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Photochromic Ionophores: Synthesis, Photoinduced Isomerization and Cycloaddition of Crown Ether Styryl Dyes

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PHOTOCHROMIC IONOPHORES: SYNTHESIS, PHOTOINDUCED ISOMERIZATION AND CYCLOADDITION OF CROWN ETHER STYRYL DYES

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Abstract The synthesis and structure of crown ether styryl dyes representing a novel class of dyes are considered. Data on photoisomerization and photo-induced 1,2-cycloaddition with formation of cyclo-butane derivatives are briefly analyzed.

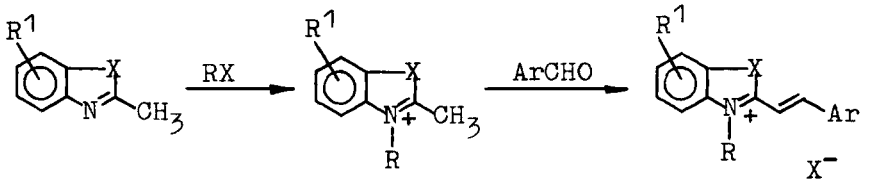
INTRODUCTION

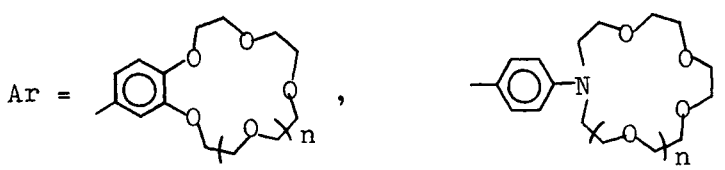
The molecular design and fine organic synthesis of supra-molecular devices with a capacity for photoswitching are the urgent problems in current researches.[1] Photocontrol of the physical and chemical properties of supramolecules may be attained by introduction into their molecules of functional groups capable of photoswitching. Up to now the major attention was given to photoswitch crown ether based on azobenzene derivatives.[2] At the same time different photoinduced and thermal pericyclic reactions of compounds containing C=C double bond exist and occur in nature. It shoud be noted such transformations as 1,2-photocycloaddition that leads to cyclobutane derivatives. So synthesis and photochemistry of crown ether styryl dyes are a new region for investigation.

SYNTHESIS OF CROWN ETHER STYRYL DYES

For these purposes we synthesized bifunctional derivatives of ethylenes - the crown ether containing styryl dyes with

unsaturated dye and crown ether residues as the structure fragments. Such structure does these compounds effective photochromic systems and photosensitive ionophores. A method of obtaining the above dyes involves the interaction of active methylene group of the quaternary salt of a heterocyclic base with a formyl derivative of benzocrown or phenylazacrown ether with formation C=C bond. The dyes prepared have an intense color in regions of 435-455 nm (yellow region) and 530-550 nm (red region).

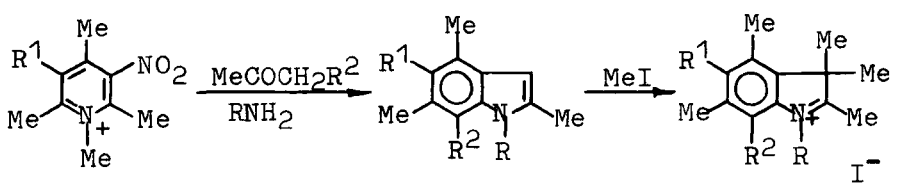




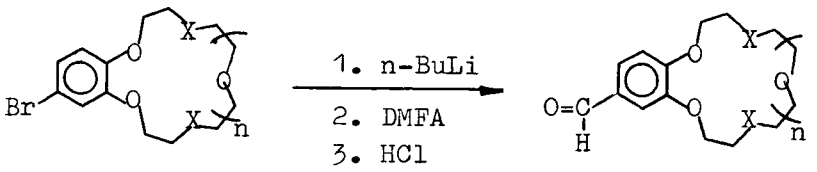
R = Alk, $(CH_2)_mSO_3^-$, $(CH_2)_mCOOH$, $(CH_2)_mP(O^-)OH$

X = CMe_2, S, O, Se, CH=CH R^1 = Me, MeO, Ph, Hal

At the same time methods of synthesis of some advanced nitrogen heterocyclic bases and their quaternary salts and unknown formyl derivatives of benzocrown ethers containing N, O and S atoms in different combinations are elaborated.



