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Abstract

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On Some Transformations of Quaternary Salts of 2-β-Chloropropenyl Derivatives of Heterocyclic Bases

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In quaternary salts of β-mono- and α,γ-disubstituted 2-propenylbenzthiazoles and other heterocyclic bases, the hydrogen atoms of the methyl or methylene group possess considerable mobility. Therefore such salts enter into condensation reactions with derivatives of heterocyclic bases and ketomethylene compounds containing readily detachable groups, with the formation of carbo- or polycarbocyanines and polymethine cyanines with the corresponding substituents in the polymethine chain ([1-10]).

It could be assumed that quaternary salts of 2-β-chloropropenyl derivatives of heterocyclic bases ([11]), e.g. I, possess analogous properties; consequently, upon their condensation with quaternary salts of bases containing a mobile group, e.g. II, one should expect the formation of as yet undescribed (cf. ([12])) mesochlorocarbocyanines, e.g. III:

[reaction scheme]

$Y - S$ or Se; $A - SAlk$, SO_3^-, OC_6H_5 and others; X –acid residue.

Upon addition of triethylamine (2 mol.) to a suspension of 2-β-chloropropenylbenzthiazole chloroethylate (I, $Y = S$; 1 mol.) and 2-sulfo-3-ethylbenzthiazolium betaine (II, $A = SO_3$, $X^- = 0$; 1 mol.) in alcohol or chloroform, and heating of the mixture on a steam bath (10 min.), an intense coloration immediately appeared (in alcohol, blue, rapidly changing to purple; in chloroform, purple). Complex mixtures of dyes were thereby formed (in alcohol, with absorption maxima at 580, 560-565, 543, 497, and 436 mμ; in chloroform, at 560-565, 580, 552-554, and 436 mμ). It was found that the dye with λ_{max}497 mμ is 3,3′-diethyl-9-ethoxythiacarbocyanine ([3]), and the substance with λ_{max}436 mμ is 1,3-bis(3′-ethylbenzthiazolylidene-2′)-acetone ([13]). The unstable dyes with λ_{max} at 560-565 and 552-554 mμ, decomposing in solutions, likewise readily pass into the latter compound. The reaction under these conditions is complicated by mutual condensation of two (or several) molecules of salt I with the formation of a very unstable dye with an absorption maximum at 688 mμ, possibly of structure V ($Y = S$) (cf. ([14])); decomposition of this gives 3,3′-diethyl-9-methylthiacarbocyanine (absorption max. at 543 mμ). A

difficultly separable mixture of dyes, mainly with λ_{max} 554 and 580 mμ (in alcohol), was also obtained upon

carrying out the process at 20–25°. The reaction proceeded considerably more uniformly at ordinary temperature in the presence of an excess of triethylamine. Thus, when 20 mol. of triethylamine was added to a suspension of the above-mentioned salts (1 mol. and 1 mol.) in chloroform, the purple color that first appeared rapidly changed to blue-violet, and shiny green crystals began to separate; after 24 hours these were filtered off and crystallized from alcohol.

It proved that this dye contains no chlorine and is the hitherto undescribed 3,3′-diethyl-9-sulfothiacarbocyaninebetaine* (IV, $Y = S$, $A = SO_3^-$, $X^- = 0$; yield 76%, m.p. 258–259°; absorption maximum in alcohol at 580 mμ).

$C_{21}H_{20}O_3N_2S_3$.	Found, %:	S 21.73; 21.81.
	Calculated, %:	S 21.63.

With a poorer yield this dye is obtained in alcoholic solution (13.6%), and also in chloroform with a smaller excess of triethylamine (10 mol.—27%; 5 mol.—13%).

