20%. On standing, the precipitated hemicellulose flocculated and was separated by centrifuging. The separated hemicellulose was treated with 95% alcohol, acetone, and ether in the usual manner. Two and five-tenths grams of dry, white hemicellulose, identified by hydrolysis and chromatography as 95% xylan, was obtained. The use of other sequences of reagents for the preparation of cellulose was not so successful as the one described above. The sequences of treatment and results are shown in Table II.

Fractionation and characterization. One-tenth gram of the cellulose obtained above was transferred into a 100-ml. centrifuge bottle to which 10 glass beads and a selected amount of water was added. The bottle was then stoppered with a serum-bottle rubber stopper.

The stopper was pierced with a syringe needle, to which, in addition to a cupriethylenediamine reservoir, nitrogen and vacuum lines with appropriate stopcocks were also connected. The air in the bottle was first evacuated and then replaced with purified nitrogen. The bottle was again evacuated and filled with cupriethylenediamine to make up 100 ml. and finally filled with nitrogen. The bottle was then shaken for 2 hr. and centrifuged. Ten milliliters of the supernatant solution was withdrawn with a syringe and transferred into an Ubbelohde viscometer in which the viscosity was determined. The transferring and the measurement of viscosity were conducted under nitrogen. The viscosities of the samples obtained with varied concentrations of cupriethylenediamine solution are shown in Table III. The residue was separated and washed with 1% acetic acid and water. Fifty milliliters of the supernatant solution was neutralized with 50% acetic acid. Precipitation occurred. The precipitate was centrifuged, separated, washed, and weighed. Thirty milligrams each of the residue and of the regenerated cellulose were hydrolyzed with sulfuric acid, chromatographed and analyzed for glucose and xylose.[5] The results are shown in Table III.

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APPLETON, WIS.

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Structure of 2,1,3-Benzoselenadiazole and Its Derivatives. III.[1] Preparation and Absorption Spectra of 5-Styryl-4-nitro-2,1,3-benzoselenadiazoles[2]

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The nitration of 2,1,3-benzothiadiazole[5] and 2,1,3-benzoselenadiazole[1] (I) has been shown to take place in the 4-position. The attack at this position is believed to be due to the greater electron density at the 4- and 7-positions of the dicationic salt of I as compared to the 5- and 6-positions.[1] Because of the ortho-para directing effect of the methyl group, the nitration of 5-methyl-2,1,3-benzoselenadiazole (II) could be expected in the 4-position. The following facts bear this out. The nitration of II gave a nitro derivative (III) whose

TABLE I

ULTRAVIOLET-VISIBLE ABSORPTION SPECTRA OF SOME 2,1,3-BENZOSELENADIAZOLE DERIVATIVES

Substituted 2,1,3-Benzoselenadiazole	λ_{max} (log ϵ)			Solvent[a]
5-Nitro-	230 (3.71)	274 (4.02)	342 (4.21)	E
	224 (3.86)	274 (4.03)	348 (4.22)	A
			400[b] (3.2)	
4-Nitro-		271 (3.57)	339 (4.19)	E
			370 (3.8)[c]	
		275 (3.73)	340 (4.16)	A
			380 (3.7)	
4-Nitro-5-methyl-			338 (4.27)	E
			370 (3.3)[c]	
		279 (3.61)	351 (4.22)	A
			380 (3.7)	
4-Nitro-5,7-dimethyl-			336 (4.26)	E
			370 (3.56)[c]	
	245 (3.56)	302 (3.81)	352 (4.31)	A
			390 (3.67)	
5-Amino-	236 (4.25)	324 (3.94)	426 (3.80)	E
	265 (3.65)			
	236 (3.97)	333 (4.10)	459 (3.74)	Ac
4-Amino-	242 (4.14)	*322* (4.00)	462 (3.28)	E
		329 (4.08)		
		336 (4.07)		
	231 (3.70)	333 (4.23)	*370* (3.1)[c]	Ac
4-Amino-5-(and 7)-methyl-	238 (4.11)	323 (4.00)	466 (3.23)	E
		329 (4.04)		
		336 (4.05)		
	232 (3.75)	330 (4.18)	*370* (3.4)[c]	Ac
5-Methyl-	*232* (3.70)	333 (4.24)	*370* (3.3)[c]	E
4-Nitro-5-styryl-		292 (4.33)	388 (4.32)	Ed
4-Nitro-5-(4′-methylstyryl)-		300 (4.26)	400 (4.23)	Ed
4-Nitro-5-(4′-chlorostyryl)-		295 (4.30)	382 (4.10)	Ed
4-Nitro-5-(3′,4′-dimethoxystyryl)-	240 (4.22)	335 (4.22)	408 (3.79)	Ed
4-Nitro-5-(4′-dimethylaminostyryl)-		340 (4.38)	489 (4.32)	Ed

[a] E = 95% ethanol; A = 95% sulfuric acid; Ac = 50% alcoholic 1.2*N* HCl; Ed = 95% ethanol containing 0.2% dioxane. [b] Underlined values are shoulders. [c] Weak inflection.

