SYNTHESIS OF THE 1-(5-TETRAZOLYL)-3,5-DIPHENYLVERDAZYL RADICAL

V. P. Shchipanov and A. A. Skachilova

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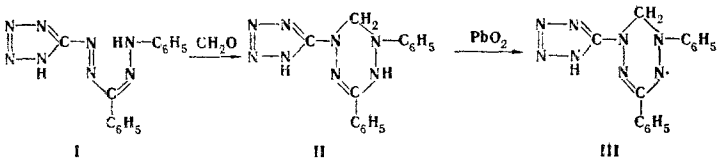
We have observed that 1-(5-tetrazolyl)-3,5-diphenylformazan (I) reacts with formaldehyde in alkaline media to give the leuco base (II) of the 1-(5-tetrazolyl)-3,5-diphenylverdazyl radical (II).



I II III

In contrast to the leuco bases of triarylverdazyl radicals, II is stable with respect to air oxygen in the crystalline state and in solution but forms verdazyl radical III, which is paramagnetic in the crystalline state and in solution (according to ESR data), on oxidation with lead dioxide in ether.

EXPERIMENTAL

Leuco Base II of the 1-(5-Tetrazolyl)-3,5-diphenylverdazyl Radical (II). A 2.1-ml sample of a 37% solution of formaldehyde was added to a solution of 2.92 g (0.01 mole) of I in 90 ml of 1% sodium hydroxide, and the mixture was maintained for 3 h without access to the air, after which it was filtered. The filtrate was acidified with acetic acid to give 1.75 g (57%) of II with mp 180.5-182.5° (decomp., colorless needles from chloroform) and R_f 0.21 in a thin layer of activity IV Al_2O_3 [acetone–chloroform–acetic acid (76:22:2)]. The chromatogram was developed with iodine vapors. UV spectrum (in alcohol), λ_{max}, nm (log ε): 230 (4.27), 305 (4.03). IR spectrum: 3321 (NH) cm^{-1}. Found: 59.0; H 4.2; N 37.0%. $C_{15}H_{14}N_8$. Calculated: C 58.8; H 4.6; N 36.6%.

1-(5-Tetrazolyl)-3,5-diphenylverdazyl Radical (III). A solution of 0.3 g of II in 200 ml of diethyl ether was shaken with 3 g of brown PbO_2 and 3 g of anhydrous Na_2SO_4 for 30 min, after which the green solution was filtered and concentrated in vacuo to 20 ml. The addition of heptane precipitated 0.2 g (66%) of III as a dark-blue powder with mp 104.5° (decomp., recprecipitation from ether solution by the addition of heptane). The product was readily soluble in most organic solvents and in aqueous alkali solution but insoluble in water and aliphatic hydrocarbons. Application of a chloroform solution of III to Al_2O_3 of any degree of activity led to rapid decolorization of the sample because of reduction of III to II (R_f 0.21). UV spectrum (in benzene), λ_{max}, nm (log ε): 380 (3.97), 690 (3.64). Found: C 59.0; H 4.5; N 36.6%. $C_{15}H_{13}N_8$. Calculated: C 59.0; H 4.3; N 36.7%.

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