Similarly, by condensation of the chloroethylate of 2-β-chloropropenylbenzselenazole (0.62 g) with 2-sulfo-3-ethylbenzthiazolium betaine (0.5 g) in chloroform (8 ml) with triethylamine (4.0 g), 3,3′-diethyl-9-sulfoselenathiacarbocyaninebetaine was synthesized (IV, $Y = Se$, $A = SO_3^-$, $X^- = 0$; shiny blue needles with m.p. 254–255°, yield 48%, absorption maximum at 592 mμ).

$C_{21}H_{20}O_3N_2S_2Se$.	Found, %:	N 5.50; 5.48.
	Calculated, %:	N 5.70.

On interaction of 1 mol. of salt I (Y—S) with 1 mol. of the ethyl-p-toluenesulfonate of 2-ethylmercaptobenzthiazole in chloroform at 20–25° in the presence of triethylamine (2 mol.), the principal reaction product isolated in the form of the perchlorate was the previously described 3,3′-diethyl-9-ethylmercaptothiacarbocyanine [15] (IV, Y—S, A—SC_2H_5, X—ClO_4; yield 48%, m.p. 208–209°, absorption maximum in alcohol at 586 and 549 mμ).

Similarly, with the ethyl-p-toluenesulfonate of 2-phenoxybenzthiazole [16] (in the presence of 20 mol. of triethylamine), a dye was obtained as the iodide, with λ_{max} at 543 and 509 mμ, which proved to be identical with 3,3′-diethyl-9-phenoxythiacarbocyanine iodide (IV, $Y = S$, $A = OC_6H_5$, $X = J$; yield 51%), previously synthesized by condensation of the iodoethylate of 2-β-phenoxypropenylbenzthiazole with salt II ($A = SO_3^-$, $X^- = 0$) [10].

Thus, in the condensation of quaternary salts of 2-β-chloropropenylbenzthiazole or -benzselenazole and benzthiazole derivatives with an alkylmercapto-, sulfo-, or phenoxy group in the 2-position (II), instead of the expected 9-chlorothia- or

-thiaselenacarbocyanines (III), dyes (IV) are obtained that contain in the meso position the group split off from salt II (A).

The mechanism of formation of these dyes is as yet insufficiently clear. It may be assumed that they are formed as a result of interaction with ions of sulfurous acid and, respectively, of mercaptan or phenol, of the meso-chlorocarbocyanine (III) formed initially. It is also possible that the latter reacts with triethylamine, giving a dye with a triethylammonium group, which is then replaced by the group (A) split off from the quaternary salt (II).

It is interesting that on interaction of the chloroethylate of 2-β-chloropropenylbenzthiazole (1 mol.) with 2-sulfo-3-ethylbenzthiazolium betaine (1 mol.) at 20–25° in the presence of triethylamine (20 mol.) in chloroform containing phenol (20 mol.), along with 9-sulfothiacarbocyanine (IV, $Y = S$, $A = SO_3^-$,

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* Previously, thiacarbocyanines with electronegative substituents (CN, $COOC_2H_5$, NO_2) in the meso position were obtained mainly by condensation of quaternary salts of 2-methylbenzthiazole and its derivatives with the corresponding trihalomethanes [17,18].

$X^- = 0$; yield 9%) it was possible to isolate, in the form of the iodide, 3,3′-diethyl-9-phenoxythiacarbocyanine (yield 27%).

Thus, the chlorine atom can be replaced not only by a group splitting off from salt II, but also by the residue of another compound with a labile hydrogen atom present in the reaction mixture.

