

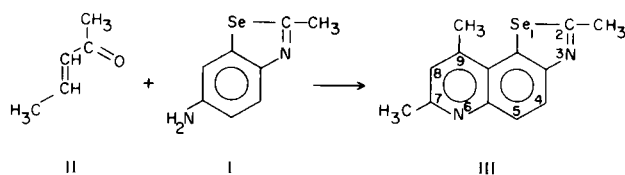
The Synthesis and Properties of 2,7,9-Trimethylselenazolo[5,4-*f*]quinoline (I)

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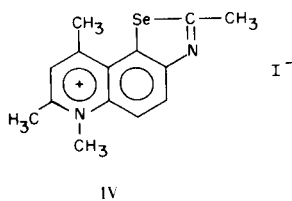
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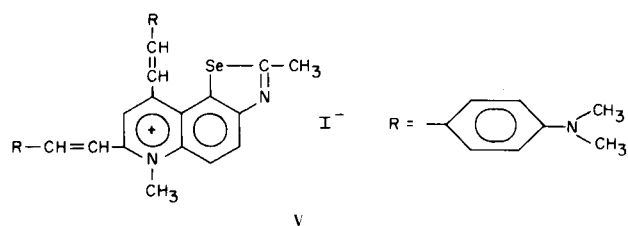
The reaction of 2-methyl-6-aminobenzoselenazole (I) (2) with 3-penten-2-one (3), gave *via* a simple Doebner-Miller type reaction the trimethyl substituted selenazoloquinoline (III).



Reaction of III with an excess of methyl iodide gave a crude product from which, after crystallization from absolute ethanol, was obtained the monomethiodide (IV).



The structures of the base III and its quaternary salt (IV) were established by nmr spectra as previously accomplished in the case of analogous sulphur derivatives (4-6). In Table I are reported nmr spectroscopic data. The $J_{H_4-H_5}$ values confirm the proposed angular structure, and the strong deshielding effect observed for protons and methyl protons in the pyridine ring of the methiodide indicate that quaternization takes place on this nitrogen atom. The enhanced reactivity of the 7- and 9-methyl groups in the methiodide enabled us to obtain, under suitable experimental conditions, the trinuclear styryl derivative (V) which is the main product in the reaction



of IV with *p*-dimethylaminobenzaldehyde. The absorption of this dye, shown in Fig. 1, owing to the complexity of the chromophoric system, is characterized by a broad absorption band with two main peaks in the green region of the spectrum.

TABLE I

H ₈		H ₄ -H ₅ (q)		C ₂ -Me		⁺ N ₆ -Me	C ₇ -Me		C ₉ -Me		J _{H₄-H₅} (c.p.s.)	
2.60	1.77	1.92	1.34	7.12	7.00	5.50	7.37	6.94	7.30	6.60	9.0	9.5
0.83		0.58		0.12			0.43		0.70		0.5	

Nmr spectral data of compounds III and IV. The spectra were determined in 6% hexadeuteriodimethylsulphoxide solution at 60 Mc with a Varian A-60 spectrometer; chemical shifts are reported in p.p.m. (τ scale) relative to tetramethylsilane as an internal standard. The left hand of each column gives values for the free base (III), the right hand gives values for the methiodide (IV), and the intermediate position gives $\Delta\tau$ values, being $\Delta\tau = \tau_{\text{free base}} - \tau_{\text{methiodide}}$. Singlets are unmarked, (q) = quartet.

