Studies on Seven-membered Heterocyclic Compounds Containing Nitrogen. VII. Thiazolocyanine Dyes

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(Received January 28, 1963)

No such thiazolocyanine dyes as condensed with the nitrogen-containing seven-membered ring have been synthesized. The present authors report here about the syntheses of these dyes.

Ethiodide (II) of 5-ethoxycarbonyl-2-methyl-5, 6, 7, 8-tetrahydro-4(*H*)-azepino [4, 3-d] thiazole (I)[1] was converted to 2-phenylaminoethenyl derivative (III). II and III reacted to yield 5, 5'-diethoxycarbonyl-1, 1-diethyl-(5, 6, 7, 8-tetrahydro-4(*H*)-azepino [4, 3-d] thiazolo)-carbocyanine iodide (IV), m. p. 193~195°C (decomp.). 2-Phenylaminoethenyl derivative (VII) was derived likewise from 2-methyl-5, 6, 7, 8-tetrahydro-4(*H*)-azepino [4, 3-d] thiazole (V)[1] via its methiodide (VI). VI and VII gave a dye assumed to be 1, 1', 5, 5'-tetramethyl-(5, 6, 7, 8-tetrahydro-4(*H*)-azepino [4, 3-d]-thiazolo)carbocyanine iodide dimethiodide (VIII), m. p. 230~234°C (decomp.).

Another cyanine dye, 11-bromo-5, 5'-diethoxycarbonyl-1, 1'-diethyl-(5, 6, 7, 8-tetrahydro-4(*H*)-azepino [4, 3-d] thiazolo)-pentamethinecarbocyanine iodide (X) was also obtained from II and 2-bromo-3-anilino-2-propen-1-ylidenaniline (IX), m. p. 162~165°C (decomp.).

1) A. Yokoo and S. Morosawa, This Bulletin, 33, 1118 (1960).

Experimental

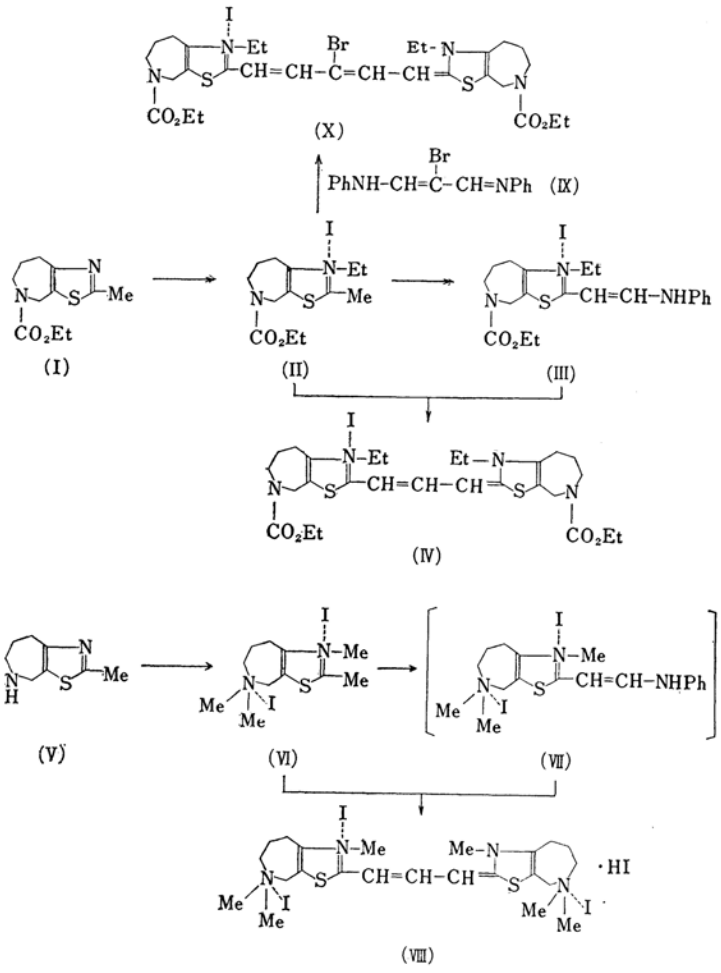
5-Ethoxycarbonyl-2-methyl-5, 6, 7, 8-tetrahydro-4(*H*)-azepino[4, 3-d]thiazole Ethiodide (II).—A mixture of 2 g. of I and 4 g. of ethyl iodide was heated under reflux for 4 hr. in a thick, round-bottomed flask. The flask was then stoppered tightly and heated for 5 hr. in a water bath. Precipitates, which formed on adding ether to the reaction mixture, were separated by decantation, and recrystallized from a small amount of ethanol to give 1.3 g. of light yellow crystals, m. p. 157~159°C.

Found: N, 6.94. Calcd. for $C_{13}H_{21}O_2N_2SI$: N, 7.07%.

2-Phenylaminoethenyl-5-ethoxycarbonyl-5, 6, 7, 8-tetrahydro-4(*H*)-azepino[4, 3-d]thiazole Ethiodide (III).—A mixture of 0.5 g. of II and 0.3 g. of diphenylformamidine was heated at 165°C for 20 min. The reaction mixture was dissolved in 2 cc. of absolute ethanol, and 2 cc. of ether was added. Crystals deposited were separated and recrystallized from ethanol to give 0.41 g. of orange crystals, m. p. 185~187°C.