It turned out that in 9-sulfothia- and -thiaselenacarbocyanines, e.g. in VI, the sulfo group is very labile and is readily replaced by various groups. Thus, when dye (VI) (1.1 g) was introduced at 20–25° into a solution of sodium methylate (0.06 g of sodium in 130 ml of methanol), the mixture was boiled for 5 min, and 10% aqueous potassium iodide solution (400 ml) was added, pure 3,3′-diethyl-9-methoxythiacarbocyanine iodide separated (VII, yield 85%, shiny red crystals, m.p. 167–168°; λ_{max} 497 mμ [3,5]). Similarly, on heating dye (VI) (0.55 g) for 30 min with potassium phenolate (0.2 g) in phenol (5.0 g) on a boiling water bath, followed by addition of sodium iodide (1.1 g) and dilution of the reaction mass with ether, 3,3′-diethyl-9-phenoxythiacarbocyanine iodide was obtained (VIII, yield 76%; violet needles, m.p. 249–250°; λ_{max} at 543 and 509 mμ [10]). When benzylamine (0.5 ml) was added at 20° to an alcoholic solution of dye VI (0.70 g in 60 ml), the color of the solution rapidly changed from blue to orange; after boiling for 15 min and adding sodium iodide (1.0 g), 3,3′-diethyl-9-benzylaminothiacarbocyanine iodide separated (IX, yield 47%, orange prisms, m.p. 249–250°, λ_{max} 474 mμ [13]). Similarly, by heating (1 h) dye VI in aniline (0.5 g in 5.0 ml) at 80°, 3,3′-diethyl-9-phenylaminothiacarbocyanine iodide was synthesized (IX, 57%, m.p. 235–236°; λ_{max} 501 mμ [13]). On addition to an alcoholic solution of the same dye (1 mol.) of 20% aqueous sodium hydrosulfide solution (1.5 mol.), orange crystals of 1,3-bis(3′-ethylbenzothiazolinylidene-

2′)propanthione-2 separated almost immediately (XI, 90%, m.p. 273-274° (273-275° ([13]), 291-292° ([19]))).

Reaction scheme shown on the page: central compound **(VI)**, bearing SO_3^-, is converted by the reagents indicated in the arrows into the following products:

- with CH_3ONa → **(VII)**, the 9-methoxy derivative (iodide);
- with C_6H_5OK → **(VIII)**, the 9-phenoxy derivative (iodide);
- with $C_6H_5CH_2NH_2$ → **(IX)**, the 9-benzylamino derivative (iodide);
- with $C_6H_5NH_2$ → **(X)**, the 9-phenylamino derivative (iodide);
- with NaSH → **(XI)**, the corresponding propanthione derivative;
- additional transformations in the scheme give compounds **(XII)** and **(XIII)**, with the structures and iodide counterion shown in the figure.

Further experiments showed that 9-sulfothia- and -thiaselenacarbocyanines enter unusually readily into a condensation reaction with quaternary salts of 2- or 4-methyl-substituted heterocyclic bases, with formation of trinuclear dyes which previously could be synthesized by other methods only in substantially lower yields (cf. [20–24]). Thus, upon 5-minute boiling of a methanolic solution of dye VI (0.22 g in 6 ml), 2-methylbenzthiazole iodoethylate (0.15 g), and triethylamine (0.10 g), dye XII separated in almost quantitative yield—green needles (from alcohol), mp 223-224° (197° [21]). Absorption maximum at 562 mμ.

Found, %: J 18.79.
$C_{31}H_{30}N_3S_3J$. Calculated, %: J 19.04.

Under analogous conditions with 3-ethylrhodanine, dye XIII was synthesized (92.5%, mp 252-253°, λ_{max} in alcohol at 558 mμ [22]); with 1,3-dimethylthiohydantoin—3,3′-diethyl-9-(1″,3″-dimethylimidazolidinethion(2″),on(4″)ylidene(5″))-thiacarbocyaninebetaine (yield 100%, bronze prisms, mp 238-239°, λ_{max} in alcohol at 546 mμ).

Found, %: N 11.22; 11.14.
$C_{26}H_{26}ON_4S_3$. Calculated, %: N 11.06,

the corresponding carbocyanine with a 3-ethyloxazolidinethione(2)one(4) residue in the 9-position (92%, green needles, mp 218-219° (190° [22]), λ_{max} in alcohol 530 mμ), and a number of other trinuclear dyes.