(1) Paper II: E. Sawicki and A. Carr, *J. Org. Chem.*, **22**, 507 (1957).

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(4) Taken in part from the dissertation to be submitted by Albert Carr in partial fulfillment of the requirements for the Doctor of Philosophy Degree at the University of Florida.

(5) L. Efros and R. Levit, *Zhur. Obshcheĭ Khim.*, **23**, 1552 (1953); *Chem. Abstr.*, **48**, 12091 (1954).

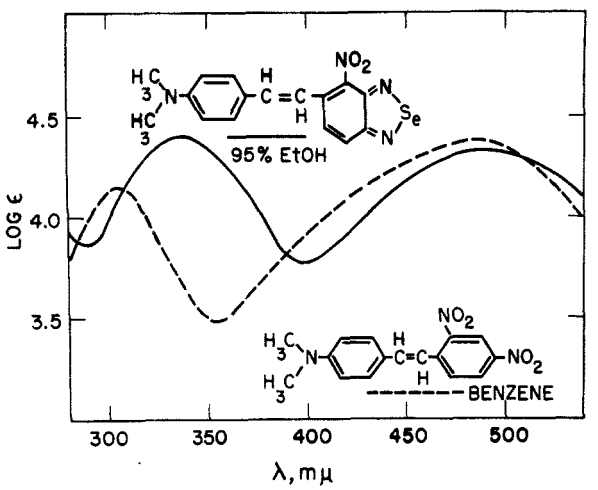
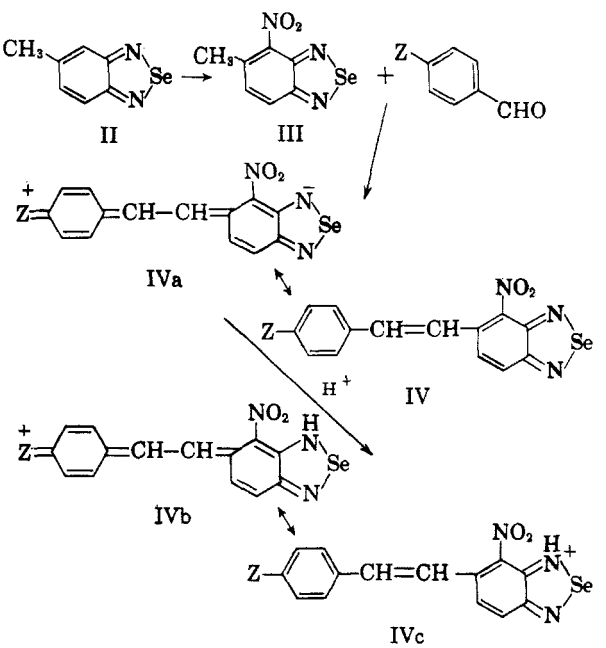


Fig. 1. Absorption spectra: 5-(4′-Dimethylaminostyryl)-4-nitro-2,1,3-benzoselenadiazole in 95% ethanol (———); 4-Dimethylamino-2′,4′-dinitrostilbene in benzene (- - - -)

spectra in alcoholic and sulfuric acid solutions more closely resembled the spectra of 4-nitro-2,1,3-benzoselenadiazole in these same solvents than the spectra of the 5-nitro isomer, Table I. For the same reasons the nitration of 4,6-dimethyl-2,1,3-benzoselenadiazole is believed to take place in the 7-position, Table I. Reduction of III to the triamine followed by reaction with selenium dioxide gave a mixture of amino-5-methyl-2,1,3-benzoselenadiazoles that was difficult to separate. The mixture of amino-5-methyl-2,1,3-benzoselenadiazoles was found to be closely similar spectrally in alcoholic and acidic solution to 4-amino-2,1,3-benzoselenadiazole in the same solvents and entirely different spectrally from 5-amino-2,1,3-benzoselenadiazole, Table I. As III undergoes condensation with aldehydes (and II does not under identical conditions), the nitro group must be ortho to the methyl. This means that nitration of II takes place in the 4-position.