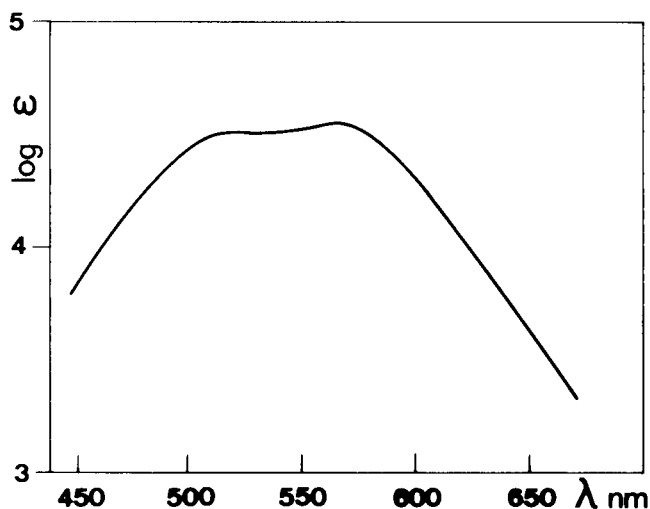


Figure 1. Absorption spectrum in ethanol of dye V.

EXPERIMENTAL

The spectrum of dye V was determined in 95% ethanol with a Beckman DU spectrophotometer. The melting points were taken on a Kofler apparatus and are uncorrected.

2,7,9-Trimethylselenazolo[5,4-*f*]quinoline (III)

The hydrochloride of compound I (15.6 g., 0.063 mole) (obtained by running gaseous hydrogen chloride through an ethereal solution of the amine) (22.5 g., 0.1 mole) of sodium *m*-nitrobenzenesulphonate, 0.1 g. of anhydrous zinc chloride and 18 ml. of 36% hydrochloric acid, suspended in 90 ml. of absolute ethanol, were treated at 65° over a period of 30 minutes with 4.2 g. (0.05 mole) of II. The mixture was stirred at 65° for one hour, then refluxed for four hours and finally let to stand overnight. After filtration, an alcoholic solution of 2,4,6-trinitrophenol was added to the solution and the yellowish picrate was collected by filtration. By decomposition of the picrate with aqueous sodium hydroxide (3%) the free base was isolated and crystallized from aqueous ethanol, yield 5.9 g. (18.6%), m.p. 178-179°.

Anal. Calcd. for C₁₃H₁₂N₂Se: C, 56.73; H, 4.40; N, 10.18. Found: C, 56.89; H, 4.38; N, 10.07.

The picrate crystallized from absolute ethanol as yellow needles, m.p. 249-250°.

Anal. Calcd. for C₁₉H₁₅N₅O₇Se: C, 45.25; H, 3.00; N, 13.89. Found: C, 45.22; H, 3.22; N, 13.60.

2,6,7,9-Tetramethylselenazolo[5,4-*f*]quinolinium Iodide (IV)

The base (III) was refluxed with an excess of methyl iodide over a period of four hours. The crude product was washed with anhydrous acetone and ethyl ether and twice crystallized from absolute ethanol, m.p. 258-259°.

Anal. Calcd. for C₁₄H₁₅IN₂Se: C, 40.31; H, 3.62; N, 6.72. Found: C, 40.55; H, 3.52; N, 6.53.

2,6-Dimethyl-7,9-bis[2-(4-dimethylamino)styryl]selenazolo[5,4-*f*]quinolinium Iodide (V)

The methiodide (IV) (0.250 g., 0.0006 mole) was dissolved with stirring in 100 ml. of boiling acetic anhydride: 50% of the solvent was then removed by distillation. *p*-Dimethylaminobenzaldehyde (0.358 g., 0.0024 mole) was added to the solution and the mixture was heated under reflux for six hours; during this period another portion of the solvent was removed by distillation to a final volume of 20 ml. After cooling, anhydrous ethyl ether was added and the dye was collected by filtration. The crude dye which is accompanied by minor amounts of side products (*i.e.* starting materials, monostyryl derivatives) was purified by column chromatography over alumina (Brockmann); eluates with benzene, chloroform, ethyl acetate, acetone and acetone-ethanol (9:1) were neglected while the subsequent fraction acetone-ethanol (6:4) which contained the dye was recovered and the solvent removed. The residue was crystallized from ethanol, m.p. 213-215°.

Anal. Calcd. for C₃₂H₃₃IN₄Se: C, 56.56; H, 4.90; N, 8.25. Found: C, 56.78; H, 4.92; N, 8.05.

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