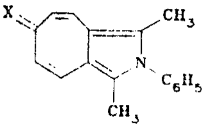
POLYMETHINE DYES BASED ON CYCLOHEPTA[*c*]PYRROLE

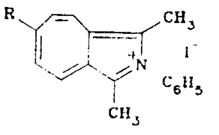
Yu. L. Briks and N. N. Romanov UDC 547.913.5

Polymethine dyes based on azulene are quite deeply colored and hence the synthesis of their aza-substituted analogs is of interest. With this in mind, we have examined the possibility of using derivatives of cyclohepta[*c*]pyrrole for the synthesis of new polymethine dyes.

The thione II is obtained by the reaction of the ketone I [2] with phosphorus pentasulfide in dioxane and this can be alkylated at the sulfur atom in the usual way with the formation of the alkylthiosubstituted derivative III.



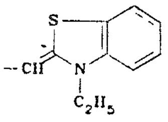
I, II, IV



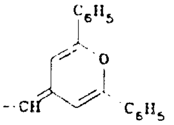
III, V, VI

I X=C; II X=S; IV X=C(CN)2; III R=SCH3

V R=

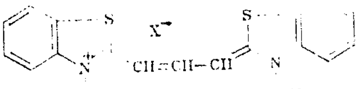


VI R=



The iodide of III, like the normal quaternary salts of 2-methyl-substituted nitrogen heterocycles, readily reacts with the nucleophilic reagents used in the preparation of polymethine dyes. Thus, on reacting with malonic dinitrile, the merocyanine IV is formed, and with 2-methyl-3-ethylbenzothiazolium or 4-methyl-2,6-diphenylpyrylium salts, the monomethinecyanines V and VI.

The azaazulene-based dyes are deeply colored. In fact, the monomethinecyanine V has practically the same absorption maximum (553 nm) as the thiatrimethinecyanine VII (558 nm [3]) which has a polymethine chain not of one methine group but of three:



VII

Thus, it has been shown that derivatives of cyclohepta[*c*]pyrrole can be used for the synthesis of deeply-colored dyes with short polymethine chains.

1,3-Dimethyl-2-phenyl-6H-cyclohepta[*c*]pyrrole-6-thione (II). Mp 212-214°C (from toluene). PMR spectrum ($CDCl_3$ (δ, ppm): 2.21 (6H, s, CH_3), 7.00 (2H, d, J = 11.5 Hz, 5- and 7-H), 7.20 (2H, m, *o*-H_{Ar}), 7.44 (2H, d, 4- and 8-H), 7.55 (3H, m, *m*- and *p*-H_{Ar}). Yield 47%.

1,3-Dimethyl-6-methylthio-2-phenylcyclohepta[c]pyrrolium Iodide (III). Mp 190-191°C, PMR spectrum ($CDCl_3$): 2.61 (6H, s, CH_3), 2.93 (3H, s, SCH_3), 7.35 (2H, m, *o*-H_{Ar}), 7.52 (2H, d, J = 14 Hz, 5- and 7-H), 7.69 (3H, m, *m*- and *p*-H_{Ar}), 8.69 (2H, d, 4- and 8-H). UV spectrum (in acetonitrile): λ_{max} 595 nm. Yield 80%.

6-Dicyanomethylene-1,3-dimethyl-2-phenyl-6H-cyclohepta[*c*]pyrrole (IV). Mp 268-270°C (from DMF). PMR spectrum (CF_3COOD): 2.36 (6H, s, CH_3), 6.90 (2H, d, J = 11.4 Hz, 5- and 7-H), 7.29 (2H, m, *o*-H_{Ar}), 7.60 (3H, m, *m*- and *p*-H_{Ar}), 7.67 (2H, d, 4- and 8-H). UV spectrum (in acetonitrile): λ_{max} 423 nm (log ε4.59). Yield 61%.

1,3-Dimethyl-2-phenyl-6-[(3-ethyl-2(3H)-benzothiazolylidene)methyl]cyclohepta[*c*]pyrroliumIodide(V). Mp 263-265°C (from pyridine). UV spectrum (in acetonitrile): λ_{max} 553 nm (log ε 4.73).

6-[(2,6-Diphenyl-4(4H)-pyranylidene)methyl]-1,3-dimethyl-2-phenylcyclohepta[*c*]pyrroliumIodide(VI). Mp 188-190°C (from CH_3CN). UV spectrum (in acetonitrile): λ_{max} 553 nm (log ε 4.73). Yield 26%.

Institute of Organic Chemistry, Ukrainian Academy of Sciences, Kiev 252660. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1432-1433, October, 1991. Original article submitted December 10, 1990; revision submitted March 22, 1991.

LITERATURE CITED

1. K. Venkataraman (ed.), *Chemistry of Synthetic Dyes* [in Russian], Vol. 4, Goskhimizdat, Leningrad (1975), p. 251.
2. A. V. El'tsov, L. N. Kovokurtseva, and A. A.Ginesina, *Zh. Org. Khim.*, **4**, 907 (1968).
3. K. Miz, *Theory of the Photographic Process* [in Russian], Moscow—Leningrad (1949).