SYNTHESIS OF A WATER-SOLUBLE VERDAZYL RADICAL

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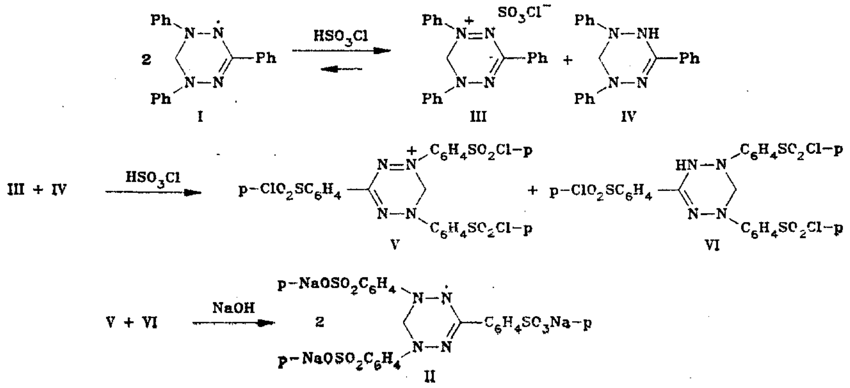
Verdazyl [2,4-diphenyl-6-aryl-3,4-dihydro-sym-tetrazin-1(2H)-yl] radicals (I) are used as instruments and subjects of the investigation of the mechanisms of organic reactions [1]. Compounds of the I type are usually insoluble in water, and they therefore cannot be used in the study of redox processes in biological systems. The previously described [2] 2,4-diphenyl-6-pentahydroxypentyl-3,4-dihydro-sym-tetrazin-1(2H)-yl radicals are only slightly soluble in water (~10^{-5} mole/liter), which makes it possible to use them for the indicated purposes.

We have synthesized the sodium salt (II) of 2,4,6-tris(p-sulfophenyl)-3,4-dihydro-sym-tetrazin-1(2H)-yl radical, the solubility of which in water is no less than 10^{-1} mole/liter:



A 0.5-g (1.6 mmole) sample of verdazyl radical I was added with stirring in the course of 10 min to 3.16 ml (48 mmole) of chlorosulfonic acid, after which the mixture was stirred at 20°C for 1.5 h. It was then poured over ice (50 g), and the aqueous mixture was neutralized with 10 N NaOH until the color changed from violet (the verdazylium cation) to green (the verdazyl radical). The frozen solution with dried lyophically, and the residue was extracted with methanol. The solvent was evaporated *in vacuo*, the residue was dissolved in 3 ml of distilled water (the water was made alkaline with ammonia to pH 8), and the solution was purified with a chromatographic column (1.5 by 25 cm) packed with Reanal Acrilex P-2 gel and equilibrated with water with pH 8. Salts were eluted initially, after which a yellow-brown impurity and (with overlapping of the zone of the impurity) green radical II were eluted. Lyophilic drying and reprecipitation from ethanol–methanol (2:1) gave 0.4 g (80%) of a finely crystalline green substance. The structure of II ($C_{20}H_{14}N_4Na_3O_9S_3$) was confirmed by spectral data. EPR spectrum [10^{-3} mole/liter in a physiological solution buffered with 0.01 mole/liter phosphate, pH 7.15 (BPS), 20°C]: nine lines, $A_{iso} = 5.7$ G, $\Delta H_0 = 3.3$ G. IR spectrum (KBr): 1045, 1076, 1127, 1185 (SO_3^-); 830 (para substitution); 750 cm^{-1} (ortho substitution; virtually absent). NMR spectrum (in CF_3COOH): 8.2 (broad m, 12H, aromatic) and 6.7 ppm (broad s, 2H, CH_2). Electronic spectrum (in BPS): λ_{max} 720 nm (log ε 3.18). The corresponding verdazylium salt was formed when bromine was added to verdazyl radical II in BPS. Electronic spectrum of the verdazylium salt in FRZ: λ_{max} 550 nm (log ε 3.59).

LITERATURE CITED

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2. R. Kuhn and G. Fischer-Schwarz, Monatsh. Chem., 97, 517 (1966).

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