R^1 = Me, H R^2 = Alk R = Alk

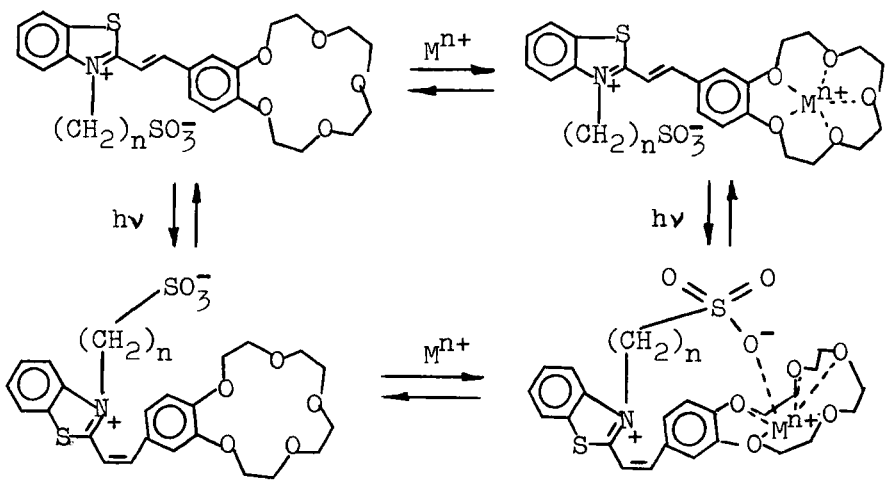


X = O, S, NMe

The synthesized novel type of dyes exhibit a high selectivity to metal cations which depends on the ionic radius of metal cation and the macrocycle size of the crown ether cavity.

PHOTOINDUCED ISOMERIZATION

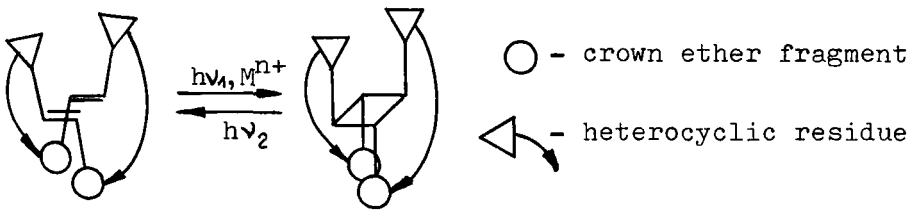
It has been shown and then it has been confirmed by theoretic calculations that among the compounds synthesized, dyes "anion covered" are the most promise.[3] This made possible at first synthesis one of the simple photo- and thermochromic unsaturated crown ethers capable of "taking off" and "putting on" their anionic "cap" thus providing the means of photocontrolling the association of metal cations.



PHOTOCYCLOADDITION

X-Ray analysis data and photochemical investigations showed that our molecules are able to self-congregate in crystal and in solution in presence of metal cations in pairs such as "head-to-tail" and in this case ethylene bonds are in position one under another. It is discovered that upon irradiation of such dimers solutions the rare observed photochemical regio- and stereospecific 1,2-cycloaddition (Φ = 0.01) of a "head-to-tail" type takes place, and it gives rise to only one of eleven possible isomers of cyclobutane.[4]

The structures of all prepared cyclobutane derivatives have been undoubtedly proved by NMR method. The irradiation of cyclobutane derivatives with more short wavelength light leads to quantitative forming of initial styryl dyes.



Discovered unique stereo- and regiospecific reaction of 1,2-photocycloaddition is predetermined by high degree of self-organization of obtaining the above dye molecules in dimers.

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