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REFERENCES CITED

1 H. W. J. Cressman (Kodak Ltd.), Brit. pat. 613458; Chem. Abstr., **43**, 4159 (1949).

2 J. D. Kendall, H. W. Wood (Ilford Ltd.), Brit. pat. 553993. Chem. Abstr., **39**, 1296 (1945); J. D. Kendall, H. G. Suggate, H. W. Wood, Brit. pat. 555936; Chem. Abstr., **39**, 1546 (1945); U. S. pat. 2455420; Chem. Abstr., **43**, 4157 (1949).
3 a) N. N. Sveshnikov, I. I. Levkoev et al., DAN, **88**, 281 (1953); b) N. N. Sveshnikov, A. F. Vompe, I. I. Levkoev, USSR Author' s Certificate 93341, 93582.
4 V. G. Zhiryakov, Dissertation, Moscow, 1952.
5 Gevaert Photo-Prod. N. V., U. S. pat. 2557806; Chem. Abstr., **46**, 47 (1952); Brit. pat. 633824; Chem. Abstr., **44**, 9840 (1950); Fr. pat. 930514; Chem. Abstr., **43**, 5684 (1949); Fr. pat. 908750.
6 J. D. Kendall, D. J. Fry, A. J. Morgan (Ilford Ltd.), Brit. pat. 675227; Chem. Abstr., **47**, 988 (1953).
7 Gevaert Photo-Prod. N. V., Brit. pat. 625907; Chem. Abstr., **44**, 4357 (1950); Fr. pat. 929969.
8 I. K. Ushenko, ZhOKh, **29**, 3364 (1959); **31**, 2869 (1961); A. I. Kiprianov, I. K. Ushenko, G. M. Oksengendler, USSR Author' s Certificate 95286.
9 F. S. Babichev, A. I. Kiprianov, ZhOKh, **28**, 209 (1958).
10 S. A. Kheifets, N. N. Sveshnikov, N. A. Damir, Journal of the All-Union Chemical Society named after D. I. Mendeleev, **7**, 582 (1962).
11 N. N. Sveshnikov, I. I. Levkoev, N. I. Shirokova, USSR Author' s Certificate 136375 (1960); N. N. Sveshnikov, I. I. Levkoev et al., DAN, **148**, 1091 (1963).
12 M. Coenen, Ang. Chem., **61**, 11 (1949); Lieb. Ann., **633**, 102 (1960).
13 N. N. Sveshnikov, I. I. Levkoev et al., DAN, **84**, 733 (1952).
14 L. G. S. Brooker, F. L. White (E. Kodak Co), U. S. pat. 2231659.
15 D. J. Fry (Ilford Ltd.), Brit. pat. 678626.
16 Kodak Pathé, Fr. pat. 1242962.
17 Zeiss Ikon A. G., Deutsch. Pat. 725825; Chem. Zbl., 1943, 1, 242.
18 A. I. Kiprianov, Yu. S. Rozum, Collection of Papers of the IOC, Academy of Sciences of the Ukrainian SSR, **13**, 29 (1947).
19 L. G. S. Brooker, F. L. White (E. Kodak Co), U. S. pat. 2520358; Chem. Abstr., **45**, 3274 (1951).
20 J. G. Farbenind. Akt. Ges., Brit. pat. 373160; Chem. Zbl., 1932 II, 1527; T. Ogata, K. Tamura, Bull. Inst. Phys. Chem. Res. (Tokyo), **13**, 475 (1934).
21 J. D. Kendall (Ilford Ltd.), U. S. pat. 2397014.
22 L. G. S. Brooker, F. L. White (E. Kodak Co), U. S. pat. 2739964.
23 Gevaert Photo-Prod. N. V., (J. Nys, Th. Ghys), Belg. pat. 521309.
24 L. G. S. Brooker, F. L. White (Kodak Pathé), Fr. pat. 1107457. E. Kodak Co, Belg. pat. 519147.

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