, m.p. 238–240° (233–234 (11))) and 3,3′-diethyl-β,β'-dimethoxythiatricarbocyanine iodide (75%; golden-green prisms, m.p. 162–163°).

$$C_{27}H_{29}O_2N_2S_2J \cdot C_2H_5OH.$$

Found, %: J 19.46;
Calculated, %: J 19.37

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Note: Figure translations are in progress. See original paper for figures.