

Synthesis of Dyes with the Neocyanine Structure Presented by Brooker, and Related Dyes. V. Synthesis of the Brooker-type Dyes from the Anil of 3-Ethyl-2-formylbenzothiazolium Iodide

By Shiro KIMURA

(Received November 17, 1959)

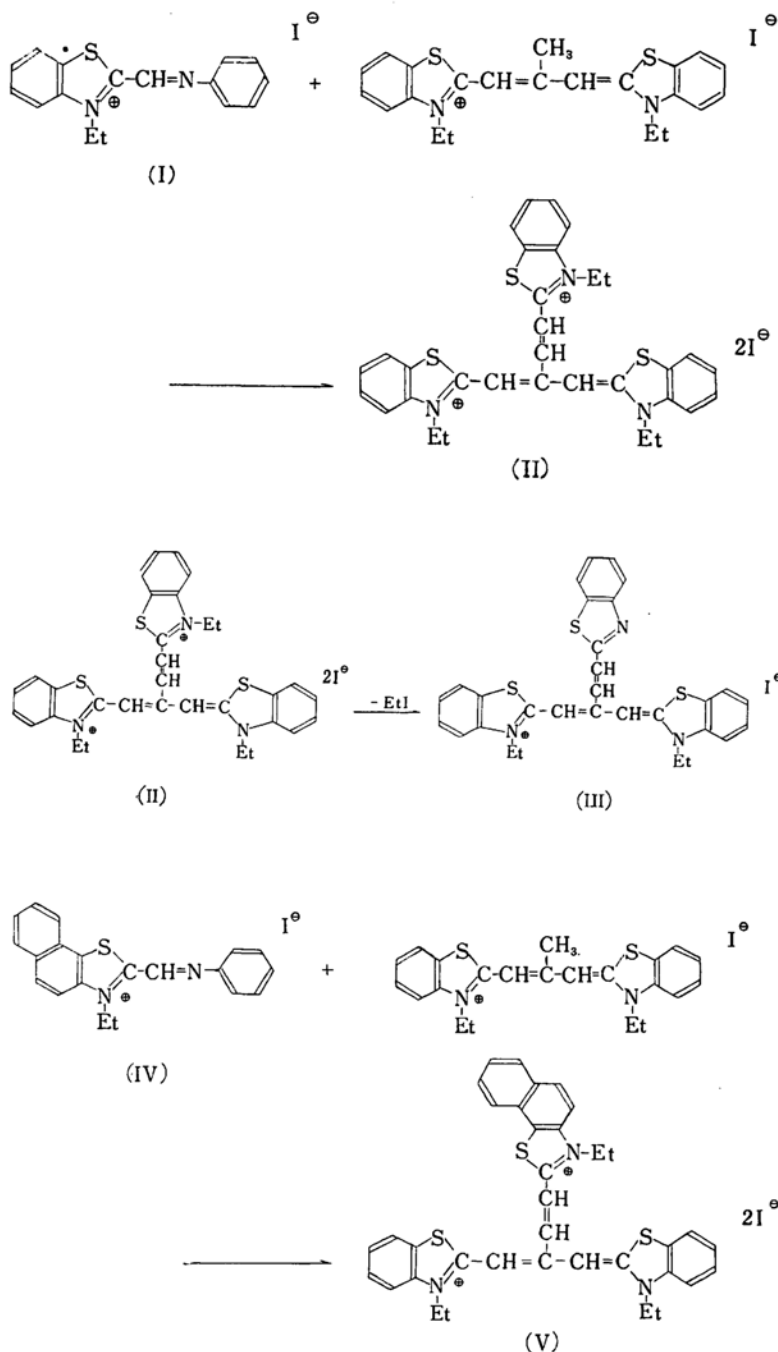
Synthesis of the Brooker-type dye, 3,3'-diethyl-9-[2-(3-ethyl-1-thia-3-azoniainden-2-yl)vinyl]thiacarbocyanine diiodide (II) in a good yield from the anil I of 3-ethyl-2-formylbenzothiazolium iodide and 3,3'-diethyl-9-methylthiacarbocyanine iodide is described in this paper and this is the reverse of the reaction given in Part II of this series¹⁾ for synthesis of the Brooker-type dyes from the nitron of 3,3'-diethyl-9-formylthiacarbocyanine bromide. At the same time, properties of the dye and synthetic process for similar dyes are described. Pure synthetic process for the anil I was de-

scribed in the preceding paper²⁾. An equimolar mixture of this anil and 3,3'-diethyl-9-methylthiacarbocyanine iodide was warmed in piperidine at 80~100°C for 5 min. and the dye II was obtained as brownish black leaflet crystal with copper luster, m. p. 257°C (decomp.).

It was shown in II that, during the course of the synthesis of this dye, heating of the mixture in a basic solvent for a long period of time or development of the product through alumina column afforded a dye of m. p. 219°C (decomp.). It was assumed that, similar to the case of 3,3'-diethyl-9-(3-ethyl-1-thia-3-azonia-

1) S. Kimura, *Bull. Soc. Sci. Phot. Japan*, **9**, 45 (1959).