Examination of the absorption spectra of the stilbene derivatives (IV) in alcohol discloses that the long wave length band shifts toward the visible in the order Z = H = 4′-Cl < 4′-Me < 3′,4′-$(OMe)_2$ ≪ 4′-NMe_2, Table I. It would seem that in this series the long wave-length band is associated with a zwitterionic resonance structure which contributes mainly to the excited state and decreases in energy with the increasing electron donor strength of Z in IV. This would involve a closing up of the electronic levels of the ground and excited states with the increasing electron donor strength of Z.

4-Dimethylamino-2′,4′-dinitrostilbene and IV, Z = 4′-$N(CH_3)_2$, have closely similar visible absorption spectra, Fig. 1. This is not surprising, for it has been shown that a nitro group and a N_2Se group are both strong electron-attracting groupings. The compound IV, Z = 4′-$N(CH_3)_2$, absorbs in the following solvents at the indicated wave length maximum in millimicrons: acetone, 335, 480; dimethylformamide, 340, 487; dimethylaniline, 340, 498; dimethyl sulfoxide, 349, 501; chloroform, 337, 501; pyridine, 347, 502; anisaldehyde, 505; 50% aqueous acetone, 349, 513; 50% aqueous dimethylformamide, 347, 513;. and 50% aqueous pyridine, 350, 520. In the pure solvents the long wave-length band was slightly more intense than the shorter wave-length band; in the aqueous solutions the long wave-length band was relatively less intense and shifted further into the visible. Apparently the water molecules arrange themselves so as to stabilize dipolar structures, such as IVa, to a somewhat greater extent in the excited state. This "closing up" of the energy levels is reflected in the red shift.



Two protons add to the heterocyclic nitrogens of I in sulfuric acid[1] while only one proton adds to III in the same solvent. In the styryl derivatives there must be an increase in the basicity for two protons can add to the molecule in sulfuric acid, Table II. The spectra of the bases, monocationic and dicationic salts of the styryl derivative (IV) are given in Table II. In the dimethylamino derivative the first proton adds to the amino nitrogen to give the salt absorbing at λ 374 mμ; in trifluoroacetic a second proton adds to the ring 1-nitrogen to form a dicationic salt, λ_{max} 441 mμ. Addition of the third proton (even in concentrated sulfuric acid) is not complete. A shoulder at 575 mμ is believed to be due to the tricationic salt.

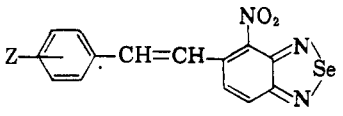
EXPERIMENTAL[6]

4-Nitro-5-methyl-2,1,3-benzoselenadiazole (III). A stirred solution of 2.0 g. (0.01 mole) of 5-methyl-2,1,3-benzo-

(6) Melting points are uncorrected. Analyses are by Peninsular ChemResearch, Inc., Gainesville, Fla.

TABLE II

COLOR AND LONG WAVE-LENGTH MAXIMA OF 4-NITRO-5-STYRYL-2,1,3-BENZOSELENADIAZOLE DERIVATIVES

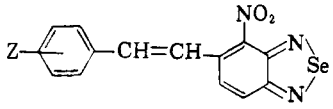


Z	Color (λ_{max}, mμ) Base[a]	Mono-cation[b]	Di-cation[c]
H	Yellow (392)	Orange-red (505)	Blue (673)
4′-Cl	Yellow (382)	Red (515)	Blue (685)
4′-CH_3	Yellow (400)	Violet (548)	Blue (723)
3′,4′-$(OCH_3)_2$	Yellow (408)	Blue (595)	Blue —
3′,4′-(O_2CH_2)	Yellow —	Blue —	Blue —
4′-$N(CH_3)_2$	Orange (489)	Light yellow (374)	Yellow (441)

[a] In 95% ethanol. [b] In trifluoroacetic acid except Z = 4′-$N(CH_3)_2$ which is in 50% alcoholic 1.2*N* HCl. [c] In concentrated sulfuric acid except Z = 4′-$N(CH_3)_2$ which is in trifluoroacetic acid. This latter compound is orange in concentrated sulfuric acid with λ_{max} 476 mμ due to the dication and a shoulder at 575 mμ due to the trication.

