CYANINE DYES BASED ON THE ACID DICHLORIDES OF o- AND p-CARBOXYPHENYLAZOCHLOROACETIC ACIDS

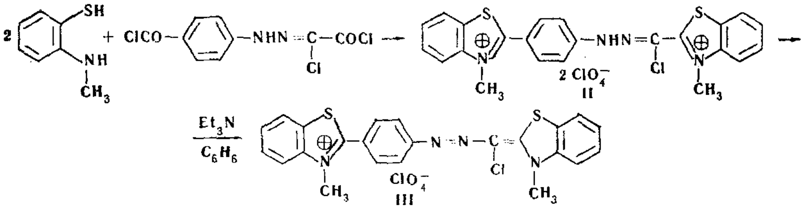
M. O. Lozinskii, S. N. Kukota,
and P. S. Pel'kis

UDC 547.789.6.07:668.8

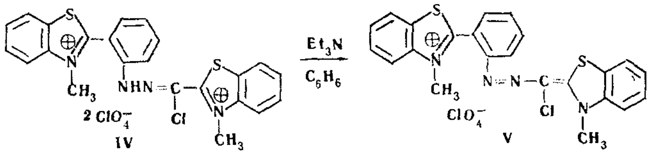
Cyanine dyes that contain chlorine, an azo group, and a phenyl ring in the conjugation chain have been synthesized for the first time.

In a continuation of our previous research [1], we have studied the cyclization of the acid dichlorides of o- and p-carboxyphenylazochloroacetic acids with N-alkyl-o-aminophenyl mercaptan via the method in [2].

We obtained cyanine dyes that contain chlorine, an azo group, and a phenyl ring in the conjugation chain for the first time (see [3]).



Diquaternary salt IV and dye V were similarly obtained.



The dyes are finely crystalline, green (III) or light-brown (V) products that are readily soluble in dimethylformamide, nitromethane, and acetonitrile, and slightly soluble in benzene and carbon tetrachloride. They decompose when they are heated in alcohol. The chlorine atom in the conjugation chain of dye III induces a bathochromic shift of the absorption maximum with respect to the unsubstituted dye [4] by 48 nm. In contrast to V, the color of III depends appreciably on the solvent polarity; it is deeper in slightly polar solvents (chloroform) and rises on passing to polar solvents (alcohol and nitromethane).

EXPERIMENTAL

Acid Dichloride of p-Carboxyphenylazochloroacetic Acid (I). This was obtained in 57% yield by the method in [5] as yellow crystals with mp 206 deg (from benzene–chloroform). Found: Cl 37.24%. $C_9H_5Cl_3N_2O_2$. Calculated: Cl 38.05%.

Acid Dichloride of o-Carboxyphenylazochloroacetic Acid. o-Carboxyphenylazochloroacetic acid [3.6 g

---

Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1048-1049, August, 1971. Original article submitted June 4, 1970.

(0.015 mole)] in 5 ml of absolute benzene was stirred with 6.24 g of phosphorus pentachloride, and the mixture was allowed to stand, with periodic shaking, for 3 days. The precipitate was filtered by suction and washed with dry benzene to give yellow crystals with mp 139 deg (from benzene). Found: Cl 38.12%. $C_9H_5Cl_3N_2O_2$. Calculated: Cl 38.05%.

4-(2-Benzothiazolyl)benzeneazo(3'-methyl-2'-benzothiazolidene)chloromethane Methylperchlorate (III). A solution of 1.2 g (0.086 mole) of N-methyl-o-aminophenyl mercaptan in 10 ml of chloroform was added in the course of 14 min to a solution of 1.2 g (0.043 mole) of acid dichloride I in a mixture of 190 ml of chloroform and 20 ml of dry benzene. The mixture was stirred for 1 h at room temperature, for ~1.5 h at 70-80 deg, and cooled. The precipitate was filtered, washed with benzene, and dried to give a quantitative yield of unpurified dichloride. The dichloride was converted by the usual method to the diperchlorate (II) with mp 225-228 deg (dec., from nitromethane–dioxane). λ_{max} 429 nm (nitromethane). Found: Cl 15.05%. $C_{23}H_{19}Cl_3N_4O_8S_2$. Calculated: Cl 16.36%.

A 1.08 g sample of II was triturated in 35-40 ml of dry benzene with 0.4-0.5 ml of triethylamine. The mixture was stirred at room temperature for 1 h and allowed to stand overnight for 12 h. The dark-red precipitate was filtered, washed with benzene, and refluxed for 4 h with 220 ml of chloroform. The precipitate was filtered to give 0.76 g (84.5%) of impure III. Compound III was purified by three reprecipitations by the addition of benzene to a solution of it in dimethylformamide or by chromatography on aluminum oxide. Pure III melted at 207-209 deg (dec.). λ_{max} (nm): 543 (alcohol), 544 (nitromethane), 564 (chloroform). Found: Cl 12.81; N 9.98; S 11.52%. $C_{23}H_{18}Cl_2N_4O_4S_2$. Calculated: Cl 12.90; N 10.19; S 11.67%.

2-(2-Benzothiazolyl)benzeneazo(3'-methyl-2'-benzothiazolidene)chloromethane Methylperchlorate (V). This was similarly obtained.

A) Diquaternary salt IV was obtained in quantitative yield and had mp 203 deg. λ_{max} 420 nm (nitromethane). Found: Cl 15.99%. $C_{23}H_{19}Cl_3N_4O_8S_2$. Calculated: Cl 16.36%.

B) Dye V was obtained in 27.4% yield and had mp 191-192 deg (by reprecipitation by the addition of benzene to a solution of V in nitromethane). λ_{max} (nm): 504 (ethanol) (ε 39,000), 507 (chloroform), 506 (nitromethane). Found: Cl 12.83%. $C_{23}H_{18}Cl_2N_4O_4S_2$. Calculated: Cl 12.90%.

LITERATURE CITED

1. M. O. Lozinskii and P. S. Pel'kis, Zh. Organ. Khim., 1, 1793 (1965).
2. A. I. Kiprianov and Z. N. Pazenko, Zh. Obshch. Khim., 19, 1515 (1949).
3. F. M. Hamer, The Cyanine Dyes and Related Compounds, Vol. 4, Interscience (1964), pp. 375, 440, 583, and 639.
4. A. I. Kiprianov and T. M. Verbovskaya, Zh. Organ. Khim., 1, 13 (1965).
5. M. O. Lozinskii and P. S. Pel'kis, Zh. Organ. Khim., 1, 1976 (1965).