2) S. Kimura, *This Bulletin*, **33**, 872 (1960).



inden-2-yl)thiacarbocyanine diiodide described in the preceding paper, this dye II might also have undergone liberation of ethyl iodide to form 3,3'-diethyl-9-[2-(2-benzothiazolyl)vinyl]thiacarbocyanine iodide (III). This dye III had already been synthesized by Hamer³⁾ and examination of her synthetic process showed

that they are identical dyes.

Condensation of 3-ethyl-2-formylnaphtho-[2,1-*d*]thiazolium iodide (IV) and 3,3'-diethyl-9-methylthiacarbocyanine iodide in pyridine similarly afforded 3,3'-diethyl-9-[2-(3-ethyl-1-thia-3-azoniacyclopenta[*a*]naphth-2-yl)vinyl]thiacarbocyanine diiodide (V) as purplish black crystalline powder of m. p. 257°C (decomp.): λ_{\max} 650 m μ .

3) F. M. Hamer, *J. Chem. Soc.*, 1952, 3197.

This synthetic process for the Brooker-type dyes from anils gives the product in comparatively good yield and can be recommended as a general method of synthesis of this type of dyes.

Experimental

Preparation of 3,3'-Diethyl-9-[2-(3-ethyl-1-thia-3-azoniainden-2-yl)vinyl]thiacarbocyanine Diiodide (II).—A solution of 0.95 g. of the anil I of 3-ethyl-2-formylbenzothiazolium iodide and 1 g. of 3,3'-diethyl-9-methylthiacarbocyanine iodide in 80 ml. of pyridine was heated at 80–100°C for 5 min. and cooled; ether was added to the reaction mixture to precipitate the dye formed. The precipitate was collected by filtration, washed with water, and 1.2 g. of the crude dye was obtained as purplish black powder, m.p. 180–190°C (decomp.). Recrystallization from methanol afforded 0.045 g. (yield, 2.8%) of brownish black leaflets, m.p. 257°C (decomp.). Paper chromatogram showed a single zone of violet color at R_f 0.37 (butanol: water = 6:1), λ_{\max} 560 m μ . This was identified with the dye II whose preparation was described in Part II of this series¹.

Found: C, 47.48; H, 3.91; N, 5.48; I, 30.94. Calcd. for $C_{32}H_{31}N_3I_2S_3$: C, 47.60; H, 3.81; N, 5.21; I, 31.50%.

Formation of 3,3'-Diethyl-9-[2-(2-benzothiazolyl)vinyl]thiacarbocyanine Iodide (III) by Liberation of Ethyl Iodide from the Dye II.—Examinations were made on elementary analytical values of the green needles, m.p. 219°C (decomp.), isolated during alumina chromatography of the product obtained from preparation of the dye II, described in Part II¹, and the values were found to be close to those calculated for III.

Found: C, 55.60; H, 4.82; N, 6.44. Calcd. for $C_{30}H_{26}N_3IS_3$: C, 55.29; H, 4.02; N, 6.45%.

The dye of m.p. 218°C (decomp.), obtained on following the synthetic process of Hamer, exhibited the same absorption curve as this dye III with λ_{\max} at 563 m μ , proving these dyes to be identical.

Preparation of 3,3'-Diethyl-9-[2-(3-ethyl-1-thia-3-azoniacyclopenta[a]naphth-2-yl)vinyl]thiacarbo-

cyanine Diiodide (V).—A mixture of 1 g. of the anil IV of 3-ethyl-2-formylnaphtho[2,1-d]thiazolium iodide and 1 g. of 3,3'-diethyl-9-methylthiacarbocyanine iodide in 80 ml. of pyridine was heated in an oil bath of 115–120°C for 10 min. Insoluble matter was filtered off, ether was added to the filtrate to precipitate the dye formed, and the mixture was allowed to stand over night. The precipitate was collected by filtration, washed with ether, and 0.8 g. of crude dye, m.p. 185–195°C (decomp.), was obtained. Recrystallization from 50 ml. of methanol afforded, as the first crop, the starting dye as indigo prisms, m.p. 275°C (decomp.), and concentration of this mother liquor to one-half the original volume afforded 0.17 g. of crystals of m.p. 195°C (decomp.). Recrystallization of this second crop of crystals from 30 ml. of methanol gave 0.05 g. of purplish black crystalline powder, m.p. 257°C (decomp.): λ_{\max} 650 m μ .

Found: C, 50.00; H, 3.94; N, 5.00. Calcd. for $C_{36}H_{33}N_3I_2S_3$: C, 50.40; H, 3.86; N, 4.90%.

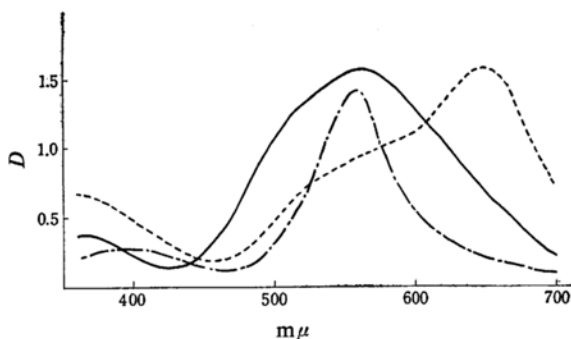


Fig. 1. Absorption spectral curves of II, III and V (in ethanol).

— (II) - - - (III) ····· (V)

Research Laboratory
Fuji Photo Film Co. Ltd.
Minami-Ashigara-machi
Kanagawa-ken