Found: N, 8.15. Calcd. for $C_{20}H_{26}O_2N_3SI$: N, 8.42%.

5, 5'-Diethoxycarbonyl-1, 1'-diethyl-(5,6,7,8-tetrahydro-4(*H*)-azepino[4, 3-d]thiazolo)carbocyanine Iodide (IV).—A mixture of 180 mg. of II, 170 mg. of III, 250 mg. of anhydrous potassium acetate and 1.5 g. of acetic anhydride was heated at 63~65°C for 3 hr. The solid reaction mixture was washed with ether and then with water by decantation, and



dried in a vacuum desiccator. The solid was dissolved in 1 cc. of absolute ethanol and 1.5 cc. of ether was added to the solution. The solution was left to stand in a refrigerator to cause crystallization. The crystals were collected and dissolved in 0.5 cc. of methanol, followed by the addition of 1 cc. of ether. The resulted solution was filtered and left to stand in a refrigerator. The crystals thus obtained were again crystallized as above to give 18 mg. of dark purple crystals, m.p. 193~195°C (decomp.). UV λ_{max}^{MeOH} mμ(log ε) : 575 (4.99).

Found: C, 47.74; H, 5.81; N, 8.19. Calcd. for $C_{27}H_{39}O_4N_4S_2I$: C, 48.08; H, 5.84; N, 8.31%.

2, 5-Dimethyl-5, 6, 7, 8-tetrahydro-4(*H*)-azepino-[4, 3-d]thiazole Dimethiodide (VI).—To a solution of 2.1 g. of V in 5 cc. of methanol was added 9 g. of methyl iodide. After having been left to stand overnight, methanol was removed and the residue was heated with 5 g. of methyl iodide in a sealed tube for 3 hr. on a water bath. The excessive methyl iodide was removed and the remainder was recrystallized twice from methanol to yield 2.9 g. of light yellow crystals, m. p. 245~248°C (decomp.).

Found: C, 28.30; H, 4.19; N, 6.08. Calcd. for $C_{11}H_{20}N_2SI_2$: C, 28.32; H, 4.33; N, 6.01%.

2-Phenylaminoethenyl Derivative (VII) of V, and 1, 1', 5, 5'-Tetramethyl-(5, 6, 7, 8-tetrahydro4-(*H*)-azepino[4, 3-d]thiazolo)carbocyanine Iodide Dimethiodide (VIII).—A mixture of 300 mg. of VI and 300 mg. of diphenylformamidine was heated at 155°C for 10 min. The reaction mixture was dissolved in methanol and a large amount of ether was added. The resulting precipitates were collected, washed with ether and dried well in a vacuum desiccator to give 380 mg. of VII as an amorphous powder. A mixture of 300 mg. of VII, 230 mg. of VI, 230 mg. of anhydrous potassium acetate and 1.5 g. of acetic anhydride was heated at 70°C for 5 hr. The reaction mixture was washed three times with each 5 cc. portion of ether and dissolved in 1.3 cc. of water. To the solution were added 5 cc. of ethanol and 15 cc. of ether, and decanted after having been left to stand. The remaining crystals, after drying, were dissolved in 4 cc. of methanol and recrystallized by adding 6 cc. of benzene and leaving to stand in a refrigerator for 5 days. After collecting and washing with a mixture of methanol and benzene (1 : 1), the crystals were dissolved in 6 cc. of methanol and 6 cc. of benzene was added. The solution was left

to stand in a refrigerator for 2 days and the crystals formed were collected, dissolved in 3 cc. of methanol and filtered. The solution was left to stand as above and the resulted crystals were further recrystallized twice from methanol to give 18 mg. of dark purple crystals which turn light brown at about 220°C, m. p. 230~234°C (decomp.). UV λ_{max}^{MeOH} mμ (log ε): 575 (4.58).

Found: C, 29.53; H, 4.69; N, 6.02; S, 6.68; I, 52.38. Calcd. for $C_{23}H_{37}N_4S_2I_3 \cdot HI$: C, 29.30; H, 4.07; N, 5.95; S, 6.81; I, 53.85%

11-Bromo-5, 5'-diethoxycarbonyl-1, 1'-diethyl-(5,6, 7, 8-tetrahydro-4(*H*)-azepino[4, 3-d]thiazolo)pentamethinecarbocyanine Iodide (X). — A mixture of 200 mg. of II, 80 mg. of IX, 100 mg. of piperidine and 2.5 g. of pyridine was heated at 50°C for 2.5 hr. After cooling, a large amount of ether was added and decanted. This was repeated three times, followed by further washing with 2 cc. of water (twice) and with 1 cc. of hot water (twice). After drying in a vacuum desiccator, the crude product was dissolved in 1.5 cc. of methanol and the solution was left to stand in a refrigerator for 2 days. The crystals formed were collected and washed with methanol. Recrystallization (twice) as above gave 60 mg. of green crystals, m. p. 162~165°C (decomp.). UV λ_{max}^{MeOH} mμ (log ε): 635 (5.12).

Found: C, 44.05; H, 5.48; N, 7.13. Calcd. for $C_{29}H_{40}O_4N_4S_2BrI$: C, 44.64; H, 5.17; N, 7.18%.

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