TABLE III

5-SUBSTITUTED 4-NITRO-2,1,3-BENZOSELENADIAZOLES



Z	M.P., °C.	Yield, %	Formula Wt.	Analyses Theory N	Found N
H	232–234	61	$C_{14}H_9N_3O_2Se$	12.7	12.4
4′-Cl	240–241	61	$C_{14}H_8ClN_3O_2Se$	11.5	11.2
4′-Me	252–253	76	$C_{15}H_{11}N_3O_2Se$	12.2	12.0
4′-NMe_2	246–247	47	$C_{16}H_{14}N_4O_2Se$	15.0	14.7
3′,4′-$(OMe)_2$	249–251	51	$C_{16}H_{13}N_3O_4Se$	10.8	10.8
3′,4′-(O_2CH_2)	254–255	60	$C_{15}H_9N_3O_4Se$	11.2	11.0
2′,3′-$(CH)_4$	255–256	45	$C_{18}H_{11}N_3O_2Se$	11.0	10.8

selenadiazole[1] in 4 ml. of concentrated sulfuric acid was treated with a mixture of 1 ml. of nitric acid (d. 1.4) and 2 ml. of sulfuric acid at 0–10°. The mixture was allowed to stand 30 min. at room temperature, then was poured on ice and filtered. Two crystallizations from xylene gave 1.5 g. (62%) of light yellow crystals, m.p. 192–194°.

Anal. Calcd. for $C_7H_5N_3O_2Se$: N, 17.4. Found: N, 17.2.

4-Amino-5-methyl-2,1,3-benzoselenadiazole and 4-amino-7-methyl-2,1,3-benzoselenadiazole. To a suspension of 2.42 g. of 4-nitro-5-methyl-2,1,3-benzoselenadiazole in 70 ml. of hot water and 20 ml. of concentrated hydrochloric acid was added 8 g. of zinc dust. The mixture was vigorously refluxed for 30 min. and filtered hot. To the cold filtrate was added an equal volume of concentrated hydrochloric acid. The mixture was cooled to 0° and filtered. The residue was washed with 20 ml. of cold 25% hydrochloric acid dissolved in a minimum amount of water and neutralized with potassium acetate. A solution of 1 g. of selenium dioxide in 2 ml. of water was added at 0–5°. Quick filtration gave 1.4 g. of crude product, m.p. 135–139°. Several crystallizations from heptane gave yellow crystals, m.p. 138–142°.

Anal. Calcd. for $C_7H_7N_3Se$: N, 19.5. Found: N, 19.9.

4,6-Dimethyl-2,1,3-benzoselenadiazole. To a solution of 98 g. of 2-nitro-4,6-dimethylacetanilide[7] in 200 ml. of hot Methyl Cellosolve was added 100 ml. of concentrated hydrochloric acid. Following 90-min. reflux, excess water was added. The crude 2-nitro-4,6-dimethylaniline (85 g.) was dissolved in 50 ml. of concentrated hydrochloric acid. A solution of 450 g. of stannous chloride in 400 ml. of hydrochloric was cautiously added. The mixture was boiled to one half volume, cooled and filtered. The residue was treated with cold aqueous sodium hydroxide solution until the mixture was definitely alkaline. The residue was extracted with alcohol, the extract treated with a concentrated aqueous solution containing 65 g. of selenium dioxide, cooled and filtered. Two crystallizations from heptane gave 44 g. of colorless crystals, m.p. 154–155°.

Anal. Calcd. for $C_8H_8N_2Se$: N, 13.3. Found: N, 13.2.

4-Nitro-5,7-dimethylbenzoselenadiazole. To a stirred solution of 2.11 g. (0.01 mole) of 4,6-dimethyl-2,1,3-benzoselenadiazole in 4 ml. of concentrated sulfuric acid at 0–10° was added a mixture of 1 ml. nitric acid (dec. 1.4) and 2 ml. of sulfuric acid. The mixture was allowed to stand at room temperature for 30 min., poured on ice, and filtered. Crystallization from Methyl Cellosolve followed by heptane gave 1.8 g. (71%) of light yellow crystals, m.p. 164–165°.

Anal. Calcd. for $C_8H_7N_3O_2Se$: N, 16.4. Found: N, 16.0.

4-Nitro-5-styryl-2,1,3-benzoselenadiazole (IV, Z = H). A mixture of 0.24 g. (0.001 mole) of 4-nitro-5-methyl-2,1,3-benzoselenadiazole and 0.9 ml. (0.009 mole) of benzaldehyde was heated in an oil bath at 150° until homogeneous. Two drops of piperidine were added and the mixture was heated at 150° for 30 min. Two ml. of methanol was added to the cold mixture. The residue obtained from the mixture was washed well with methanol. Crystallization from Methyl Cellosolve (β-methoxyethanol) gave glistening yellow crystals, m.p. 232–234°.

This general procedure was followed for all the styryl derivatives, Table III.

Anal. Calcd. for $C_{14}H_9N_3O_2Se$: N, 12.7. Found: N, 12.4.

Ultraviolet-visible absorption spectra. A Beckman Model DU quartz spectrophotometer with 1-cm. silica cells was used by the procedure described in previous publications.

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